INVESTIGATIONS OF METAL OXIDE NANOSTRUCTURES FOR SOLAR-DRIVEN GREEN ENERGY APPLICATIONS

A THESIS

Submitted in partial fulfillment of the requirements for the Award of the degree of

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By

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DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY, 2024



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "INVESTIGATIONS OF METAL OXIDE NANOSTRUCTURES FOR SOLAR-DRIVEN GREEN ENERGY APPLICATIONS" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, INDIAN INSTITUTE OF TECHNOLOGY **INDORE**, is an authentic record of my own work carried out during the time period from July 2019 to February 2024 under the supervision of Prof. Rupesh S. Devan and Prof. Parasharam M. Shirage, Department of Metallurgical Engineering and Materials Science.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

05/07/2024

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Dedicated to my

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LIST OF PUBLICATIONS

A] On thesis work

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- 1. **Bimli S**., Manjunath V., Mulani S. R., Game O. S., Shaikh P. A., Devan R. S., Multifunctional photodetector based on Ag/MAPbBr₃/Ni heterostructure: a magnetically tunable photocurrent. (Communicated).
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NOMENCLATURE

Α	
ABPE	Applied Bias to Photon Conversion Efficiency
Aq.	Aqueous
AO	Ammonium Oxalate
Ag	Silver
Au	Gold
В	
BET	Brauner-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BSO	Barium Stannate
BTO	Barium Titanate
BE	Binding Energy
BQ	Benzoquinone
С	
CA	Chronoamperometry
CBM	Conduction Band Minimum
CB	Conduction Band
CBO	Copper Bismuth Oxide
CdS	Cadmium Sulfide
CNT	Carbon Nanotube
COD	Chemical Oxygen Demand
CO_2	Carbon di-oxide
CR	Congo Red
Cs_2SnI_6	Cesium Tin Iodide
CV	Crystal Violet
CuAlO ₂	Copper Aluminum Oxide
Cu ₂ O	Copper Oxide
D	
D^*	Detectivity
DI	Deionized
DOS	Density of States
DSSC	Dye-Sensitized Solar Cell
DRS	Diffused Reflectance Spectra
E	
EDS	Energy Dispersive Spectroscopy
EQE	External Quantum Efficiency

ESI	Electrospray Ionization
EDL	Electric Double Layer
EIS	Electrochemical Impedance Spectroscopy
ETL	Electron Transport Layer
eV	Electron Volt
F	
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine doped Tin Oxide
G	
Gof	Goodness of fitting
GO	Graphene Oxide
н	1
HTM	Hole Transport Material
НМТА	Hexamine
H2O2	Hydrogen Peroxide
HTL	Hole Transport Laver
T	
1 T	Photo Current
IPh I	Short Circuit Current
IFA	Incident Photon to Current Conversion Efficiency
IFCL	Indium Tin Oxide
-	Indium Thi Oxide
J	
J _{SC}	Short Circuit Current Density
L	
LCMS	Liquid Chromatography Mass Spectroscopy
LSPR	Localized Surface Plasmon Resonance
L _d	Diffusion Length
LSV	Linear Sweep Voltammetry
LZO	Lanthanum doped Zinc Oxide
Μ	
MAPI	Methyl ammonium lead triiodide
MEA	Monoethanolamine
MB	Methodia
MO	Metal Oxides
MOF	Metal Organic Framework

MOCTL	Metal Oxide Charge Transport Layer
MoS_2	Molybdenum Sulphate
Ν	
NHE	Normalized Hydrogen Electrode
NA	Acceptor Density
ND	Donor Density
NFs	Nanoflakes
NPs	Nanoparticles
NiO	Nickel Oxide
NRs	Nanorods
NPt	Nano petal
NIR	Near Infrared
NF	Nickel Foam
0	
1D	One-dimensional
O ₃	Ozone
Р	
PbI ₂	Lead Iodide
PD	Photodetector
P _{in}	Incident Power
PO	Perovskite Oxide
PCE	Power Conversion Efficiency
PV	Photovoltaic
PPM	Parts Per Millions
PEC	Photo-electrochemical
PPy	Polypyrrole
PVA	Poly Vinyl Alcohol
PVDF	Poly Vinylidene Fluoride
Pt	Platinum
R	
R	Responsivity
Rct	Charge transfer resistance
Rs	Series Resistance
Rsh	Shunt Resistance
RE	Reference Electrode
ROS	Reactive Oxygen Species
RNL	Remazol Golden Yellow
RO	Reverse Osmosis
rGO	Reduced Graphene Oxide

S	
S	Sensitivity
SCR	Space Charge Region
SAXS	Small Angle X-Ray Scattering
SCAPS 1D	Solar Cell Capacitance Simulator-1D
SCE	Saturated Calomel Electrode
SnO_2	Tin oxide
Т	
2D	Two-dimensional
TiO ₂	Titanium dioxide
U	
UPS	Ultraviolet Photoelectron Spectroscopy
V	
VB	Valence Band
V _{OC}	Open Circuit Voltage
VBM	Valence Band Maximum
V_2O_5	Vanadium Pentoxide
W	
WO ₃	Tungsten Trioxide
WE	Working Electrode
X	
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
Z	
ZnO	Zinc Oxide
0D	Zero Dimensional

Chapter 1

Introduction

1.1 Overview of green energy

The worldwide energy demand is projected to reach 46 terawatts (TW) by the year 2100 due to rapid industrialization and population growth [1]. At present, the majority of global energy requirements are fulfilled by crude oil, coal, natural gas, and other fossil fuels, but they are drastically diminishing due to continuously increasing consumption [2]. Moreover, the utilization of these fossil fuels generates greenhouse gases, leading to global warming and many other ecological difficulties, which need to be regulated for our ecosystem. The surge in energy demand, coupled with the dwindling supply of fossil fuels, is prompting the world to move towards renewable energy sources being the only solution to tackle the energy crisis. Renewable energy resources like hydro, biomass, solar, and wind have the potential to produce energy without carbon emissions. Currently, only 14% of global energy requirements are accomplished by various renewable energy sources, suggesting major reliance on non-renewable energy sources [3], and thus, the production of renewable energy sources at large scale is mandatory. Achieving efficiencies of various renewable energy technologies beyond certain limits has posed a significant challenge. This has directed researchers to make efforts to innovate new technologies or enhance the efficiency of existing ones.

Among various available sources of renewable energy, solar stands out as a more economical, clean, and viable way to produce green energy over other renewable techniques. Solar-driven electricity generation using photovoltaic (PV) cells, hydrogen (H₂) production through photoelectrochemical (PEC) cells [4], and wastewater purification and photodetectors (PDs) are some of the prominent real-time applications of solar energy. The PV cell technology that directly converts sunlight into electricity has evolved with time from bulky crystalline silicon (Si) to flexible thin film solar cells. The incident photons create electron–hole (e^- – h^+) pairs within the light harvester, which get separated and collected by the charge collectors. Therefore, the efficiency of solar cells majorly relies on the ability to convert incident sunlight into photogenerated current. Being availability of sun light, the PV cells can produce electric energy only in daylight, and therefore, external storage is required. Nowadays, grid-connected PV systems are widely used to supply excess power to the grid, thus moving towards high-quality flexible power systems [5]. However, the high energy density and minimal carbon footprint of abundantly available

 H_2 sources make them valuable alternative fuels for energy production. The evolution of green H_2 from carbon (C) free fuels is crucial for a self-sustainable future. The electrolysis of water under sunlight is the cost-effective, clean, and efficient approach for producing H_2 and O_2 from abundant water. [6]. This environmentally friendly process facilitates easy collection and storage of produced green H_2 to generate electricity (through fuel cells) with minimal post-combustion pollutants. Therefore, PEC water splitting and PV cells utilizing sunlight are cost-effective and viable ways of generating green energy.

Furthermore, the p-n junction PDs, akin to solar cells, transform incident light energy into electrical output signals. The PDs work on the principle of absorption of incident photons and consequent excitation of e⁻ from VB to the CB. These photogenerated e⁻ under photoexcitation give rise to the photocurrent and represent the photo-response of PDs. These PDs are commonly employed to detect the light of specific wavelengths depending on the optical characteristics of the absorber materials. The optical bandgaps of the materials decide the interaction regions of the solar spectrum, and hence, the choice of materials depends on the wavelength under detection. Further, the self-powered PDs are capable of detecting incident light without an external power source, which makes them suitable to operate at remote locations. The PDs are also used in combination with solar cells to determine the incident light intensity and power generation of the PV cell.

Moreover, most of the difficulties confronting civilization in the current scenario are associated with the quality and supply of water. The rapid industrialization and increased global population have also created a scarcity of fresh drinkable water. The three responsible components for water scarcity intricately interconnected with the expansion of population and economic development are limited pure water resources, increased water demand, and increasing water pollution [7]. ~ 80% of the wastewater generated by industrial, domestic, and agricultural production is released in untreated form into freshwater bodies such as lakes, rivers, and oceans due to inadequate facilities and equipment to treat it. Among various industries, the dye industry related to textiles, leather tanning, and paper is identified as the most detrimental to the environment in terms of volume and composition of discharged effluent [8]. Therefore, photocatalytic wastewater purification by degrading toxic organic dye molecules into less harmful byproducts under sunlight is extremely essential to fulfill the freshwater requirements. The use of sunlight

and economical photocatalyst make this process very cost-effective and environmentally benign.

1.2 Green energy applications

The various environmentally benign green energy sources are promising alternatives to fulfill energy requirements with controlled environmental impact. Green energy sources such as solar thermal, photovoltaic cells, and green H_2 production will drastically reduce carbon emissions as compared to fossil fuel and natural gas. Moreover, photocatalytic wastewater treatment utilizes solar energy to degrade toxic organic dyes, contributing towards a sustainable environment by decreasing greenhouse gas emissions.

1.2.1 Solar cells

Solar cells are the devices that convert incident solar energy into electrical energy. Among various renewable energy harvesting approaches, solar cells have demonstrated significant potential for a self-sustainable future [9]. Currently, ~32% of the total renewable energy is generated by solar PV cells. Over the years, researchers have developed new materials, technologies, and device architectures to enhance the performance of solar cells. [10]. Silicon (Si), an indirect bandgap semiconductor having a low optical bandgap of ~1.2 eV, is the most common material used to fabricate solar cells [11]. In past years, both crystalline and amorphous Si-based solar cells have been investigated for light harvesting applications. Si solar cells, categorized as the "first generation solar cells," delivered PCE of 22.8% [12] due to the novel device architecture. However, the low power-to-weight ratio and high processing cost of single crystal Si increase the power generation cost of the cell. After that, flexible thin film based solar cells of CdTe, GaAs, amorphous-Si, CIGS, etc., categorized as "secondgeneration solar cells", relatively reduced the overall cost of electricity generation [13, 14] due to flexibility, lightweight, and low production cost [15]. However, thirdgeneration solar cells, which use polymer, organic sensitized dyes, and organometallic perovskite absorbers, have advanced significantly over the past several decades in terms of device architecture for high-performance [16-18]. Recently, organometallic perovskite has emerged as a low-cost and efficient light harvester with efficiency
(>25%), which is comparable to Si-based solar cells [19]. The chart of growth in cell efficiencies of various solar cell technologies over the years is shown in Fig. 1.1.

In third-generation solar cells, the perovskite absorber is sandwiched between the hole transport layer (HTL) and electron transport layer (ETL) to form a heterostructure device for extraction of photogenerated e^-h^+ pairs. These transport layers mainly serve to (i) assist the transportation of selective charge carriers towards the external circuit and (ii) reduce the recombination by blocking the charge of opposite polarity. The positioning or alignment of the energy band (CB and VB) of any transport layer is important in deciding the flow of charge carriers. Further, the charge carrier mobility of ETL/HTL should be comparable to the perovskite absorber to avoid charge accumulation at the perovskite/ETL and HTL/perovskite interface [20]. The transport layer should have a wide optical bandgap for complete irradiation of visible light to the perovskite absorber through it. The defect sites within the ETLs/HTLs should also be minimal. Apart from assisting in charge transportation, ETLs/HTLs also protect the perovskite layer from UV-assisted degradation [21]. Further technological advancement in solar cells is needed for sustainable energy generation in the near future. Overall, PV cells provide a cost-effective and renewable way to harness solar energy.



Fig. 1.1. Best efficiencies report for various generations of solar cells. (NREL website).

1.2.2 Photodetector

Photodetectors (PDs) are semiconductor devices that convert optical signals into electrical impulses and, therefore, are used to detect the optical power of incident light. PDs) are essentially used in telecommunication, night vision, video imaging, optical communication, and microelectronics. The PDs with lateral or vertical device architecture are classified as broadband and narrowband based on the bandwidth of their spectral response window [22]. The broadband PDs capable to responds over wide range of solar spectrum are typically used for multicolor light detection and imaging. On the other hand, narrowband PDs that are able to detect only selective wavelengths are utilized for intelligent monitoring, biological detection, and security systems. Furthermore, the single junction (homojunction) PDs are fabricated by sandwiching the absorber between the metal electrodes, and heterojunction PDs are formed by depositing different materials over one another, such as perovskite/MOs, dichalcogenide/MOs, p-MO/n-MO, etc. The heterostructure PDs exhibit broadband responsivity and high sensitivity due to improved charged separation. The key parameters to determine the performance of any PD system are responsivity (R), detectivity (D), and external quantum efficiency (EQE). An EQE of >100% desirable for highly sensitive PDs [23] can be achieved by the photomultiplication (PM) phenomenon, which corresponds to the flow of a large number of charge carriers per incident photon across PDs. Further, the charge collection efficiency of the photogenerated electrons and holes depends on the built-in potential, which is tailored by doping, forming heterostructures, and the work function of the metal electrodes in symmetric and asymmetric device configuration. However, an additional bias voltage needs to be applied to enhance the charge collection efficiency. Self-biased PDs that give photo response by collecting charges without any bias potential, are crucial for remote sensing applications.

1.2.3 Photoelectrochemical water splitting

H₂ fuel, which can easily be stored and transferred in gaseous form, has very high energy density (~three times) compared to other fossil fuels, which makes it more efficient than coal and natural gas [24, 25]. Currently, several processes, such as methane cracking, catalytic steam reforming, gasification, and partial oxidation of

heavy oil, etc., employed for H_2 production rely on natural gas, coal, and other fossil fuels, releasing harmful greenhouse gases during the production of H_2 fuel [26]. The purity of H₂ is the main concern for these techniques, and therefore, finding environmentally benign, sustainable, and renewable approaches to produce highquality H_2 fuel is of scientific importance. Electrochemical, photocatalytic, and photoelectrochemical (PEC) water splitting has the potential to address these issues for green H_2 production. Two half-reactions, i.e., hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) take place at cathode and anode, typically liberating H_2 and O_2 , respectively. [27]. However, most of H_2 is produced by steam reforming (47%) followed by partial oxidation of oil (31%) and gasification (18%), and only 4% of H_2 is currently produced by water splitting. Therefore, increasing the production of H₂ fuel by employing renewable energy sources is timely need. Presently, electrocatalysis is suffering from significant overpotential and limited selectivity for the oxygen evolution reaction (OER) despite the use of noble metals as catalysts [28]. Likewise, photocatalytic water splitting is significantly challenged by unfavorable thermodynamics, slow kinetics (particularly for the OER), dissolved oxygen, and severe reverse reactions [29]. Therefore, the sustainable and eco-friendly PEC water splitting technique, which is known for high energy conversion efficiency, carbon-free hydrogen generation, scalability, versatility in electrode materials, and the use of abundant solar energy as a feedstock, is occupying the desks of various laboratories. The three fundamental steps of PEC water splitting are (a) absorption of incident light, (b) separation of charge carriers, and (c) charge injection through electrolyte. The photogenerated charge carriers (e^--h^+ pairs) diffuse to the electrode surface and flow through the external circuit as well as the electrolytic medium to participate in the water electrolysis. Therefore, efficient charge separation and reduced interfacial recombination determine the efficiency of the PEC cell. Further, high photoactivity of electrodes lead to more generation of charge carriers, thus enhancing the PEC performance [24]. Typical PEC water-splitting cell is the three-electrode assembly of a working photoelectrode (WE), counter electrode (CE), and reference electrode (RE). The OER and HER half-reactions take place at WE and CE, respectively, and are expressed as follows,

In acidic electrolyte,

$$2H_20 + 4e^- = 4H^+ + O_2 \uparrow \tag{1.1}$$

$$4H^+ + 4e^- = 2H_2 \uparrow \tag{1.2}$$

In alkaline medium,

$$40H^{-} = 2H_20 + 4e^{-} + O_2 \uparrow \tag{1.3}$$

$$2H_2O + 4e^- = 4OH^- + 2H_2 \uparrow \tag{1.4}$$

The photogenerated e^-h^+ pair takes part in these half-reactions in acidic or alkaline electrolytes to evolve H₂ and O₂. The h⁺ generated at the photoanode (WE) oxidizes the water molecule to generate H⁺ ions and liberate O₂. These H⁺ ions travel through the electrolytic medium towards the Pt electrode. Conversely, the photo-generated e⁻ will travel to CE (Pt) through an external circuit and react with H⁺ ions. The complete reactions for PEC water splitting are given by Eq. 1.5-1.8.

$$Photoanode + h\nu \to (e^- + h^+) \tag{1.5}$$

$$H_2 O + h^+ \rightarrow H^+ + O_2 \uparrow \qquad (at anode) \qquad (1.6)$$

$$H^+ + e^- \rightarrow H_2 \uparrow \qquad (at cathode) \qquad (1.7)$$

$$2H_2 O \rightarrow 2H_2 + O_2 \qquad (overall reaction) \qquad (1.8)$$

Overall, PEC water splitting is a cost-effective and renewable technology for generating green hydrogen fuel. The complete mechanism of PEC water splitting is shown in Fig. 1.2.



Fig. 1.2. Schematic of PEC water splitting mechanism.

1.2.4 Photocatalytic dye removal

Every year, approximately 100,000 tons of dyes are discharged into effluents due to dyeing and finishing inefficiencies, accounting for ~20% of total water pollution

[30]. Extreme pollution is caused by industrial release, particularly by industries that emit persistent and toxic effluents. As a result, millions of people worldwide consume severely contaminated drinking water, putting them at risk of variety of diseases and severe health problems, including carcinogenic and mutagenic. Among several classified dyes, the most commonly used organic azo dyes share $\sim 60\%$ of total dye usage [31]. Furthermore, the wastewater contains textile pigments and dyes that are extremely colorful and have a high amount of total organic carbon (TOC), suspended particles, chemical oxygen demand (COD), and biological oxygen demand (BOD). These can block the effective penetration of light into aquatic, causing a disturbance in photosynthesis activity [32]. Considering these issues, it has become critical in today's world to address the problem of textile wastewater pollution by developing efficient wastewater treatment technologies. Over the years, various methods have been invented to accomplish this. Traditional physical techniques include reverse osmosis, ion exchange, membrane filtration, and activated carbon adsorption. However, these techniques do not degrade toxic organic dye molecules completely but rather transfer them from one medium to another, resulting in secondary pollution [8]. Biological methods, including the degradation of dye molecules into non-toxic byproducts using enzymatic decomposition or yeast or fungi-assisted decomposition, suffer from disadvantages like the requirement of specific reaction conditions being totally reliant on the use of living microorganisms for the dye treatment. Other methods used for the removal of dye molecules include ozonation, Fenton processes, photochemical oxidation, electrochemical destruction, and advanced oxidation processes (AOP) [31]. Among all these methods of dye degradation, the photocatalytic AOP, which relies entirely on a renewable source of energy, i.e., natural sunlight, offers several merits like complete detoxification of organic molecules, low cost, and sustainable [33]. The basic principle of photocatalytic dye degradation involves the utilization of UV or visible light to produce highly reactive oxygen species (ROS), which act as powerful reducing or oxidizing agents to degrade organic dye molecules into less harmful and eco-friendly byproducts. Photocatalysts can degrade the complex and persistent organic compounds found in textile dye effluent, which are difficult to eliminate using

conventional wastewater treatments [34]. The schematic of the photocatalytic dye degradation process is shown in Fig. 1.3.



Fig. 1.3. Schematic of mechanism for photocatalytic degradation of organic dyes [7].

1.3 Role of metal oxides for green energy applications

Metal oxides (MOs) are chemical compounds formed by metal cations and oxygen anions. Depending on the close-packed array of metal and oxygen ions, these MOs can have cube, tetragonal, orthorhombic, hexagonal, monoclinic, etc., crystal structures. Their physicochemical and optoelectronic properties can be controlled through chemical composition by altering the oxidation states (which typically vary between +1 to +6 for different elements) and type of bonds (ionic, covalent, etc., between metal and oxygen ions) and, therefore, extensively investigated for multifunctional applications. Among the most studies metal oxides, the oxides of Sn, Ti, Fe, W, Ba, Zn, Ni, Cu, etc., provide excellent control optoelectronic and physicochemical properties. Further, their nanostructured morphology offers a high surface-to-volume ratio, better charge transportation properties, higher active sites, and control over the optoelectronic properties [35]. The controlled optical bandgap of these MOs allows the harvest of solar energy in various forms and hence has been explored for applications in energy conversion, light sensing, and wastewater purification [20, 36-38].

1.3.1 Charge transport layers in solar cells

The main component of solar cells is the light absorber layer that utilizes incident photons to excite the e^- from VB to CB, thus generating e^--h^+ pairs, which need to be separated for the generation of electricity. In PSCs, various metal oxide charge

transport layers (MOCTLs) have been used to transport the photogenerated electrons and holes from light absorber material. MOCTLs/perovskite interface and band energy of MOCTLs with perovskite light absorber are crucial to achieving highly efficient PV cells. The schematic representation of the working of PSCs is depicted in Fig. 1.4. These CTLs will allow smooth extraction of photogenerated electrons and holes [39]. The MOCTLs allow complete visible light to irradiate onto the perovskite absorber. Moreover, MOCTLs absorb UV radiation, thus optically protecting the perovskite layer from UV degradation. Further, the existence of impurities, defects, and non-uniformity within MOCTLs hampers the device's performance. The presence of oxygen vacancies in MOCTLs will create deep or shallow energy levels that act as recombination centers [40]. Therefore, selecting suitable MOCTLs having charge mobilities comparable to absorbers with minimal defect sites is crucial for lower recombination and better device performance. The optoelectronic properties of MOCTLs can be engineered by preparing core-shell heterostructure and nanocomposites and substituting a suitable dopant to minimize charge recombination [41-44]. Various MOs have been explored to transport charge carriers from perovskite absorbers to metal contacts. The optical bandgap and energy alignment of the MOCTLs with light harvester are crucial prerequisites for constructing a functional device [45]. The wide optical bandgap of the MOs allows complete transmission of visible spectra on the perovskite. Moreover, the MOCTLs should be earth-abundant and easy to synthesize with high chemical and thermal stability. These MOCTLs can be categorized into electron transport layers (ETLs) and hole transport layers (HTLs).



Fig. 1.4. Schematic of working principle of a PSC with charge transport layers [39].



Fig. 1.5. Schematic representation of band-energy alignment of various ETLs with MAPI light harvester [20].



Fig. 1.6. Schematic representation of band-energy alignment of various HTLs with MAPI light harvester [20].

Oxides of several metals like Tin (Sn) [46], Tungsten (W) [47], Zinc (Zn) [48], Titanium (Ti) [49], Strontium (Sr) [50], Barium (Ba) [51], Iron (Fe), Indium (In), and Aluminium (Al) has been as an efficient ETLs for high-performance PSCs [52]. The band energy alignment of various MOs as ETLs is represented in Fig. 1.5. These ETLs can be used in a variety of morphological forms and have the capability to alter the charge carrier dynamics. Further, these ETLs will provide a favorable template with better interfacial characteristics to the perovskite absorber layer. Similar to ETLs, several inorganic semiconductors have been extensively utilized as HTLs for PSCs.

The band energy alignment of various inorganic HTLs with perovskite absorbers is represented in Fig. 1.6. The inorganic HTLs are more economical and have superior stability over organic-based HTLs [53]. Therefore, several inorganic HTLs such as NiO, CuO, VO_X, CuI, CoO_X, and CuSCN [52, 54-56] have been engineered to tailor charge carrier dynamics for efficiently extracting the photogenerated holes in the PSCs.

Among these ETLs, zinc oxide (ZnO), an n-type semiconductor, offers high crystallinity at low processing temperature and favorable band alignment with hybrid perovskite. A direct bandgap of ~3.2 eV, the electron mobility of 205–300 cm²/Vs, and an electron diffusion co-efficient of 1.7×10^{-4} cm²/s are the other major characteristics of ZnO attracting research to explore it as a potential ETL to improve the PSCs performance [20, 57]. Various methods have been explored widely to process and coat ZnO films under ambient atmosphere, and each method provides a unique way of controlling the structure, electronic properties, and surface defects, which strongly affect the charge carrier transfer at the ZnO/perovskite interfaces [48, 58]. Furthermore, various morphologies (nanorods, nanosheets, monolayers, nano-flowers, etc.) of ZnO have been explored to improve charge carrier collection efficiency at this interface. A simple and cost-effective approach to process the ZnO hole-blocking layer is repeated spin coating of ethanol mixed solution of zinc acetate as a precursor with intermediate drying to achieve the desired thickness [59]. Son et al. [48] introduced the Solution-Immersion Method for one-dimensional (1D) ZnO nanorods as an ETL to use in PSCs, which resulted in faster charge collection efficiency, leading to improved efficiency than that of TiO₂ nanorods as ETL. The single-crystalline 1D ZnO nanorods offered smooth charge transfer across the ZnO/perovskite interface due to an internal electric field along the c-axis, i.e., common growth direction for ZnO nanorods and absence of grain boundaries [60]. The compact and uniform planar ZnO films have indeed delivered relatively high-efficiency solar cells.

Tseng et al. [61] produced uniform ZnO films using RF sputtering under pure Argon (Ar) and Ar+O₂ working gas to tune the surface electronic properties that resulted in downshifting of band structure, improving the electron injection and rendering ~16% efficiency combined with methylammonium lead iodide (i.e., MAPbI). However, since the high-energy ions used during sputtering damage the substrate and deteriorate the

ZnO film quality; therefore, ALD has been utilized to obtain high-quality ZnO films [62]. The optimized thickness of 30 nm for ALD grown ZnO films attained high V_{OC} (i.e., 0.97 V), FF (i.e., 48%), and J_{SC} (i.e., 14.15 mA/cm²) of the PSCs. The study revealed a better excitation dissociation rate at the ZnO/perovskite interface, hinging on the exciton lifetime and photo-induced absorption strength. Nevertheless, an increase in thickness beyond 30 nm caused high series resistance, and the performance of PSCs decreased. Apart from this, the spray coating technique is also explored for the mass production of planar ZnO films over a larger area [63]. Hydrothermally grown 1D hexagonal ZnO nanorods exhibited high charge conduction due to their sparsely populated conduction band and showed a good agreement between experimentally measured JSC and integrated current density calculated from external quantum efficiency [48].

The two major drawbacks of the ZnO ETLs are the severe charge recombination at the ZnO/perovskite interface due to the high-density of surface defect states and the poor chemical stability due to the presence of hydroxyl group as well as organic residual on the surface of ZnO, which deteriorate cell efficiency. Notably, the presence of volatile organic residue on the surface of ZnO grants penetration to atmospheric water/oxygen at the ZnO/perovskite interface and degrades the perovskite, leading to operational instability of PSCs [64]. It has stimulated researchers to investigate other possibilities of ZnO surface control on the interface stability. The chemical behavior of the ZnO surface, basic in nature, is responsible for the deprotonation of methylammonium cation to form methylamine through an acid-base reaction, which leads to the perovskite undergoing thermal decomposition even in the absence of hydroxyl group and residual organic ligand at the ZnO surface [65, 66]. Density functional theory (DFT) calculations for the geometry optimization of the ZnO/perovskite structure have revealed that the deprotonation of methylammonium ion is a constructive guide to develop the PSCs capable of withstanding harsh temperature conditions. Moreover, creative strategies such as doping and surface passivation of ZnO have been effectively used to achieve excellent performance as ETL in PSCs. Both planar and nanostructured ZnO ETLs were doped with elements like Mg [67], Al [68, 69], I [70], Ag [71], Ga [72], and Sn [73], etc., to develop low defect sites, larger surface

area, and rapid electron extraction, which are some of the prerequisites for efficient ETLs. Apart from this, recently, the ZnO surface was modified with methylammonium chloride (MACl) [74], carbon nanotubes (CNTs) [75], and ethylenediamine tetraacetic acid (EDTA) [76] to eliminate the deprotonation ability and achieved enhanced stability of the ZnO/perovskite interface.

Separately, the most widely studied optoelectronic material, aluminium-doped ZnO (i.e., AZO), is put forth as an ETL as well as the transparent conducting electrode in PSCs, which has also improved thermal stability by decreasing Lewis acid-base chemical reaction at ZnO/perovskite interface [69]. The monolayer of Cs and Li-doped ZnO as ETL in PSC has delivered PCE of 18% that is comparable to well-accepted TiO₂, which is attributed to increased electron density due to decrease in trap density by reducing oxygen vacancies at the ZnO surface [77]. The doping of iodine serves to render dense growth of ZnO:I nanopillars and leads to matching work functions between ETL and perovskite, which results in a PCE of around 18% [70]. The doping of ZnO [78] is a common and effective approach to fine-tune the position of Fermi level (EF) and band structure and increase the conductivity to avoid interface charge recombination by achieving optimized CB edge difference between ZnO and perovskite. However, the surface passivation strategy helps to enhance thermal stability during annealing [79], improving the morphology of the perovskite layer [80] and reducing the back electron transfer and charge recombination [60]. ZnO ETLs passivated with thin layers of MgO [81], TiO₂ [79], Zn₂SnO₄ [82], Nb₂O₅ [80], SnO₂ [60], etc., were used to limit the degradation of perovskite absorber due to surface defects of ZnO at the perovskite/ZnO interface. The well-optimized passivation of ZnO with TiO₂ using the wet chemical approach of the layer-by-layer absorption and reaction (LBLAR) method [83] achieved an efficiency of ~13.5% with better long-term stability as compared to un-passivated ZnO NRs.

Overall, the degradation and thermal decomposition of perovskite due to the ZnO surface prevents long-term stability and outdoor applications of ZnO-based PSC devices. Therefore, more efforts by the broader research community are required to search for novel ways other than passivation that can stop the deprotonation of methylammonium and also provide smooth charge transfer across the ZnO/perovskite

interface. The comparison of performance parameters of various PSC devices with ZnO as ETLs is tabulated in Table 1.1.

S.N.	Device Configuration	Voc	Jsc	FF	PCE	Ref.
		(V)	(mA/cm ²)		(%)	
1.	FTO/ZnO/2-	1.16	22.9	0.77	20.6	[84]
	$TA/Cs_{0.05}(FA_{0.9}MA_{0.1})_{0.95}PbI_{2.55}Br_{0.45}/$					
	Spiro-OMeTAD/Au					
2.	FTO/AZO/CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD:	1.05	23.16	0.74	18.1	[85]
	Li-TFSI:TBP/Au					
3.	FTO/Mg:ZnO/CH ₃ NH ₃ PbI ₃ /Spiro-	0.83	25.06	0.65	13.5	[86]
	OMeTAD: Li-TFSI:TBP/Au					
4.	ITO/ZnO/ZnO-Cl-Phen/FA _{0.9}	1.16	22.88	0.80	21.1	[87]
	$Cs_{0.1}PbI_{2.7}Br_{0.3}/Spiro-OMeTAD/Ag$					
5.	FTO/ZnO/ZnS/TiO2/Spiro-OMeTAD/Au	1.12	24.07	0.77	20.6	[88]
6.	FTO/ZnO/IBA/CH3NH3PbI3/Spiro-	1.12	21.93	0.75	18.8	[89]
	OMeTAD/Au					
7.	FTO/MLG/ZnO/FAxMA1-xPbI3-yBry/Spiro-	1.15	23.42	0.78	21.0	[90]
	OMeTAD/Au					
8.	FTO/ZnO-MgO-	1.12	23.86	0.79	21.1	[81]
	EA+/TiO2/(CsFAMA)Pb(BrI)3/spiro-					
	OMeTAD/Au/Graphene					
9.	ITO/ZnO-K/CH ₃ NH ₃ PbI ₃ /spiro-	1.13	23.0	0.77	19.9	[91]
	OMeTAD/Au					
10.	ITO/c-ZnO/ZnO:I/CH ₃ NH ₃ PbI ₃ /Spiro-	1.13	22.42	0.72	18.2	[70]
	OMeTAD/Ag					
11.	ITO/AZO/CH ₃ NH ₃ PbI ₃ /spiro-OMeTAD/Ag	1.07	21.5	0.73	17.6	[68]
12.	ITO/Mg-ZnO/CH3NH3PbI3/Spiro-	1.07	20.6	0.74	16.5	[67]
	OMeTAD/Ag					
13.	PEN/ITO/ZnO/CH3NH3PbI3/PTAA/Au	1.10	18.7	0.75	15.6	[92]
14.	ITO/PEDOT:PSS/CH3NH3PbI3/ZnO/Ag/Al2	1.02	20.73	0.76	16.5	[93]
	O ₃ -PET					
15.	ITO/c-ZnO/CH ₃ NH ₃ PbI ₃ /spiro-	1.03	20.4	0.75	15.7	[94]
	OMeTAD/Ag					
16.	FTO/c-ZnO/ZnO NR/CH3NH3PbI3/spiro-	0.991	20.08	0.56	11.1	[48]
	OMeTAD/Au					
17.	$FTO/ZnO/CH_3NH_3PbI_3/spiro-OMeTAD/Au$	1.02	16.98	0.51	8.9	[95]

Table 1.1. A brief comparison of performance parameters of ZnO ETLs-based PSCs.

1.3.2 Photodetector

Depending on the optical bandgap, various materials have been explored to detect a wide range of spectra. Several MOs such as titanium oxide (TiO_2), tin oxide (SnO_2), zinc oxide (ZnO), gallium oxide (Ga₂O₃), etc., are commonly used to detect ultraviolet (UV) range of spectrum due to their wide optical bandgap [96]. Further, to detect the visible spectrum range, MOs having low optical bandgap, such as tungsten oxide (WO₃), bismuth oxide (Bi₂O₃), etc., have been explored [97]. Moreover, various morphological forms are also explored to achieve good photo-response. Tunable optoelectronic properties of MOs by employing doping or oxygen vacancies allow to achieve higher photodetection ability [37, 98]. The 1D ZnO has caught the attention of PD applications due to its excellent charge transportation ability [99]. The light induce conductivity in ZnO nanowire (NW) provides the ability to switch between ON and OFF states with high sensitivity and excellent wavelength selectivity [100]. The PDs of Pt metal decorated ZnO NWs using the focused ion beam (FIB) exhibit a high gain of $\sim 10^8$ and, thus, high photodetection ability [101]. Several dopants, such as Al and Cu, have been introduced within the ZnO nanostructure to enhance the photodetection ability further [102, 103]. Moreover, the heterostructure of ZnO with Cu₂O leads to the formation of a self-powered p-n junction PD. The p-n junction provides a wide spectral response and generates a high built-in field of 2.2 eV [104]. However, the inability of MOs to absorb infrared (IR) light forced researchers to look for other materials to detect the IR spectrum range.

Antimony triselenide (Sb₂Se₃), an earth-abundant and non-toxic p-type photo absorber semiconductor material having a high absorption coefficient of $\sim 10^5$ cm⁻¹ and a low optical bandgap of ~ 1.1 eV, has been extensively used for Visible to IR light detection [105]. Thermally deposited Sb₂Se₃ thin film over silicon Nitride (Si₃N₄, (100)) substrate results in highly responsive PD. The self-powered PD exhibits a high responsivity of 0.924 A/W [106]. Hydrothermally grown single crystalline Sb₂Se₃ NWs exhibit a high responsivity of 8 A/W. The 1D morphology of Sb₂Se₃ provides better charge separation, which results in a lower response time of 300 ms [107]. Further, to enhance the photo-response, heterostructure with wide bandgap MOs has been investigated for self-powered PD applications. The thin film of MOs acts as a buffer layer, which assists in charge transportation and enhances the photo-response of the PDs. The vapor transport deposited Sb₂Se₃ over the spin-coated film of the SnO₂ buffer layer forms ITO/SnO₂/Sb₂Se₃/Au device architecture. The SnO₂/Sb₂Se₃ heterostructure results in highly responsive (0.312 A/W) PD [108]. Similarly, flexible and self-powered PD by thermally deposited films of ZnO and Sb₂Se₃ exhibits excellent performance by showing ultrabroad response with a high responsivity of 77.66 mA/W and detectivity of 2.45×10^{11} jones [109]. Therefore, exploration of the heterostructure of ZnO and Sb₂Se₃ for the applications in PD is a timely need. The PD performance of some selective heterostructures of various MOS and metal dichalcogenides are listed in Table 1.2 for better understanding of their responsivity and detectivity.

S.N.	Device architecture	Incident	Intensity	Responsivity	Detectivity	Ref.
		light (nm)	(mW/cm ²)	R (mA/W)	D (Jones)	
1.	FTO/β-Bi ₂ O ₃ /Pt	365-850	-	29.92	7.46×10 ¹⁰	[97]
2.	Si/Cu-ZnO/Au	365	10	10000	-	[102]
3.	ITO/Cu ₂ O/ZnO	380	-	240	-	[104]
	NR/Pt	450		60		
4.	Si ₃ N ₄ /Sb ₂ Se ₃ /Pt	532	0.05	346	1.0×10^{10}	[106]
		1064		924	2.7×10^{10}	
5.	Si/SiO ₂ /Sb ₂ Se ₃ /Ti/Au	600	-	8000	-	[107]
6.	ITO/SnO ₂ /Sb ₂ Se ₃ /Au	750	-	312	-	[108]
7.	ITO/Sb ₂ Se ₃ /ZnO/Au	905		77.66	2.45×10 ¹¹	[109]
		532	0.1	0.7	~10 ¹²	

 Table 1.2. Comparison of performance of various photodetectors.

1.3.3 PEC water splitting for hydrogen fuel

The abundantly available MOs are ideal candidates for cost-effective photoelectrode, unlike costly Pt electrodes, due to their stable chemical/thermal properties and visible light active optical bandgap. MOs having optical bandgap >1.23 eV are favorable for overall water splitting reaction [36]; nevertheless, band energy alignment is important in deciding the PEC activity. Typically, the CB should be above the H⁺/H₂ reduction potential for H₂ evolution, and the VB should be below the H₂O/O₂ oxidation potential for O₂ evolution. Several binary and ternary MOs have been broadly investigated as photoelectrodes for PEC water splitting (Fig. 1.7). Nevertheless, ZnO nanostructures have been extensively explored for PEC water splitting applications

[110-112] owing to the high electronic mobilities (200-300 cm²/Vs), large exciton BE (60 meV), and high chemical/thermal stability[57]. However, the wide optical bandgap of 3.1-3.4 eV has restricted the photoactivity of ZnO. Therefore, in the quest to enhance the photoactivity of ZnO, various researchers across the globe have incorporated the decoration of plasmonic NPs, doping metals, core-shell heterostructures, and nanocomposite formation. The incorporation of Au and Ag on the ZnO surface induces the plasmonic effect, i.e., surface plasmon resonance (SPR), and assists in enhancing the PEC water splitting performance. Au loading on the tip of ZnO NRs to from matchlike ZnO/Au heterostructure improved charge separation and resulted in enhanced photocurrent of ~9.1 mA/cm² and 16 times higher photoconversion efficiency (0.48%) as compared to pristine ZnO [113]. The core-shell nanoelectrode of ZnO NWs uniformly deposited with thin Fe₂O₃ layer exhibited the shift in onset potential due to n-n heterojunction, which resulted in smooth charge transportation and improved PEC performance. [114] Similarly, the ZnO/ZnS heterostructure grown over a silicon substrate delivered high photocurrent of 1.21 mA/cm² [115].



Fig. 1.7. Energy band alignment of various metal oxide photoelectrodes for solardriven water splitting [36].

The substitution of suitable dopants helps in achieving better PEC performance by shifting the energy band level and lowering the optical bandgap of the pristine ZnO. Several dopants, such as Al, N, Mg, and Sn, have been explored to enhance PEC performance. The Mg-doped ZnO nanostructure results in a longer electron lifetime and improves the stability of the photoanode [116]. The inverse opal structure of Al-doped ZnO increases the charge diffusion length and results in improved PEC activity. The Al-doped ZnO photoanode delivered an excellent photocurrent density of 1.5 mA/cm² [117], which was improved further to 1.87 mA/cm² after Sn and Al co-doping [118]. Likewise, Al-doped ZnO (AZO) acted as a template for the growth of various ZnO nanostructures, further improving PEC activity [119].

S.	Photoelectrode	Electrolyte	Photo-	Donor	Flat band	Ref.
N.			current	density	potential	
			(mA/cm^2)	N_{D} , (/cm ³)	V _{fb} , (V)	
1.	10 % Mg ZnO NRs	0.1 M NaOH	0.35	4.4×10^{21}	1.341	[116]
2.	ZnO pin hole (ZP)	0.5 M Na ₂ SO ₄	0.62	1.1×10^{20}	-0.5	[125]
	Aminated ZP (A-ZP)		1.02	1.7×10^{20}	-0.55	
	ZnO rosette sheets (ZS)		0.76	1.4×10^{20}	-0.5	
	Aminated ZS (A-ZS)		1.27	3.4×10^{20}	-0.55	
3.	ZnO rods	0.5 M Na ₂ SO ₄	0.019	1.8×10^{18}	-0.22	[119]
	AZO flower		0.18	9.0×10 ²⁰	-0.32	
4.	SILAR ZnO NRs	0.5 M Na ₂ SO ₄	0.19	2.2×10^{21}	-0.29	[112]
5.	ZnO NRs	0.1 M KOH	0.17	2.3×10^{20}	-0.11	[118]
	Sn0.05Al0.03Zn0.92O NRs		1.87	4.4×10^{21}	-0.69	
6.	BaSnO ₃ NPs	1 M K ₃ BO ₃	0.81	2.16×10 ¹⁸	-0.52	[123]
7.	BaSnO _{3-δ} NPs		7.32	8.47×10^{18}	-0.24	
8.	BaSnO ₃ NWs	0.35 M Na ₂ SO ₃	0.5	-		[124]
9.	BaSnO ₃ NRs/CdS QD	+ 0.25 M Na ₂ S	4.8			
10.	BiVO ₄ particles		0.53	-	-	[117]
	BiVO ₄ /AZO inverse	H4NaO5P	1.5			
	opal					
11.	Cu ₂ O/SrTiO ₃		2.52	-	0.91	[122]
	microparticle					

Table 1.3. Comparison of PEC performance of various MOs based photoanodes.

Moreover, ternary MOs like SrTiO₃, KTaO₃, and BaSnO₃ have been investigated for solar water splitting due to suitable CB and VB potentials [120]. Several dopants and core-shell nanostructures with other MOs are also investigated for PEC water splitting [121]. The nanostructured film of Cu₂O/SrTiO₃ heterostructure delivers an excellent photocurrent of 2.52 mA/cm², which is 25 times higher than that of pristine Cu₂O film. The enhanced charge separation due to the difference in the electronic mobility of SrTiO₃ and Cu₂O results in enhanced photocurrent [122]. Similarly, BaSnO₃ shows excellent solar water splitting activity due to high electronic mobility and appropriate band offset potentials. The oxygen vacancies introduced within the BaSnO₃ nanostructure tune the band structure and result in an enhanced photocurrent of 7.32 mA/cm² [123]. Further, the QDs of CdS decorated over BaSnO₃ nanowires improve the effective charge separation, which results in an enhanced photocurrent of 4.8 mA/cm² [124]. The performance of various MOs photoelectrode for solar water splitting is tabulated in Table 1.3.

1.3.4 Photocatalytic dye degradation

The photocatalytic removal of azo dyes requires reactive oxygen species (ROS) to degrade the dye molecule. The ROS, i.e., h^+ , $\cdot OH^-$, and $\cdot O_2$ radicals, are typically generated by the dissociation of H_2O molecules in the presence of photogenerated charge carriers. The photocatalytic effect observed in TiO_2 is considered one of the milestones in this field. Therefore, the scientific community started hunting various catalysts in the domain of water purification by means of dye degradation and water splitting. The binary MOs semiconductors like zinc oxide (ZnO), tungsten trioxide (WO_3) , zirconium oxide (ZrO_2) , manganese oxide (MnO_2) , tin oxide (SnO_2) , and titanium oxide (TiO_2) are utilized for photocatalytic dye removal owing to their merits like low cost, easy availability, good photo-oxidation ability, higher efficacy, nontoxicity, and ecofriendly nature [126]. However, the main drawback in utilizing these MOs is their wide optical bandgap (2.4-5 eV), which makes them active only in the UV spectrum, allows photo corrosion, and is not applicable for dye degradation at various pH ranges. Therefore, to enhance the photocatalytic performance of MOs and make them active in visible light, various strategies are employed, which include doping with rare earth, nanocomposites, heterostructures, and morphology engineering [127-129]. The MOs are doped with numerous rare earth metals like Ce, Er, Yb, La, and Gd to introduce defects for oxygen vacancy formation, which lower the optical band gap in the visible region [130]. The photocatalytic degradation efficiency was studied for coprecipitation synthesized pristine ZnO and La and Gd co-doped (Gd/La@ZnO) nanoflowers for the rhodamine B (RhB) dye degradation under direct sunlight illumination. Gd/La@ZnO delivered 91% degradation in 100 min., which is much higher than the pristine ZnO (20%) [131]. Further, the photocatalytic degradation activity of toluidine blue O (TBO) organic dye was analyzed in the presence of the Ce³⁺ and Eu³⁺ doped TiO₂ nanowire arrays. The >90% degradation observed in 80 and 120 min for Ce³⁺@TiO₂ and Eu³⁺@TiO₂, respectively, was attributed to the large aspect ratio providing more active sites for photocatalytic activities [132]. Similarly, Smdoped ZnO nanofibers showed excellent degradation activity for Congo red (CR, 95.8% in 240 min) by altering the surface morphology of ZnO with Sm doping concentration [133].

Moreover, composite formation with transition metal oxides and nanostructure of graphene were adopted by the scientific community to reduce the electron-hole pair recombination, improving the optoelectronic properties. In this regard, ZnO QDs/rGO nanocomposite has been utilized for the degradation of Rhodamine 6G (Rh6G), MB, and Safranin O (SO). The composite of rGO sheets with ZnO QDs limits the QDs agglomeration, thus enhancing the effective number of active sites, which resulted in complete dissociation of MB, Rh6G, and SO in 15, 30, and 25 min, respectively [134]. The visible light illuminated degradation of malachite green (MG) and MB was studied using rGO-Fe₃O₄/TiO₂ composite and exhibited 99 and 97% degradation, respectively, which is much higher than that of pristine TiO_2 (~67%). The visible light activity of pristine TiO₂ (~3.2 eV) was significantly improved by lowering the bandgap to 2.6 eV after forming the composite nanostructure [135]. CuO decorated ZnO NRs delivered 98.5% degradation activity in 150 min for MB dye under sunlight and Xenon lamp exposure. The synergistic effect of ZnO and CuO interaction enhanced the photoactivity and resulted in highly stable cyclic degradation performance [136]. Similarly, the core-shell formation significantly improves the photocatalytic activity towards the degradation of organic dye molecules by reducing the recombination of the electron and holes. The hierarchical Ag/diatomite/ZnO core-shell array delivered complete degradation of MB with rate constant of 0.0246 min⁻¹, which is ascribed to

the photonic structure of regular frustules, prohibited oxidization of Ag, and suppressed back electron transfer [137]. A recent study reported 95.11% degradation of RhB dye within 25 min using Ag/ZnO@ZIF-C core-shell, which is ~2.27 times higher than the standard P25. In this ZIF modified in core-shell structure, graphene carbon acts as photoexcited charge bridge, and the synergetic interface between ZnO@ZIF-C and Ag NPs delivers enhanced photocatalytic activity [138].

Among all reported MO catalysts, the ABO₃ perovskite oxides have attracted researchers due to their superior chemical and structural stability, high charge carrier mobility, morphological tunability, ease of synthesis, and modifiable bandgap energy [7]. BaSnO₃, an n-type semiconductor, exhibits excellent photocatalytic activity owing to the wide optical bandgap (\sim 3-3.4 eV), higher electronic mobility (\sim 150 cm²/V·s), better charge separation, suitable CB edge potential (~0.69 V), and a greater number of active sites [124, 139]. Further, high tilting of Sn-O-Sn in SnO_6 octahedra allows charge carriers to migrate easily, which results in higher photocatalytic activity [140]. The creation of oxygen vacancies in the BaSnO₃ crystal due to the substitution of Fe³⁺ at Ba^{2+} site resulted in lowering the optical bandgap and enhanced the visible lightfostered photocatalytic activity, which leads ~93% degradation of Remazol golden yellow (RNL) dye in 240 min [141]. Composite nanostructures of BaSnO₃ with rGO exhibited ~94% degradation of MB dye in 180 min, which is relatively higher compared to pristine $BaSnO_3$ (~46%). The smooth charge transportation at BaSnO₃/rGO due to the higher conductivity of rGO leads to enhanced photocatalytic activity [142]. Similarly, to improve the effective charge separation, TiO_2 was infused with BaSnO₃ nanostructures, which resulted in achieving higher photocatalytic activity. The BaSnO₃/TiO₂@HNTs exhibits ~92% degradation of MB dye in 300 min [143].

1.4 Motivation

(a) MOs have shown great potential for multifunctional applications due to their superior physico-chemical properties and can be easily synthesized in various nanostructured morphologies.

- (b) The one-dimensional (1D) nanostructure has excellent charge transport characteristics along the length due to reduced grain boundaries-assisted recombination and, therefore, can preferably be used for various optoelectronic applications.
- (c) The optoelectronic properties of MOs can be boosted by introducing suitable dopants, forming nanocomposites, and modifying and controlling the defects and interfaces at the nanoscale. Further, the band engineering of these MOs will tailor the CB edge potentials and help in achieving better photocatalytic activity by improving interfacial charge transportation.
- (d) The nanostructured MOs can efficiently harvest solar energy using PEC water splitting, serve as a charge transport/buffer layer in PV cells and PDs, and can be utilized as a photocatalyst for wastewater purification.

Therefore, it is important to investigate the effect of doping and heterostructure formation of the MOs on the performance of solar-driven water splitting for green H_2 production, water remediation, solar cells, and photodetectors.

One of the critical challenges in photovoltaics is developing high-efficiency, cheap, and durable thin-film solar cells. Recently, halide perovskite solar cells have shown tremendous progress with high efficiency. Nevertheless, all high-performing perovskite solar cells contain toxic lead and lack stability. Further advancement in perovskite solar cells requires cautious optimism. Therefore, to explore the thin film solar cells of ZnO and MAPbI₃ and finding alternatives to MAPbI₃ is a timely need. We have introduced a lowcost Cs_2SnI_6 light harvester and various MO charge transport layer based all-inorganic double perovskite solar cells to overcome the downsides of organometallic halide perovskite solar cells. Nevertheless, all high-performing perovskite solar cells contain toxic lead and are prone to degrade due to environmental effects such as temperature, moisture, and UV irradiation, which dissociate the perovskite structure to form PbI₂ at the interfaces, which questions their reliability in real-time performance. Thus, further advancements in perovskite solar cells require cautious optimism. Therefore, we have introduced low-cost all-oxide heterostructure solar cells (AOHSCs) with CuBi₂O₄ (Kusachiite) light harvester and ZnO and other MO transport layers to overcome the downsides of halide PSCs.

Likewise, it is highly desirable to develop robust photodetectors (PDs) that can substantially detect low-intense light and have broadband responsivity, thereby maintaining long-term photoactivity at reasonably good photo-response and recovery. Accordingly, efficient PDs necessarily should possess an effective large surface area, robust charge transport paths, lesser charge recombination, low external bias voltage, and enhanced light harvesting capability. Moreover, considering the commercial aspects, the design and synthesis of the PDs should be simple and eligible for large-area fabrication. Previous reports related to cadmium chalcogenides (viz. CdTe, CdSe, CdS, etc.) PD devices fabricated using combinations of CdS/Sb₂Se₃ indicated excellent device efficiency. However, the toxic nature of cadmium limits its use on a large-scale. Therefore, a heterojunction of several different non-toxic materials combined with Sb₂Se₃ was proposed. Among them, $Sb_2Se_3/AgSbSe_2$ was proposed as alternative, which helped in solving the low intrinsic electrical conductivities of Sb_2Se_3 , thereby enhancing the PD device efficiency and stability. Apart from this, ZnO, when combined with the Sb₂Se₃, indicated an excellent alternative to fabricating photovoltaic devices. However, the important issue that still remains in order to have a perfect PD device is the formation of suitable interfaces. When the semiconductor PD device is developed with the combination of different heterostructures, the surface, and the interface define the functionalities of the device because they provide a potential driving force, which facilitates the separation of photoexcited charge carriers, dominates the transfer direction, increases the contact interface, and accelerates the rate of charge transfer within the heterojunction compartment. Nevertheless, the fabrication of suitable heterostructure in all respects is one of the major challenges that researchers face. Particularly, the nanostructured p-n heterojunction between two semiconductors has been reported as the most challenging. However, if the heterojunctions are properly designed, an effective space charge region can be fabricated owing to the depletion of electrons from the n-type semiconductor and holes from the ptype semiconductor near the interface.

The industrialization of the current technological world demands a continuous supply of fresh water and green energy. Therefore, researchers are exploring hydrogen production and wastewater treatment using solar energy in combination with cost-effective and environmentally friendly photocatalytic materials. The various photocatalytic materials, such as metal oxides (MO), metal sulfide (MS), dichalcogenides, metal-organic frameworks (MOF), etc., have a wide bandgap of ~1-4 eV, are capable of harvesting a wide

range of the solar spectrum, and therefore, extensively engaged for multifunctional photocatalytic applications. However, MOs are given priority due to their environmentally friendly and thermally stable nature and tunable bandgap to harvest solar energy via photovoltaic cells, solar thermal, and PEC water splitting. Several MOs (i.e., NiO, TiO₂, CuO, ZnO, BiVO₄, WO₃, etc.) have also been explored for various sustainable energy applications like solar cells, PEC water splitting, solar steam generation, light sensing, and photocatalytic dye removal. Among these metal oxides, environmentally benign earthabundant ZnO is a promising photoanode for PEC water splitting due to superior optoelectronic properties. An exciton binding energy of 60 meV, an affinity towards various dopants, good mechanical stability, the high electronic mobility of $\sim 300 \text{ cm}^2/\text{V} \cdot \text{s}$, and suitable CB edge potential with H⁺/H₂ offered by ZnO make it promising and versatile candidate for better H_s evolution activity through advancement in PEC water splitting. Additionally, the one-dimensional (1D) morphology significantly enhances its photoelectric performance arises from a blend of factors, including high electron mobility (1D ZnO, 1000 $\text{cm}^2/\text{V}\cdot\text{s}$), a low onset potential, intrinsic stability, and a large surface area. These attributes facilitate visible light activity by multiphoton absorption and scattering effect. The 1D morphology provides a continuous pathway for efficient electron transportation with fewer grain boundaries and surface states, allowing better charge extraction at the electrode/electrolyte interface. The band engineering of ZnO can enhance the electronic conductivity and light harvesting activity, extend the photo-response to visible light, and improve the water-splitting performance, and hence suitable dopants like La, Sn, Al, Mg, and Ga are adopted for ZnO. Moreover, perovskite oxides having a chemical composition of $A^{2+}B^{4+}O_3$ or $A^{3+}B^{3+}O_3$ are also striking for hydrogen and oxygen evolution due to their unique structural and compositional flexibility, offering controlled charge transfer at the interface. The greater charge carrier mobility, lower charge recombination, and higher thermal stability of the ABO₃ materials also make them an ideal contender for photocatalytic water splitting and dye degradation. Ba and Sn based perovskite exhibit excellent electronic mobility due to the Sn(5s) orbitals on the bottom of the conduction band. Furthermore, the optoelectronic properties, i.e., bandgap and electronic mobility of these perovskite oxides, can be engineered through suitable doping and heterostructure for enhanced photocatalytic activity.

1.5 Thesis objectives

The present thesis examines the following objectives. The hydrothermally grown ZnO NRs are used to form a p-n heterojunction with thermally evaporated Sb₂Se₃ NFs for photodetection application. The ZnO NRs were also used as charge transport layer with MAPbI₃ absorber layer to fabricate an HTL free PSC. Moreover, a theoretical investigation has been performed to evaluate the best device configuration of all inorganic double perovskite solar cells and all oxide heterostructure solar cells to find a suitable alternative to the MAPbI₃ absorber. Likewise, La doping was introduced in ZnO nanorods photoanode by hydrothermal method to achieve enhanced photoelectrochemical water splitting performance. Furthermore, perovskite BaSnO₃ NPs were also used for solar-driven water splitting and photocatalytic wastewater purification.

The primary objectives of my thesis work are:

- Low-temperature synthesis of pristine and La-doped ZnO NRs and perovskite BaSnO₃ NPs by cost-effective hydrothermal and co-precipitation methods and further explore their physicochemical, morphological, and optoelectronic properties.
- Investigation on the photovoltaic performance of ZnO NRs with CH₃NH₃PbI₃ absorber layer in FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au device configuration. Further, numerical investigations are performed on ZnO/Cs₂SnI₆ double perovskite and ZnO/CBO all oxide heterostructure solar cells to avoid the degradation of the absorber layer and hence device efficiency by introducing alternative absorber layers to CH₃NH₃PbI₃.
- Formation of heterostructured p-n junction diode using 1D ZnO NRs and 2D Sb₂Se₃ nanosheets and evaluate their light sensing performance.
- Band engineering to probe the physicochemical properties through La doping in ZnO NRs photoanode for PEC water splitting performance.
- Investigations on the PEC performance of BaSnO₃ photoanode for green H₂ and photocatalytic degradation of azo dyes for wastewater purification.

1.6 References

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Chapter 2

Experimental techniques

2.1 Introduction

Higher active surface area and superior optoelectronic properties are essential for various energy conversion and photocatalytic applications. Especially, high surface area and porous structure provide more active sites for catalytic activities, and therefore, synthesizing the nanostructured morphology of MOs is one of the prerequisites for superior solar-driven applications such as PEC water splitting and photocatalytic wastewater treatment. Several methods, like sol-gel, co-precipitation, hydrothermal, etc., have been explored in the past for synthesis of various MO nanostructures to achieve desirable physicochemical and optoelectronic properties. Similarly, thin films of MOs are widely used to form p-n junctions in various optoelectronic devices like solar cells and photodetectors. In this chapter, we discussed various chemical approaches utilized to synthesize MOs nanostructures for solar-driven applications.

2.2 Synthesis techniques

Nanostructures of ZnO and BaSnO₃ are explored for applications in light sensing, solar cells, PEC water splitting, and photocatalytic dye removal. 1D ZnO NRs were grown over the ZnO seed layers. Initially, the spin coating technique was used for the synthesis of ZnO NP seed layer, which was further subjected to grow 1D NRs of ZnO using the hydrothermal method that allows precise control over the nanostructure morphology with ease of operation and reproducibility. Further, the Sb₂Se₃ NFs/ZnO NRs heterostructure has been fabricated by thermally depositing the Sb₂Se₃ NFs over ZnO NRs. The ZnO NRs are used as the efficient charge transport layer for perovskite solar cell applications. Further, Ladoped ZnO NRs are also synthesized using the hydrothermal method. Likewise, BaSnO₃ NPs were synthesized using a cost-effective and low-temperature co-precipitation technique. This chapter details the synthesis and characterization of these MOs.

2.2.1 Synthesis of ZnO seed layer by spin coating

Spin coating is one of the most precise, cost-effective, and productive techniques used for depositing thin films over any substrate, and it often rules out the need for post-deposition heat treatment. It also provides thin, uniform, and multilayer coating of variable thicknesses of a variety of materials [1]. Therefore, the seed layer of ZnO NPs was synthesized using solution solution-processed spin coating approach. The

schematic of the solution process approach is illustrated in Fig. 2.1 (left panel). Zinc Acetate Dihydrate $(Zn(CH_3COO)_2 \cdot 2H_2O, ACS \text{ reagent} \ge 98\%)$ and 2-Methoxyethanol (CH₃OCH₂CH₂OH, Anhydrous, 99%) are purchased from Sigma Aldrich. Monoethanolamine (MEA, C₂H₇NO, extrapure, 99%) was purchased from Sisco Research Laboratories (SRL) Chem. All the chemical precursors were used as received without further purification. Further, all the glassware used for the synthesis of ZnO seed solution was chemically and physically inert. Herein, Zinc acetate was firstly dissolved in 20 ml of 2-Methoxyethanol, and the solution was constantly stirred at 60 °C for 30 min. MEA was added dropwise in Zinc acetate to obtain 1:1 molar ratio, and the resultant solution was reacted at 60 °C under continuous stirring for an additional 2 h to transform solution from milky white to transparent. The seed solution was allowed to age for 24 h prior to use. Subsequently, fluorine-doped tin oxide (FTO) coated glass substrates (Sigma Aldrich) were sequentially ultrasonicated for 5 min each with soap solution, DI water, acetone, and ethanol. After that, 50 μ l of seed solution was spincoated at 3000 rpm for 30 sec on FTO-coated glass substrates with an active area of 1×1 cm² and dried at 130 °C for 10 min. This process was repeated thrice to ensure a uniform, pin-holes free, and compact thin film (seed layer) of ZnO NPs. Finally, the ZnO seed layer coated films were annealed at 400 °C for 30 min in muffle furnace to obtain compact and highly crystalline thin film of ZnO NPs.

2.2.2 Synthesis of pristine and La-doped ZnO NRs by hydrothermal method

Hydrothermal synthesis represents a heterogeneous process of synthesizing inorganic compounds in aqueous systems above ambient temperatures and pressure conditions. The reaction solution is kept in a Teflon liner and sealed packed in a stainless steel (SS) autoclave. The morphological shape and size of the nanostructures can be controlled by adjusting the precursor concentration, reaction temperature, time, and pH of the solution [2]. Here, a low-temperature hydrothermal technique was used for the growth of ZnO NRs over seed layer coated substrates. The schematic representation of the growth mechanism of pristine and La-doped ZnO NRs is depicted in Fig. 2.1 (middle and right panel). The solution for ZnO NRs is prepared by dissolving equimolar (25 mM) amount of Zinc Nitrate Hexahydrate (Zn(NO₃)₂· $6H_2O$, Reagent grade, 98%, Sigma Aldrich) and hexamine (HMTA, $C_6H_{12}N_4$, Extra pure AR, 99.5%,

SRL Chem) in DI water under constant stirring at room temperature. This solution was transferred to Teflon lined autoclave, and the seed layer coated FTO substrates facing downwards were immersed in it. The autoclave was reacted in hot air oven at optimized 90 °C for 2 h to grow ZnO NRs. For the synthesis of La-doped ZnO NRs, various concentrations of 1, 5, and 9 wt.% of Lanthanum Nitrate Hexahydrate (La(NO₃)₃·6H₂O, extra pure AR, 99%, SRL Chem) were mixed with Zinc nitrate solution and HMTA. The solution was then reacted at same optimized conditions of ZnO NRs (i.e., 90 °C for 2 h) to grow La-doped ZnO NRs. After the completion of the reaction, the pristine and La-doped ZnO samples were rinsed thoroughly with DI water and ethanol several times and left to dry in hot air at 80 °C for 2 h. Finally, the samples were annealed at 450 °C for 30 min. in muffle furnace. The 1, 5, and 9 wt.% La doped ZnO samples were coded as 1LZO, 5LZO, and 9LZO, respectively.



Fig. 2.1. Schematic representation of spin-coated ZnO seed layer and hydrothermal synthesis of pristine and La-doped ZnO nanorods (NRs).

2.2.3 Synthesis of Sb₂Se₃ nanoflakes by thermal evaporation method

(a) Preparation of Sb₂Se₃ precursors by electrodeposition and selenization

Electrodeposition is a large-area deposition technique that results in a uniform deposition of MOs and their nanocomposites. This process takes place in a three-electrode electrochemical cell consisting of conducting substrate (working electrode), platinum (Pt) mesh (counter electrode), and Ag/AgCl (reference electrode) electrode. The morphology, uniformity, and thickness of the depositing film can be controlled by optimizing the solution concentration, applied potential, and current. The deposition of desired material occurs through the process of chemical bonding [3]. Here, our aim was merely to produce high-purity Sb₂Se₃

compounds (that were not morphologically or crystallographically controlled), which will play the role of initial (or target) material to produce Sb₂Se₃ crystals on suitable substrates using thermal transfer process in controlled manner. Hence, individual Sb and Se precursors were initially synthesized on a working electrode (Mo/glass) via three-electrode electrodeposition using a VersaSTAT 3 potentiostat system (AMETEK). The electrodeposition of an Sb–Se precursor was carried out at -0.95 V with an electric charge density of 0.5 C/cm² in an electrolyte containing 0.055 M antimony potassium tartrate (K(SbO)C₄H₄O₆·0.5H₂O), 0.045 M selenous acid (H₂SeO₃), and 1 M ammonium chloride (NH₄Cl). Next, additional 3 µm Se layers for copious Se supply were deposited on the Sb–Se coating using a thermal evaporation system. The Sb–Se/Se bi-stacking samples were recrystallized at 350 °C for 1 hr using a rapid thermal annealing (RTA) system in a vacuum (~10⁻³ torr), and excess Se residues were evaporated at 250 °C in a vacuum atmosphere. The schematic representing these steps involved in the synthesis of Sb₂Se₃ precursors is shown in Fig. 2.2.



Fig. 2.2 Schematic representation of synthesis of ZnO/Sb₂Se₃ heterostructure.

(b) Thermal evaporation of Sb₂Se₃ and control of wettability via substrate surface modification

Well-established thermal evaporation process is employed for depositing nanomaterials, where the source material undergoes thermal heating and sublimation (evaporation) using an electric current under high vacuum environment (~10⁻⁵ Torr). The sublime vapor particles move towards the target (substrate) material and solidify in thin films (Fig. 2.2) [4]. In order to get elevated melting points for metals, the boat or coil is electrified with a substantial direct current

(DC). Herein, the synthesized high-purity Sb₂Se₃ was again evaporated onto 1D ZnO NRs at 400 °C using an RTA system in a vacuum. The Sb₂Se₃ flakes were coated on the 1D ZnO NRs, and consequently, these samples were tested for hydrophobic characteristics. The vertically aligned Sb₂Se₃ flake structure was preferentially produced, and their surfaces monotonously exhibited typical hydrophilicity. Usually, it is reported that the crystallographic orientation of Sb₂Se₃ structures shows either hydrophobicity or hydrophilicity. In our case, the deposited sample showed good hydrophilicity.

2.2.4 Fabrication of CH₃NH₃PbI₃ based solar cells

CH₃NH₃PbI₃ was deposited over ZnO NR substrates using a two-step deposition process in ambient conditions. Lead iodide (PbI₂, perovskite grade, 99.99%), N,N-Dimethylformamide (DMF, anhydrous, 99.8%), Dimethyl sulfoxide (DMSO, anhydrous, 99.9%), and 2-Propanol (IPA, anhydrous, 99.5%) are purchased from Sigma Aldrich. Methylamine hydroiodide (MAI, low water content, 99.9%) was purchased from TCI chemicals. 1.2 M solution of PbI₂ was prepared by dissolving 552 mg of PbI₂ in 19:1 (DMF: DMSO) solution. This solution was reacted at 80 °C for 2 h and filtered through 0.45 mm PVDF filter. PbI₂ solution was spin-coated on ZnO NR samples at 1500 rpm for 25 sec. and further dried at 70 °C for 90 sec. PbI₂ coated films were dipped in freshly prepared MAI solution in IPA with 10 mg/ml concentration for 30 sec to obtain deep reddish-brown films and further rinsed in IPA to remove the excess deposition and dried at 100 °C for 30 min. Finally, Au was deposited using a thermal evaporator to form the metal contacts. The schematic of the CH₃NH₃PbI₃ based solar cell is provided in Fig. 2.3.



Fig. 2.3 Schematic of the ambient fabrication process of HTL free ZnO/CH₃NH₃PbI₃ heterostructure perovskite solar cells.

2.2.5 Synthesis of perovskite BaSnO₃ NPs using co-precipitation techniques

(a) Synthesis of perovskite BaSnO₃ NPs

Co-precipitation is an efficient and cost-effective method used for the synthesis of high-purity MOs nanostructure at ambient pressure and low temperatures. This process involves nucleation, growth, and coarsening, followed by the agglomeration process. Numerous nucleation sites create a variety of tiny particles known as insoluble species under supersaturation conditions during the coprecipitation process. The process of aggregation and Ostwald ripening will dictate the morphological shape, size, and characteristics of the nanomaterial [5]. BSO NPs were synthesized using co-precipitation process in hydrogen peroxide solvent. Initially, the stoichiometric amount of 10 mM Barium salt (BaCl₂.2H₂O, extra pure AR, 99%, SRL Chem) was mixed in 50 ml Hydrogen Peroxide (H₂O₂, 30%, AR, Loba Chemie) at ambient conditions. Similarly, 10 mM Tin salt (SnCl₄.5H₂O, 98%, Sigma Aldrich) was also mixed in 50 ml H_2O_2 solution in another beaker, under constant stirring for 30 min at 50 °C to achieve the better solubility of SnCl4 avoiding the impurity phase formation Further, both solutions were mixed together to form homogenous solution of Ba^{2+} and Sn^{4+} ions, and 5 mM citric acid (anhydrous, extra pure AR, 99.5%, SRL Chem) was added slowly and continued to stir for another 30 min. After that, liquid ammonia (NH₃, AR, SRL Chem) was added dropwise to the above solution until pH reached ~10 for precipitation to occur. The precipitated solution was left overnight (12 h) under constant stirring to gain the precipitated powder, which was further washed with ethanol and DI water to remove the impurities. It was successively dried in ambient conditions at 70 °C for 10 h in a hot air oven and then kept for annealing at 900 °C for 3 h in a muffle furnace to form crystalline BSO NPs. Most of the previous reports used expensive and tedious freeze-drying processes to collect BSO NPs. However, here, we gained highly crystalline BSO NPs without any secondary impurities using economical hot air drying. The schematic representing these steps involved in the synthesis of the BSO NPS is shown in Fig. 2.4.

(b) Synthesis of BaSnO₃ NPs thin film

Initially, FTO-coated glass substrates (surface resistivity ~7 \Box /cm², Sigma Aldrich) were sequentially ultrasonicated with soap solution, DI water, acetone, and ethanol for 20 min. each. 20 mg BSO powder mixed with 1 ml of 2-Methoxyethanol (CH₃OCH₂CH₂OH, AR, 99%, SRL Chem) in a glass vial stirred overnight to disperse uniformly was used for thin film formation. 60 µl of this solution was spin-coated over the FTO substrates at 3000 rpm for 20 sec. to gain uniform films (1×1.5 cm²) of BSO NPs. The BSO films prepared were further dried at 140 °C for 15 min. to evaporate the residual solvent. This process was repeated four times to gain uniform BSO films of the required thickness for PEC water splitting analysis.



Fig. 2.4. Schematic representation of co-precipitation synthesis of BaSnO₃ NPs.

2.3 Material characterization techniques

The synthesized nanostructures of ZnO, La-doped ZnO, BaSnO₃, Sb₂Se₃, Sb₂Se₃@ZnO, and organometallic halide perovskite were characterized to evaluate their physicochemical and optoelectronic properties. The X-ray diffraction (XRD) patterns (Empyrean, PANalytical, Cu-Ka) were recorded to investigate the phase purity and crystal structure. Various surface morphologies were confirmed using Field Emission Scanning Electron Microscopy (FESEM, JEOL, JSM-7610 F+). Energy dispersive X-ray spectroscopy (EDX, Oxford Instruments, X-Max^N) was used to characterize the elemental composition of various nanostructures. Absorption and reflectance spectra were recorded using UV–Visible spectrophotometer (Shimadzu, UV-2600) to evaluate the optical bandgap of the materials. Raman spectrum (HORIBA-JY LABRAM-HR) was recorded with an excitation wavelength of 633 nm to investigate the defect level of the pristine and La-doped ZnO samples. The presence of various functional groups was confirmed by the Fourier

transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One). Ultraviolet photoelectron spectroscopy (UPS, AIPES, 40 MeV, 1 = 61Å, and I = 100 mA) was performed to evaluate the fermi level and valance band (VB) edge potential. The oxidation/electronic state and chemical composition were confirmed from X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc. Al-k \Box). N₂ adsorption-desorption isotherm were performed using BET analysis (QUANTACHROME Autosorb iQ2) to evaluate the active surface area and pore size distribution of the BaSnO₃ NPs. Small Angle X-ray Scattering (SAXS, Empyrean-DY2528, Malvern Panalytical) data was analyzed to evaluate the size distribution of BaSnO₃ NPs. Liquid chromatography mass spectroscopy (LCMS, (Bruker Daltonik, micrOTOF-QII) was used to analyze the fragmentation of dye molecules into several intermediates formed during the degradation process. These techniques are widely used in literature; thus, their details are not included in the thesis. However, application-oriented techniques such as photoelectrochemical measurements, photocatalytic dye degradation, photovoltaic measurements, and light sensing analysis are discussed in the following sections.

2.3.1 Light sensing analysis

Light sensing studies of a PD were performed in the ambient environment utilizing a system source meter (2611B, Keithley) in conjunction with a computer to record the electrical signals. An optical chopper was used to cut off the light source periodically. The light intensity was acquired by a lux meter and a laser power meter. Note that for solar irradiance, while measuring the dynamic response of the PD, the light intensity was varied from $0.25 - 1.75 \text{ mW/cm}^2$. On the other hand, in the case of different spectral responses at different wavelengths, the light intensity was 0.15 mW/cm^2 . Capacitance-frequency tests were carried out using a 2611B, Keithley Semiconductor Characterization System with 0 V DC bias and 30 mV AC amplitude for the range of 1 Hz to 1 MHz in darkness. The various performance parameters such as responsivity (R) and detectivity (D) of a PD were evaluated by [6],

$$R = \frac{J_{ph}}{P_{in}} \tag{2.1}$$

$$EQE = \frac{R_{\lambda}}{\lambda} \times 1240 \tag{2.2}$$

$$D = \frac{R}{(2qJ_d)^{1/2}}$$
(2.3)

Where J_{ph} is the photogenerated current density, P_{in} is the incident power, q is the electronic charge, l is the incident wavelength, and J_d is the dark current density.

2.3.2 Photovoltaic studies

The photovoltaic measurements of ZnO/MAPbI₃ based perovskite solar cells were performed using a class AAA solar simulator. The photograph of the class AAA solar simulator is provided in Fig. 2.5. The solar simulator has a spectral response that roughly corresponds to the solar spectrum. A standard solar simulator comprises a xenon lamp as the light source, an AM 1.5 G filter with an intensity of 100 mW/cm², a collimator, and a Keithley meter for measurement. The simulator's design assures a spectrum that closely resembles a blackbody temperature of ~5800 K. In order to determine the performance, we have analyzed the various parameters, such as open-circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF), and power conversion efficiency (PCE), of the solar cell from the I-V characteristic acquired after illuminating the device under the solar simulator [7]. The I-V plot of the solar cell under dark and illumination conditions is shown in Fig. 2.6.



Fig. 2.5 Photographic image of Class AAA solar simulator.

(a) Open circuit voltage (Voc)

 V_{OC} is described as the maximum potential across the solar cell under open circuit conditions, i.e., when the current is 0 A and is expressed as,

$$V_{OC} = \frac{kT}{q} ln \left(\frac{l_L}{l_S} + 1\right) \approx V_{OC} = \frac{kT}{q} ln \left(\frac{l_L}{l_S}\right)$$
(2.4)

(b) Short circuit current (Isc)

I_{SC} is described as the maximum current flowing through the solar cell under short circuit conditions, i.e., when applied bias potential is 0 V and is expressed as, $I_{sc} = I_s (e^{(qV/kT)} - 1) - I_L$ (2.5)

Where, I_S represents the diode current (A), q is the charge of an electron (eV), V is the open-circuit voltage (V), k is the Boltzmann constant $(1.380649 \times 10^{-23} \text{ m}^2 \cdot \text{kg/s}^2 \cdot \text{K})$, T is the temperature (K), and I_L is photogenerated current (A).

(c) Fill factor (FF)

FF is described as the ratio of actual maximum power generated by the solar cell to the ideal power, is expressed as,

$$FF = \frac{V_{mp} \times I_{mp}}{I_{SC} \times V_{OC}}$$
(2.6)

where, I_{mp} and V_{mp} are short-circuit current (A) and open-circuit voltage (V) at maximum power, respectively.

(d) Power conversion efficiency (PCE)

PCE is described as the ratio of output power delivered by the solar cell to the incident power (100 mW/cm^2), is expressed as,

$$PCE = \frac{I_{SC} \times V_{OC} \times FF}{P_{in} \times A}$$
(2.7)

where, P_{in} is incident input power, and A is the active area of the solar cell (cm²).



Fig. 2.6 I-V characteristics of a solar cell under dark and illumination condition [8].

2.3.3 Numerical analysis of PV cells using SCAPS-1D

We have performed a numerical analysis to evaluate the performance of lead-free all-inorganic Cs₂SnI₆ (CSI) double perovskite solar cell (DPSC) with the device architecture as Glass/FTO/ZnO/CSI/HTL/Au. The schematic of device architecture, along with the energy band (EB) level of various layers, is illustrated in Fig 2.7. Moreover, to replace toxic and unstable Pb-based perovskite light harvester, p-type kusachiite CuBi₂O₄ (CBO) absorber layer has been investigated for designing an all oxide heterostructure solar cell (AOHSC) with device architecture Glass/FTO/ETL/CBO/Au (Fig. 2.8). We have modeled and analyzed the device architectures using SCAPS-1D software developed by Mark Burgelman and team. Our study concentrates on exploring the relationship between the geometrical and optoelectronic properties of the absorber and transport layers and the efficiency of heterojunction solar cells. Further, it presents the researchers with guidelines for experimental investigation [9].

The charge transport characteristics are extracted by working out the steady-state Poisson equation for the device arrangement [10].

$$\frac{\partial E}{\partial x} = \frac{\rho}{\epsilon} = -\left(\frac{\partial^2 \psi}{\partial x^2}\right) = \frac{q}{\epsilon} \left[p(x) - n(x) + N_D(x) - N_A(x) + p_T(x) - n_T(x)\right]$$
(2.8)
where, ρ is the space charge density, ψ indicates the electrostatic potential, E

corresponds to the electric field, ϵ is the permittivity of the material, q represents the electronic charge, N_A (N_D) is the acceptors (donors) charge carrier density, and p (n) is the hole (electron) concentration.

Device performance can be modeled and predicted using the continuity and driftdiffusion equations, which describe the charge transport through a semiconductor device stack under steady-state conditions. These are typically represented by two sets of equations for each carrier type, as given by [11],

$$\frac{\partial n}{\partial t} = G_n - \frac{n - n_0}{\tau_n} + \mu_n E \frac{\partial n}{\partial x} + n\mu_n \frac{\partial E}{\partial x} + D_n \frac{\partial^2 n}{\partial x^2} \qquad \text{(for electron)}$$
(2.9)

$$\frac{\partial p}{\partial t} = G_p - \frac{p - p_0}{\tau_p} + \mu_p E \frac{\partial p}{\partial x} + p \mu_p \frac{\partial E}{\partial x} + D_p \frac{\partial^2 p}{\partial x^2} \qquad \text{(for holes)}$$
(2.10)

$$J_n = n\mu_n \frac{\partial E_{Fn}}{\partial x} = q[n\mu_n E + D_n \frac{\partial n}{\partial x}]$$
 (for electron) (2.11)

$$J_p = p\mu_p \frac{\partial E_{Fp}}{x} = q[p\mu_p E - D_p \frac{\partial p}{\partial x}]$$
 (for hole) (2.12)

Where, G_p (G_n) represents the hole (electron) generation rates, p_T (n_T) is the trapped hole (electron), D_p (D_n) is the diffusion coefficient for the hole (electron), τ_p (τ_n) is the hole (electron) lifetime, μ_p (μ_n) represents the hole (electron) mobilities, J_p (J_n) is the hole (electron) current density, and E_{Fp} (E_{Fn}) the quasi-Fermi levels for the hole (electron), respectively.



Fig. 2.7. (a) Device architecture of Cs_2SnI_6 DPSCs used in this study and (b) the band energy level of different layers of CSI DPSCs.



Fig. 2.8 Influence of external factors on perovskite (Scheme 1) and all oxide (Scheme 2) solar cells.

2.3.4 Photoelectrochemical measurements

The PEC water splitting measurements were performed in 0.1M Na₂SO₄ (AR, 98%, SRL Chem) electrolyte of pH ~6.8 using a three-electrode electrochemical cell assembly of BSO NPs photoanode, platinum (Pt), and saturated calomel electrode (SCE) as working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. The schematic of the photoelectrochemical cell is shown in Fig. 2.9(a). The photoanode was irradiated with a 150 W Xenon lamp (PEC-L01) of 100 mW/cm² (1 sun) intensity through a quartz window. Potentiostat (Metrohm Autolab: PGSTAT302N) was used to measure the I-V characteristics under dark and illumination conditions. Chronoamperometry (CA) measurements were performed with an ON/OFF cycle of 40 sec. at the fixed biased potential of 0.3 V. Electrochemical impedance spectra (EIS) were recorded at biased potential of 0.3 V in the frequency range of 0.1 Hz to 100 kHz, and Mott-Schottky (MS) plot ($1/C^2$ vs. bias potential) was evaluated under dark at 1 kHz. To analyze the effective use of the photogenerated e-h pair, the applied bias photon to current efficiency (ABPE) of BSO photoanode was calculated and given by [12],

$$ABPE(\%) = \frac{J_{ph} \times (1.23 - |V_b|) \times \eta_f}{P_{in}}$$
(2.13)

Where, J_{ph} is the photogenerated current density of BSO NPs (mA/cm²), V_b is the applied bias potential (V), η_f is the faradaic efficiency (~1), and P_{in} is the power of incident light (mW/cm²). The Mott-Schottky (MS) plot was analyzed to evaluate the intrinsic properties, namely space charge region (W), flat band potential (V_{fb}), and donor carrier concentration (N_D) of BSO NPs is given by the following equations [13].

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r A^2 q N_D} \left[V - V_{fb} - \frac{k_B T}{q} \right]$$
(2.14)

$$Slope\left(S\right) = \frac{2}{\epsilon_0 \epsilon_r A^2 q N_D} \tag{2.15}$$

$$W = \sqrt{\frac{2\epsilon_0 \epsilon_r}{qN_D} \left(V - V_{fb} \right)}$$
(2.16)

Where, C is the capacitance at the electrolyte/photoanode interface, V is the biasing potential, ϵ_0 is the dielectric permittivity of space, ϵ_r is the relative permittivity, A is the surface area of the photoanode, k_B is the Boltzmann's constant, q is the electronic charge, and T is the operating temperature.



Fig. 2.9. Schematic representation of (a) PEC water splitting and (b) photocatalytic dye degradation setup.

2.3.5 Photocatalytic dye removal measurements

The photocatalytic dye degradation activity of BSO NPs was evaluated for the MB and CV dyes under the Xenon lamp ($\lambda = 100-1800$ nm, 300 W) in laboratory scale photochem reactor. The schematic of the photochem reactor is shown in Fig. 2.9(b). More experimental details are provided in our earlier published articles. To achieve adsorption-desorption equilibrium, the catalyst was mixed with dye solution and stirred constantly for 60 min. under dark and then exposed for photocatalytic reaction. The catalyst dose was first optimized for 10 ppm MB dye and further reacted with 20 and 30 ppm dyes. The degradation performance was approximated at regular intervals by examining the changes in UV-visible absorbance spectra of the dye solution. The scavenging study was performed to identify the role of active radicals like photogenerated holes (h^+), hydroxyl radicals ($\cdot OH^-$), and superoxide radicals ($\cdot O_2^-$) on the photocatalytic degradation performance [14]. Further, plausible degradation pathway for the MB dye was proposed from the byproducts examined at various stages of degradation using Liquid Chromatography Mass Spectrometry (LCMS, micrOTOF-Q II, Bruker Daltonik). The degradation efficiency of dye was calculated from the UVvisible spectra using the equation,

Dye degradation (%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (2.17)

$$\ln(\frac{c_t}{c_0}) = -k_{obs} t \tag{2.18}$$

Where, C_0 is the initial dye concentration before light irradiation, C_t is the dye concentration after continuous light irradiation for t interval of time, and k_{obs} is the rate constant of pseudo-first-order reaction kinetics. The Langmuir-Hinshelwood kinetics model utilized for better comparison of dye degradation signifies the pseudo-first-order reaction kinetics for photocatalytic dye degradation [15].

2.4 References

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Chapter 3

ZnO nanorods as charge transport layer for perovskite solar cells

3.1 Introduction

Efforts have been made in recent years to discover alternative sources of clean and affordable energy to meet the growing global energy demands [1, 2]. While crystalline (mono/poly) silicon initially dominated the commercial photovoltaic industry, various PV energy conversion technologies have been developed to economically address future needs [3]. Recently, hybrid lead halide perovskites have shown potential as efficient alternatives to traditional solar cells due to their intrinsic optoelectronic properties, such as better light harvesting, long and balanced carrier diffusion lengths, alterable absorption via halide composition engineering, low density of traps within bandgap, and low exciton dissociation barrier [4-6]. Despite several advances in perovskite solar cells (PSCs) to improve the power conversion efficiency (PCE) to 25.8 % [7], interfacial recombination and obstacles to charge transport caused by perovskite degradation or the formation of secondary phases (e.g. PbI₂ and perovskite-hydrate phases) [8, 9] are limiting their practical feasibility. Therefore, exploring more stable and environment-friendly alternatives to leadbased hybrid perovskites as light-harvesting materials in PSCs is of prime importance [10-13]. The tin (Sn) based halide perovskites are one of the many alternative to lead (Pb) based perovskite for PV application [14-17]. CsSnI₃ has immense potentials to deliver competitive PCE, but suffers from the stability issue of Sn^{2+} ions, which readily oxidize into more stable Sn^{4+} ions [18]. The cubic phase Cs_2SnI_6 (CSI) has attracted widespread attention, which is a non-toxic and air-stable Sn-deficient derivative of the CsSnI3 perovskite phase [19]. This is mainly due to stable tetravalent Sn⁴⁺ and stronger Sn-I covalent bonds compared to CsSnI₃, offering relatively superior stability to the CSI under ambient conditions. Therefore, pristine and doped CSI perovskite delivering excellent optoelectronic properties has been examined for applications in alternative PV technologies [16], photodetector [20], photo-electrochemical water splitting [21], and solar cells [22]. Along with the light harvesters, charge (electron/hole) transport layers are obligatory for effective charge extraction. Wide bandgap semiconductors with appropriate work functions compared to halide perovskites deliver excellent optoelectronic properties, exist in numerous morphological forms that allow efficient light harvesting, and are widely used as electron transport layers (ETLs) and hole transport layers (HTLs) in solar cells. Oxides of Tin (SnO_X), Titanium (TiO_X) and Zinc (ZnO) are commonly used as ETL in thin

film PVs because of their interesting optoelectronic properties such as low trap assisted recombination, high conductivities and mobility.[23-27] Among these, the intrinsic charge carrier mobility (205-300 cm²/V·s) of ZnO is reasonably high to yield efficient charge transport at low recombination rates[25] and on coupling with CSI absorbers, it offers a low interfacial energy barrier at the interface.[28] Therefore, this study used ZnO as an ETL (Fig. 2.7(a)). Just as important, the Hole Transfer Layer (HTL) is necessary to create directional flow of holes (via filtering electrons due to energy alignment) to top Au electrode. For this, valance band maxima (VBM) in the case of semiconductors of HTL need to be energetically more elevated than the VBM of the absorber layer [27]. Therefore, a wide range of p-type metal oxides like, CuBi₂O₄ (CBO), Cu₂O, CuAlO₂ (CAO), and NiO are chosen as HTLs, (Fig. 2.7(b)) owing to their better stability, superior charge transfer capabilities, energy bandgap in between visible and UV region, and better band energy alignment with CSI absorber [29-33]. Fig. 2.7(a) shows the device architecture we used for CSI based double perovskite solar cells (DPSCs) with different charge transport layers. The corresponding energy level alignments of light harvester (CSI) and ETL/HTLs is shown in Fig. 2.7(b). Numerical analysis of solar cell parameters predicts solar cell performance and provides guidelines for experimental investigation. Moreover, the simulation software offers an in-depth study of different physical parameters affecting device performance before real-time fabrication. Therefore, the thin film PV device can be modelled using a numerical analysis employing basic semiconductor drift-diffusion equations [34].

Herein, p-n junction heterostructure solar cell fabricated with device architecture of FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au has delivered an PCE of ~3.13%. Therefore, p-CSI light absorber is utilized to explore its possibility as an alternative for the CH₃NH₃PbI₃ light absorber. The one-dimensional Solar Cell Capacitance Simulator (SCAPS-1D), which models PV performance parameters using elementary semiconductor second-order differential equations, *i.e.* Poisson equation and non-transient carrier flow equations for the absorber and transport layer. In light of this, SCAPS-1D is adopted to characterize the photovoltaic performance of devices formed by n-ZnO as ETL, p-CSI light absorber, and various p-type metal oxides, i.e., CBO, Cu₂O, CAO, and NiO as HTLs. The effect of thickness variation, bulk and interfacial defect doping densities, and acceptor and donor

charge carrier densities of subsequent HTL and ETLs are analyzed on the performance of DPSCs. Device performance is analyzed for real-world application, considering the impact of series and shunt resistances, top metal contact work-function, and temperature. We here show through SCAPS 1-D simulations that the well-optimized device with CSI light harvester and various metal oxides as hole extraction layers have the potential to deliver efficiency close to 30 %.

3.2 Experimental Details

3.2.1 Synthesis of ZnO seed layer by spin coating

The seed layer of ZnO NPs was synthesized using solution solution-processed spin coating approach. The details of solution process approach along with the schematic are discussed in chapter 2 (section 2.2.1).

3.2.2 Synthesis of ZnO NRs by hydrothermal method

A low-temperature hydrothermal technique was used for the growth of ZnO NRs over seed layer coated substrates. The synthesis protocol along with the schematic are discussed in chapter 2 (section 2.2.2).

3.3 Simulation Procedure

The all-inorganic DPSCs with the device architecture as Glass/FTO/ZnO/CSI/HTL/Au is considered for this numerical study. FTO-coated glass substrate offers transparent bottom contact, while n-ZnO assists electron transport (hole blocking), facilitating a smooth charge extraction towards FTO at the ZnO/CSI interface. All inorganic p-CSI double perovskite light harvesters photo-generate the electron-hole pairs upon visible light irradiation. Various p-type metal oxides are scrutinized with bandgap ranging from visible to UV region as hole transport layer (electron blocking layer) with Au as a top metal electrode. Maximizing performance in CSI-DPSCs requires optimizing the thickness, doping, and trap densities of the light harvester and transport layers. Fabricating CSI-DPSCs with varying thickness and defect/doping density to optimize performance is a myriad task. Thus, reliable software programs are essential to guide the judicious optimization of solar cells. We have modelled and analyzed the device architecture (Glass/FTO/ZnO/CSI/HTL/Au) using SCAPS-1D software. Our study concentrates on exploring the relationship between the geometrical and optoelectronic properties of the

absorber and transport layers and the efficiency of heterojunction solar cells. Further, it presents the researchers with guidelines for experimental investigation [34].

The charge transport characteristics are extracted by working out the steady-state Poisson equation (as stated in Eq. 3.1) for the device arrangement.

$$\frac{\partial E}{\partial x} = \frac{\rho}{\epsilon} = -\left(\frac{\partial^2 \psi}{\partial x^2}\right) = \frac{q}{\epsilon} \left[p(x) - n(x) + N_D(x) - N_A(x) + p_T(x) - n_T(x)\right]$$
(3.1)

Where, ρ is the space charge density, ψ indicates the electrostatic potential, E corresponds to the electric field, ϵ is the permittivity of the material, q represents the electronic charge, $N_A(N_D)$ denote the acceptors (donors) charge carrier density and p(n) is the hole (electron) concentration.

Device performance can be modelled and predicted using the continuity and driftdiffusion equations, which describe the charge transport through a semiconductor device stack under steady-state conditions. These are typically represented by two sets of equations for each carrier type (Eq. 3.2 and Eq. 3.4 for electrons and Eq. 3.3 and Eq. 3.5 for holes).

$$\frac{\partial n}{\partial t} = G_n - \frac{n - n_0}{\tau_n} + \mu_n E \frac{\partial n}{\partial x} + n\mu_n \frac{\partial E}{\partial x} + D_n \frac{\partial^2 n}{\partial x^2} \qquad (\text{for electron})$$
(3.2)

$$\frac{\partial p}{\partial t} = G_p - \frac{p - p_0}{\tau_p} + \mu_p E \frac{\partial p}{\partial x} + p \mu_p \frac{\partial E}{\partial x} + D_p \frac{\partial^2 p}{\partial x^2}$$
 (for holes) (3.3)

$$J_n = n\mu_n \frac{\partial E_{Fn}}{\partial x} = q[n\mu_n E + D_n \frac{\partial n}{\partial x}]$$
 (for electron) (3.4)

$$J_p = p\mu_p \frac{\partial E_{Fp}}{x} = q[p\mu_p E - D_p \frac{\partial p}{\partial x}]$$
 (for hole) (3.5)

Where, G_p (G_n) represents the hole (electron) generation rates, p_T (n_T) is trapped hole (electron), D_p (D_n) is diffusion coefficient for the hole (electron), τ_p (τ_n) is hole (electron) lifetime, μ_p (μ_n) represents hole (electron) mobilities, J_p (J_n) is hole (electron) current density, and E_{Fp} (E_{Fn}) is quasi-Fermi levels for the hole (electron), respectively.

The SCAPS-1D software is fed with the optoelectronic parameters of the different material systems studied in this report. Table 3.1 presents the initial or optimized values chosen for each layer in the CSI-DPSC. The corresponding defect parameters of different layers and the interfacial defect parameters for the absorber-transport layer interface are provided in Table 3.2 and Table 3.3, respectively. The initial values of these parameters are transcribed from the previously reported experimental and theoretical work. The

simulations are carried out at room temperature (300 K) under AM 1.5G illumination (100 mW/cm²), series resistance (R_s) of 2 Ω .cm², and shunt resistance (R_{sh}) of 10⁵ Ω .cm². The work function (W_F) values assigned to the top gold and bottom FTO electrodes are 5.1 and 4.4 eV, respectively.

Parameter	FTO	ZnO	CSI	CBO	Cu ₂ O	CAO	NiO
Thickness (nm)	350	100*	600*	100*	100*	100*	100*
Bandgap, E_g (eV)	3.50	3.3	1.48	1.5	2.17	2.7	3.6
Electron affinity, (eV)	4.0	4.0	4.13	3.72	3.2	2.6	1.46
Dielectric permittivity	9.0	9.0	10	34	7.1	60	10.7
CB DOS, N_c (cm ⁻³)	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	1.2×10^{19}	2.5×10^{18}	2.0×10^{18}	2.2×10^{18}
VB DOS, N_v (cm ⁻³)	1.8×10 ¹⁹	1.8×10 ¹⁹	1.8×10 ¹⁹	5.0×10 ¹⁹	2.5×10^{18}	1.8×10^{19}	1.8×10^{19}
e ⁻ /h ⁺ thermal velocity				1.0×10^{7}			
e ⁻ mobility, (cm ² /Vs)	100	100	53	1.1×10 ⁻³	200	2	12
h ⁺ mobility, (cm ² /Vs)	25	25	3.1×10 ⁻²	1.2×10 ⁻³	800	8.6	2.8
Donor density (cm ⁻³)	1.0×	10^{18*}			-		
Acceptor density(cm ⁻³)	-	-	1.0×	10^{18*}	$9.0 \times 10^{15*}$	1.0×	10^{18*}
Reference	[35]	[36]	[37,38]	[26,32]	[39]	[40]	[31,41]

Table 3.1 Input parameters for different layers used in the simulation.

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Parameters	ZnO	CSI	HTL
Defect Type	Neutral	Single Donor	
Capture cross section of e^{-}/h^{+} (cm ²)	1×10 ⁻¹⁵	1×10 ⁻¹⁵	
Reference for defect energy level Et	Above E _v	Above E _v	
Energy level with respect to Reference (eV)	0.6	0.6	
Defect Energy Distribution	Gaussian	Gaussian	
Characteristic energy (eV)	0.1	0.1	
Total defect density (cm ⁻³)	1.0×10^{14} *	1.0×10^{14} *	
Reference	[42]	[31,41,43]	

Table 3.3 Interfacial defect parameters used to analyze and optimize solar cell properties.

Parameters	ZnO/CSI	HTL/CSI	
Defect Type	Neutral		
Capture cross section of electrons (cm ²)	1×10 ⁻¹⁵		
Capture cross section of holes (cm ²)	1×10 ⁻¹⁵		
Reference for defect energy level Et	Above E _v		
Energy level with respect to Reference (eV)	0.6		

Defect Energy Distribution	Gaussian		
Characteristic energy (eV)	0.1		
Total defect density (cm ⁻³)	$1.0 \times 10^{10*}$		

* Represents the optimized value of the parameter

3.4 Results and discussions

3.4.1 Experimental investigation

3.4.1.1 Physicochemical investigation of ZnO NRs





FESEM images of the ZnO seed layer and ZnO NRs are shown in Fig. 3.1(a) and Fig. 3.1(b), respectively. The uniform coverage of ZnO particles over the FTO

glass substrate (Fig. 3.1(a)) acted as a nucleation site for further uniform 1D growth of ZnO (Fig. 3.1(b)). The cross-section FESEM image represents the deposition of ~20 nm thick ZnO seed layer on the top of FTO, which is followed by ZnO NRs of ~900 nm long (Fig. 3.1(c)) The EDS spectrum (Fig. 3.1(d)) showed the presence of elements Zn and O, along with additional peaks representing the Sn from FTO substrate. The Au is observed due to its coating during FESEM sample preparation. The absence of any foreign element confirms the purity of grown ZnO NRs. The well-indexed XPD spectra (Fig. 3.1(e)) confirm the formation of wurtzite crystalline the ZnO NRs (JCPDS 65-3411), with oriented growth along the c-axis corresponding to the (002) plane. The characteristic peaks of FTO are indexed using (*) [44]. UV-visible spectra in transmittance mode indicated the ~70% transparency of the film to the Visible light (Fig. 3.1(f)). Further, core level XPS spectra of Zn(2p) represented two different peaks corresponding to the B.E. of 1021.0 (\equiv a) and 1044.1 (\equiv b) eV, confirming the Zn²⁺(2p_{3/2}) and Zn²⁺(2p_{1/2}) states, respectively for the ZnO NRs (Fig. 3.1(g)). The peak separation of 23.1 eV observed for Zn(2p) represents the formation of ZnO [45]. Fig. 3.1(h) represents The core level XPS of O(1s) shows the single peak located at B.E. of 530.2 eV corresponds to the lattice O²⁻ anions [46]. Overall, these observations confirm the formation of wurtzite crystalline, pure-phase ZnO NRs with excellent transference to visible light.

3.4.1.2 Physicochemical investigation of CH₃NH₃PbI₃

The well-optimized 1D ZnO NRs film was further subjected to the deposition of CH₃NH₃PbI₃ perovskite film. The well-indexed peaks of CH₃NH₃PbI₃ represent the formation of pure tetragonal phase (Fig. 3.2(a)). The UV-visible diffuse reflectance spectrum of CH₃NH₃PbI₃ (Fig. 3.2(b) has a reflectance onset at ~760 nm and also depicts the high absorbance of the complete visible spectrum (400-750 nm). The corresponding Kubelka-Munk function (Fig. 3.2(c)) shows the optical bandgap of 1.58 eV, which is expected to have high photo response [47]. Further, the FESEM image of CH₃NH₃PbI₃ grown over ZnO NRs depicts the large grains of size ~600-700 nm (Fig. 3.2(d)). However, nonuniform CH₃NH₃PbI₃ film growth has been observed due to a discontinuity growth at several points. The crosssectional FESEM image (Fig. 3.2(e)), shows the complete infiltration of

CH₃NH₃PbI₃ within the ZnO NRs to form CH₃NH₃PbI₃/ZnO heterojunction. The EDS spectrum of the CH₃NH₃PbI₃ grown over ZnO NRs forming heterojunction represents the existence of C, Pb, and I corresponding to CH₃NH₃PbI₃, and Zn, Sn, and O arising from underlying ZnO NRs and FTO (Fig. 3.2(f)).



Fig. 3.2. (a) XRD pattern, (b) diffuse reflectance spectra, (c) Kubelka-Munk plot of CH₃NH₃PbI₃ perovskite absorber layer, (d) Top view and (e) cross-sectional view FESEM images, and (f) EDS spectra of CH₃NH₃PbI₃ grown over ZnO NRs.

3.4.1.3 Photovoltaic measurements

Solar cell with device architecture FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au was subjected to illumination under simulated solar light. The J-V characteristic recorded to measure the device performance is shown in Fig 3.3. The HTL-free device resulted in a V_{OC} , J_{SC} , and FF of ~0.42 V, ~19.13 mA/cm², and ~0.39, respectively. Importantly, this device fabricated at ambient conditions delivered a power conversion efficiency (PCE) of ~3.13%. Moreover, 3 independent devices considered to estimate the statistical distribution of device performance delivered uniform performance (Fig 3.4). However, the lower performance of solar cells is mainly attributed to the low V_{OC} and FF values. The roughness and discontinuity in the perovskite film may create pinholes that act as recombination centers and provide a path for leakage current, thus hampering the V_{OC} . Similarly, the quality of the perovskite also results in lower values of FF. Overall, the reduced

performance of FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au in our study compared to reported literature originated from ambient processed or deposited CH₃NH₃PbI₃ perovskite film., which can be significantly controlled under an inert atmosphere.



Fig. 3.3. J-V characteristics of HTL-free perovskite solar cell under illumination.



Fig. 3.4. Distribution of (a) V_{OC}, (b) J_{SC}, (c) FF, and (d) PCE for three PSC.

3.4.2 Theoretical investigation

3.4.2.1 Absorption coefficient and band energy diagram

In view of the above experimental observations, the simulation studies for identifying significantly better solar cells, ZnO is used as ETL along with p-CSI absorber and metal oxide HTLs. The material's absorption coefficient (α) measures its efficiency in utilizing the e-m spectrum. Therefore, a high value of absorption coefficient is preferred to harvest regions of sun spectrum with a minimum thickness of the active layer. Mathematically, α is expressed as Eq. 6.

$$\alpha = \left(A + \frac{B}{h\nu}\right)\left(\sqrt{h\nu - E_g}\right) \tag{3.6}$$



Fig. 3.5. Absorption Coefficient of various charge transport layers and CSI absorber layer of double perovskite based solar cell.

Where the symbols retain their standard interpretations except A and B which denote the fitting parameters used to simulate the absorption curve. The graph in Fig. 3.5 displays the simulated α that have been assessed for the p-CSI absorber, metal oxide HTLs, and the n-ZnO ETL. The p-CSI displays absorption across the visible spectrum, beginning at around 900 nm. The n-ZnO onset in α occurs in the UV region which allows for unimpeded penetration of visible light to the p-CSI layer resulting in efficient $e^- - h^+$ pair generation. The CSI delivers a competitive absorption coefficient of roughly ~10⁵ cm⁻¹ at ~600 nm, rivaling the absorption efficacy of traditional semiconductors (e.g. mono-Si) or lead based perovskites [48,49]. Consequently, the thickness of the light harvesting CSI layer and the ETL or HTL are optimized to increase the PCE.

Fig. 3.6 shows the energy band alignments for the device stack MO/CSI/ZnO/FTO with different HTLs is shown in. The conduction band minima (CBM) of ZnO ETL and the CBM (4.13 eV) of CSI when coupled with various HTLs, namely, CBO, Cu₂O, CAO, and NiO; demonstrate an offset of 0.11, 0.09, 0.08, and 0.10 eV, respectively. The lower CB offset at ZnO/CSI interface renders smooth extraction of the photogenerated electrons. The valence band (VB) offset at ZnO/CSI interface for devices comprising CBO, Cu₂O, CAO, and NiO is 1.93, 1.91, 1.92, and 1.89 eV, respectively, restrict the flow of positive charge carriers in

the opposite direction. Besides that, the augmented VB offset restricts photocarrier losses at the ZnO/CSI interface, escalating the device's comprehensive performance. Likewise, a narrow VB offset of 0.16, 0.11, 0.14, and 0.17 eV for CBO, Cu₂O, CAO, and NiO HTLS at the HTL/CSI interface facilitates the positive charge extraction towards the top rear metal contact [50]. This analysis signifies that the modeled CSI absorber, all considered HTLs, and ZnO ETLs in the DPSCs can efficiently drive photogenerated charges into the external load.



Fig. 3.6. Energy band alignment of the p-CSI DPSCs consisting of n-ZnO ETL and various metal oxide HTLs.



3.4.2.2 Effect of thickness on device performance

Fig. 3.7. Impact of varying the thickness of the CSI film on various PV parameters.

Absorber layer thickness has a positive correlation with efficacy of light harvesting as well as recombination losses. Therefore, the thickness of the CSI double perovskite light harvester need to be optimized to increase light harvesting while limiting the recombination losses. We varied the thickness of CSI from 100 to 1100 nm, and corresponding variation in PV parameters is shown in Fig. 3.7. The production of a greater amount of photogenerated charges in thicker CSI films causes a rise in short-circuit current density (J_{SC}), leading to improved efficiencies for all HTLs. However, both the power conversion efficiency (PCE) and J_{SC} saturate beyond the thickness of 600 nm, indicating the maximum limit for light harvesting in CSI without additional increase in the charge carrier recombination. The optimum PCE of 28.18, 29.72, 29.43, and 29.33 % is observed for 600 nm thick CSI solar cells comprising CBO, Cu₂O, CAO, and NiO HTLs of 100 nm thickness, respectively, which has reached to the range of 30 to 31 % if we increase the thickness upto 1100 nm for CSI films. The open circuit voltage (V_{OC}) of CSI devices is unchanged irrespective of the thickness variation of the light harvester, which might be due to the constant band offsets at the HTL/CSI interface. The marginal reduction in the fill factor (FF) with increase in thickness (beyond 600 nm) of the CSI light harvester is observed due to the increased series resistance. As a result, a 600 nm thickness for the CSI film was chosen for further examination.



Fig. 3.8 Variation in solar cell parameters of DPSCs with the thickness of (a) ETL layer and (b) HTL layers.

Similarly, the effect of HTL thickness variation from 50 to 400 nm on the CSI solar cell parameters is evaluated and shown in (Fig. 3.8(a)). Regardless of their thickness, all HTLs show minimal variation in all solar cell parameters. However, CuBi₂O₄ (CBO) HTL showed thickness-dependent feasible increase in performance parameters due to controlled visible light activity. Therefore, considering the experimental feasibility of HTL film deposition, a thickness of 100 nm is considered for advanced optimizations. The maximum PCE of 28.49, 29.72, 29.43, and 29.33 % was obtained for 100 nm thick CBO, Cu₂O, CAO, and NiO HTLs, respectively. Moreover, irrespective of the changes in the thickness of the
ZnO (Fig. 3.8(b)), the performance of the CSI with distinct HTLs remained practically stable. Therefore, further device performance is evaluated for an optimized 100 nm thick ZnO layer along with a 600 nm CSI absorber and 100 nm HTLs.



3.4.2.3 Effect of defect density on device performance

Fig. 3.9. Alteration in PV parameters relative to the changes in bulk defect density in (a) CSI light harvester and (b) HTL layers. The bulk defect density utilized for further optimizations is shown by the dashed-line.

The bulk defect density is anticipated in the CSI light harvester, irrespective of the optimization of synthesis protocols in various techniques [22, 51, 52]. Higher defect density within the absorber material induces defect-assisted recombination, consequently reducing the charge collection efficiency. As a result, the Shockley-Read-Hall (SRH) recombination model was utilized to examine the impact of recombination driven by bulk defect density on the device performance. (Eq. 3.7).

$$R_{SRH} = \frac{(np - n_i^2)}{\tau \left(n + p + 2n_i \cosh(\frac{E_i - E_t}{k_B T})\right)}$$
(3.7)



Fig. 3.10. Energy band alignment of the Cs₂SnI₆ DPSCs with variation in bulk defect density of absorber layer.

Where, p(n) is the concentration of holes (electron), n_i is the intrinsic carrier concentration, τ is the lifetime of the charge carrier, E_i is the intrinsic energy level, E_t is the energy level of trap states, k_B is the Boltzmann constant, and T is the operating temperature of the device. A steady decrease in solar cell parameters is observed with an increased bulk defect density of CSI from 10¹² to 10¹⁹ cm⁻³ (Fig. 3.9(a)). V_{OC}, J_{SC}, and FF of the device have decreased drastically with an increase in the bulk defect density; therefore, the maximum PCE of >30 % observed at a low bulk defect density of 10^{12} cm⁻³ for all HTLs has reduced to ~4 % for the bulk defect density of 10^{19} cm⁻³. The reduction in V_{OC} from ~1.26 to ~0.75 V at higher defect density (i.e., 10¹⁹ cm⁻³) of the CSI absorber arises due to a reduction in energy band offset between the ZnO ETL and all the HTL (Fig. 3.10). The open circuit voltage (V_{OCI}) at a defect density of 10^{12} cm⁻³ is found to be much higher compared to the final open circuit voltage (V_{OCF}) at a defect density of 10^{19} cm⁻³. The decrease in J_{SC} and FF can be attributed to the presence of localized traps that act as recombination-sites within the perovskite absorber layer, as well as an increase in charge transfer resistance at the interface [53]. Nevertheless, an optimized PCE >27 % can be achieved for 10^{14} defects per cm³. On the contrary, the bulk defect density of the HTLs (ranging from 10^{12} to 10^{18} cm⁻³) does not affect the PCE and other PV parameters for CSI solar cells, remaining constant. (Fig.

3.9(b)). A ~2 % drop in PCE is observed for CBO HTL accounting from the visible activity of the CBO films, akin to losses in the CSI light harvester. Given its experimental feasibility, 10^{14} traps per cm³ in the bulk is chosen for further optimization for all HTLs. On the other hand, while variations in population of traps within ZnO were observed, the performance of CSI solar cells remained constant, and as such, a trap population of 10^{18} cm⁻³ was selected for subsequent optimization.



Fig. 3.11. Interfacial defect density-dependent variation in solar cell parameters at (a) CSI/ETL and (b) CSI/HTL interfaces. The dotted blue line represents the defect density utilized for further optimization of devices.

Solution processed polycrystalline films might have higher defect of the order of $\sim 10^{12}$ to 10^{14} cm⁻³. Consequently, utilizing 2D perovskites for surface passivation on top of 3D perovskites may assist in managing the surface defects of the perovskite absorber layer. Additionally, passivating the surface by depositing 2D perovskites on top of 3D perovskites improves the overall stability of the device [54]. Interfacial defects play a critical role in regulating recombination losses and transport resistance, which in turn affects the device performance. Therefore, in

order to comprehend the impact of interfacial defects at the CSI/ETL and CSI/HTL interface, the defect density at the CSI/transport layer interface varied from 10^8 to 10^{20} cm⁻³ (Fig. 3.11). The increase in defect density at CSI/ETL interface steadily decline the PCE of CSI solar cells from ~ 29 % (at 10^8 cm⁻³) to ~17 % (at 10^{20} cm⁻³) for all HTLs, (Fig. 3.11(a)) which is associated with the corresponding drop in V_{oc} and FF originating from a change in built-in potentials at interfacial band edges and an increase in recombination losses, respectively.



Fig. 3.12. Energy band alignment of the Cs₂SnI₆ DPSCs with variation in interfacial defect density of (a) perovskite/ETL interface and (b) HTL/perovskite interface.

The V_{OC} reduction with an increased interfacial defect density of the CSI/ETL interface is shown in Fig. 3.12 (a). The reduced band energy level at CSI/ETL drained V_{OC} from ~1.3 V (V_{OCI}) to ~1 V (V_{OCF}). However, a slight decrease in J_{SC} is observed as the density of defects at the CSI/ETL interface

increases. Overall, a better interface of ZnO with CSI results in lower recombination and smooth charge transportation at the CSI/ETL interface. Besides, the increase in defect density at CSI/HTL interface reduces the PCE, V_{OC} , and J_{SC} for all HTLs (Fig. 3.11(b)). The reduction in V_{OC} and J_{SC} with increased interfacial defect density is attributed to the change in energy band offset (Fig. 3.12(b)) and the increase in defect-assisted recombination at the CSI/HTL interface, respectively.



3.4.2.4 Effect of carrier density on device performance

Fig. 3.13. PV parameters dependence on the acceptor carrier density in (a) CSI light absorber and (b) HTL films. The dashed-line corresponds to the acceptor carrier density utilized later for optimization of devices.

Further, in the quest for improvement in PCE, the acceptor charge carrier density of the CSI light harvester varied from 10^{16} to 10^{21} cm⁻³, and the analogous improvement in PCE, V_{OC}, and FF are observed for all HTLs (Fig. 3.13(a)). The increase in V_{OC} resulted from an improvement in energy band offsets at the interface due to the increase in the energy band level of the CSI absorber with respect to acceptor charge carrier density within the CSI (Fig. 3.14). At higher

acceptor charge carrier density, the increased energy band levels of CSI improve the V_{OC} of the device from ~1.2 V (V_{OCI}) to ~1.4 V (V_{OCF}). The FF improved due to an increase in carrier concentration in CSI films and a net reduction in the parasitic resistance of the absorber layer. At a high carrier density of 10²¹ cm⁻³, CSI light harvester renders PCE of 28.52, 33.02, 32.97, and 32.68 % with CBO, Cu₂O, CAO, and NiO HTLs, respectively. However, achieving the carrier density of 10^{21} cm^{-3} is challenging; hence, an experimentally realizable value of 10^{18} cm^{-3} is considered for further simulations. On the other hand, unlike CSI light absorbers, the increase in acceptor carrier density (from 10¹⁶ to 10²² cm⁻³) of HTLs has negligible changes in the PCE (Fig. 3.13(b)). The Voc, Jsc, FF, and PCE of all devices remained unaltered with variation in acceptor carrier density in HTLs, except CBO. The PCE increased with the increase in acceptor carrier density of CBO and further saturated $>10^{18}$ cm⁻³. Similarly, the variation in the donor carrier density in the ZnO has not affected the overall performances of CSI solar cells. Therefore, the acceptor and donor carrier density of 10¹⁸ cm⁻³ is considered for transport layers to further optimize the device performance.



Fig. 3.14. Energy band alignment of the Cs₂SnI₆ DPSCs with variation in acceptor carrier density of the perovskite layer.

3.4.2.5 Effect of parasitic resistances on device performance

Ideally, the solar cell achieves maximum efficiency at zero series and infinite shunt resistances, which is experimentally not feasible due to the limitations in obtaining ideal conformal films with precise interfaces. Therefore, the effect of series and shunt resistance on the performance of CSI solar cells is evaluated. Overall, the device performance parameters were reduced with increased series resistance (Fig. 3.15(a)). The surge in Rs escalated the ohmic loss of the device and linearly reduced FF, hence the PCE. The overall performance of the device is impacted by the presence of pinholes in low-quality films, as they provide shunting pathways that reduce the Rsh [55]. The compact and pinhole-free films ensure higher shunt resistance with reduced charge recombination and leakage current. Therefore, the PCE has improved from ~2 to 30 % along with V_{oc}, J_{SC}, and FF for all the HTL when shunt resistance increases from 10 to $10^5 \Omega/cm^2$ (Fig. 3.15(b)). Overall, a reasonable PCE of ~30 % is achievable at 2 and $10^4 \Omega cm^2$ series and shunt resistance, respectively, from the solar cells consisting of CBO, Cu₂O, CAO, and NiO HTLs, and CSI absorber.



Fig. 3.15. (a) R_S and (b) R_{SH} dependent variation in PV performance of DPSCs.

3.4.2.6 Effect of operating temperature and work function

During the real-time operation of solar cells, the increase in temperature alters the optoelectrical properties by inducing thermal stress and leads to poor device performance. Therefore, device performance is simulated for T = 270 to 450 K (Fig. 3.16(a)). The temperature rise causes a linear decrease in PCE, FF, and V_{OC} of CSI solar cells. The decrease in V_{OC} is attributed to the alteration in the energy-band offset between CSI, CBM of ZnO and VBM of HTL at elevated operating temperatures. (Fig. 3.16(b)). Moreover, the increase in reverse saturation current at higher operating temperatures results in the reduced V_{OC} of the device. The upsurge in the collisions between charge carriers at higher operating temperatures escalates the internal resistance and results in lowering the FF of the device. However, unaffected J_{SC} from rising operating temperature confirms the superior thermal stability of the CSI double perovskite light harvester.



Fig. 3.16. PCE variation of all inorganic DPSCs with (a) Operating temperature, (b) corresponding energy band diagram, and (c) W_F of back metal.

The W_F of the rear metal contact has a decisive influence on the built-in potential of a PSC. Therefore, overall PCE of all inorganic DPSCs is examined for various metals, i.e., Fe, Cu, Ag, C, Au, and Pt as back/rear metal electrodes (Fig. 3.16(c)). The PCE of the device increased up to the work function (W_F) of < 5 eV and saturated above 5 eV. The Pt and Au metal contact delivered a maximum PCE of > 29 % for CBO, Cu₂O, CAO, and NiO, respectively, but their higher cost limits the usage in device fabrication. Besides, Fe's cost advantage over other tested metals is offset by its low conductivity, leading to the lowest PCE. Nevertheless, Ag and C delivered reasonably equivalent PCE to Pt and Au, originating from better charge extraction, illustrating the suitability as back metal contact; however, device stability might be compromised by forming AgI at the interface due to the lower stability and higher reactivity of Ag [56], limits its usage in a real-time application, which one should look to overcome.





Fig. 3.17. Variation in IPCE spectra of CSI PDSCs relative to changes in CSI film thickness for different HTLs (upper panel). The JV curves of the CSI PDSCs comprises different HTLs (lower panel).

The incident photon conversion efficiency (IPCE) spectra furnish deeper insights to comprehend the photogeneration relative to the wavelength of the incident photons. The thickening of the CSI light-harvesting films leads to an improvement in the absolute number of photogenerated charges, resulting in higher IPCE for all HTLs of DPSCs, as shown in Fig. 3.17 (upper panel). Nevertheless, the IPCE nearly saturates above the thickness of ~600 nm is in line with our absorber and transport layer thickness dependent observations. Further, considering all the optimized physical parameters of the subsequent layers, the JV curves of the CSI DPSCs are illustrated in Fig. 3.17 (lower panel). At the optimized condition, the CSI DPSCs can achieve PCE of ~28.18, ~29.72, ~29.43, and ~29.33 % for CBO, Cu₂O, CAO, and NiO, respectively, which exemplifies the capability of CSI double perovskite light harvesters for solar cells.

3.4.2.8 C-V and C-f studies

Furthermore, capacitance-voltage (C-V) analysis is performed on the optimized device of Glass/FTO/ZnO/CSI/Cu₂O/Au to study the effect of a high-frequency AC signal on the DC-biased p-n junction. The capacitance at the p-n junction is evaluated at different bias potentials by neglecting the effect of small R_s and approximating the device as parallel combination of junction capacitance and R_{sh} [55]. Moreover, the built-in potential between the p-n junction, the width of the space charge region (SCR), and the apparent doping profile of the CSI perovskite absorber layer are examined. The relation between junction capacitance (C) and reverse bias voltage (V_{rb}) is given by Eq. 3.8.

$$c = \frac{c_0}{\left(1 + \frac{V_{rb}}{V_{bi}}\right)^m} \tag{3.8}$$

Where, c_0 is the capacitance at zero bias voltage, V_{bi} is the built-in potential, V_{rb} is the reverse bias voltage, and m is the grading coefficient of the device that determine the types of junctions with the value of 1/2 and 1/3 for abrupt and linear graded junction, respectively. The room temperature (300 K) C-V characteristics of all inorganic DPSCs consisting of Cu₂O HTL are simulated for R_{sh} ~10⁵ Ω -cm² (Fig. 3.18). With the rise of DC bias voltage, the capacitance increased until reaching a specific point, and then dropped as the voltage continued to increase due to the rise of dielectric dispersion [57]. The corresponding Mott-Schottky plot relating the Capacitance per unit area (C) with acceptor carrier density (N_A) at the edge of CSI SCR (Eq. 3.9) for the complete device and ZnO/CSI p-n junction is shown in the inset of Fig. 3.18(a).

$$\frac{1}{C^2} = \frac{2(V_{b_i} + V_{rb})}{q\epsilon_r A^2 N_A} \tag{3.9}$$

Where, C is the capacitance per unit area, ϵ_r is the relative dielectric permittivity of the space, V_{rb} is the applied reverse bias potential, V_{b_l} is the built potential, A is the area of the cell, q is the electronic charge, and N_A is the acceptor carrier density cm⁻³. The built-in potential of 1.34 and 1.50 eV is observed for Cu₂O based devices and ZnO/CSI p-n junction. Ideally, the V_{OC} of a device is equal to the built-in potential, but a relatively lower V_{OC} is observed due to the recombinational losses within the device [58]. Later, we simulate dark C-f characteristics of optimized device stack with Cu₂O as HTL at 300K and without any applied bias (Fig. 3.18(b)). The capacitance across ZnO/CSI p-n junction and the whole device is evaluated for the frequency range of 1 Hz to 10 GHz. The higher capacitance value at a lower frequency remained constant up to 10⁴ and 10⁶ Hz for ZnO/CSI junction and device, respectively, which reduced drastically and became constant >10⁹ Hz. The lower capacitance at frequencies above 1 MHz can be attributed to the sudden rise in the number of minority carriers leading to enhanced carrier injection within junction, which further facilitates the carrier recombination [59].



Fig. 3.18. (a) C-V and (b) C-f characteristics of CSI DPSCs.

3.4.2.9 Recombination rate

The band-offset energy and changes in the carrier mobility at the interface of the different layers leads to recombination and negatively impacts the device's overall performance by decreasing its V_{OC} [60]. The SRH mechanism was employed to quantify photocarrier losses at the CSI/ZnO interface, junction, and quasi-neutral region, considering the impact of traps/defects in trap-assisted recombination given by (Eq. 3.10-3.13) [61],

$$V_{0c} = \frac{2k_BT}{q} ln \left[\frac{1}{2} \frac{R_0^d}{(R_0^l + R_0^q)} \times \left(\sqrt{4G_a D \frac{(R_0^l + R_0^q)}{(R_0^d)^2} + 1} - 1 \right) \right]$$
(3.10)

$$V_{0c} = \frac{2k_BT}{q} \ln[k_1(\sqrt{G_a k_2 + 1} - 1)]$$
(3.11)

Where, k_1 and k_2 are given as

$$k_1 = \frac{1}{2} \frac{R_0^d}{\left(R_0^l + R_0^q\right)} \tag{3.12}$$

$$k_2 = \frac{4D(R_0^i + R_0^q)}{(R_0^d)^2} \tag{3.13}$$

Where, R_0^i is photocarrier recombination rate at CSI/ZnO interface whereas, R_0^d , and R_0^q are the corresponding rates within the junction (depletion) and quasi-neutral regions, respectively. D is the total thickness of the device and G_a is the incident intensity. It is evident from Eq. 3.11 that the V_{OC} of the device will depend on G_a and T of the cell. The variation in device's V_{OC} with temperature but under constant illumination (AM1.5G) (Fig. 3.19(a)) and under a range of illumination levels at 300 K (Fig. 3.19(b)) are studied to determine various recombination coefficients [58,62]. Table 3.4 provides a summary of the values of the various recombination rates and coefficients. This corroborates that maximum recombination occurs at the interfacial region of the CSI and HTL/ETLs. Furthermore, simulated studies indicate that the well-optimized CSI DPSCs is able to achieve better efficiency than all the previously reported work on CSI-based PSCs (Table 3.5).

Table 3.4. Extracted recombination rate and their coefficient of CSI-based DPSCs.

Device	<i>k</i> ₁	k ₂	R_0^i (/cm ² s)	R_0^d (/cm ² s)	R_0^q (/cm ² s)
Cu ₂ O/CSI	4.74×10^{6}	80869	0.027	4.4×10^{5}	1.96×10^{-2}



Fig. 3.19. V_{OC} of the DPSCs evaluated at (a) different illumination at 300 K and (b) different temperatures under constant illumination of AM1.5G (1 sun).

S.	Device stack	Voc	J _{SC}	FF	PCE	Ref.
N.		(V)	(mA/cm ²)			
1.	FTO/ZnO NR/Cs2SnI6/P3HT/Au	0.52	3.20	0.51	0.86	[28]
2.	ITO/CsSnI ₃ -SnCl ₂ /PCBM/BCP/Al	0.45	11.6	0.67	3.16	[17]
3.	FTO/TiO ₂ /Sn-TiO ₂ /Cs ₂ SnI ₄ Br ₂ /LPA/FTO	0.56	6.23	0.58	2.03	[63]
4.	FTO/TiO ₂ /Cs ₂ SnI ₆ /P3HT/Ag	0.51	5.41	0.35	0.96	[49]
5.	FTO/TiO ₂ /Cs ₂ SnI ₆ /P3HT/Ag	0.26	7.41	0.25	0.47	[64]
6.	FTO/TiO ₂ /Cs ₂ SnI ₆ /N719/Ag	0.67	16.3	0.62	6.75	[16]
7.	FTO/GO/Cs ₂ SnI ₆ /Cu ₂ O/Au	1.3	27.15	0.69	25.1	[33]
8.	FTO/GO/Cs2SnI6/Cu2O/Au	0.84	34.6	0.82	23.6	[65]
9.	FTO/ZnO/CSI/CBO/Au	1.26	27.1	0.85	28.2	This
	FTO/ZnO/CSI/Cu ₂ O/Au	1.29	26.8	0.86	29.7	Work
	FTO/ZnO/CSI/CuAlO ₂ /Au	1.29	26.8	0.85	29.4	
	FTO/ZnO/CSI/NiO/Au	1.29	26.8	0.85	29.3	

Table 3.5. Comparison of PCE of different CSI-based perovskite solar cells.

3.5 Conclusion

Many organometallic lead halide perovskites are prone to instability and sensitivity to moisture. To achieve prolonged stability in photovoltaic performance, we suggest using a CSI double perovskite light harvester as an alternative. To simulate an efficient photovoltaic device, the ZnO is considered as ETL owing to its higher charge carrier mobility, ease of synthesis, and excellent physical and chemical stability. Different p-type metal oxides such as CBO, Cu₂O, CAO, and NiO with various bandgaps ranging from UV to visible region are adopted as HTLs due to their superior optoelectronic properties and better energy band alignment with CSI perovskite. The simulated device with all HTLs has shown excellent PCE and stability at higher operating temperatures. The DPSC device was optimized for various architectural and optoelectronic parameters, including thickness, free carrier density, and trap density (in both the bulk and interfacial regions) for the charge transport and the absorber layer. Additionally, parasitic resistance, work-function, and operating temperature are simulated to aid practical fabrication of PSC. The excellent PCE for the simulated device exemplifies the capability of CSI double perovskite as light harvesters in PV devices. FTO/ZnO/CSI/Cu2O/Au device configuration delivered optimized PCE of ~30 %. To summarize, our study provides a framework for optimizing device architecture of high-efficiency lead-free all inorganic DPSCs using CSI as a light absorber, ZnO as an ETL, and different metal oxides as HTLs. All the constituents of the device architecture studied in this report are cost-effective, environmentally friendly, stable and, most importantly, could be realized experimentally.

3.6 References

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Chapter 4

All oxide heterostructure solar cells

4.1 Introduction

With the increasing energy demand and limited fossil fuel, solar energy, an alternate source of renewable energy, can fulfill the energy demand by providing clean and economical electricity. Organic-inorganic lead halide perovskite light harvesters have challenged the crystalline silicon solar cells in the last decade [1, 2]. On account of their intrinsic optoelectronic properties, namely, high absorption coefficient, long charge carrier diffusion lengths, tunable bandgap, low bulk defect density, and low exciton binding energy, the power conversion efficiency (PCE) of single-junction perovskite solar cells (PSCs) have reached 26.1 % [3, 4]. Despite this noteworthy PCE, the implementation of PSCs still has a long way to go due to the high toxicity and short-term stability of organometallic perovskite light absorbers [5, 6]. Various efforts are made to replace lead (Pb) in perovskite absorbers [7]. However, the perovskite absorbers without Pb lack efficiency, hindering their commercialization. The performance of perovskite absorbers degrades as they undergo structural changes with varying temperatures, moisture, and ultraviolet (UV) illumination, questioning their real-time reliability [8, 9]. The intrinsic hygroscopic nature of the perovskite absorber is of concern as perovskite dissociates to form PbI_2 at the interface with the transport layer, as shown in Fig. 2.8 (Scheme 1). Therefore, finding an alternate non-toxic light harvester with high efficiency and long-term stability is essential.

Upon investigating potential light harvesters with required photovoltaic properties, the non-toxic ternary metal oxide $CuBi_2O_4$ (CBO) of kusachiite tetragonal crystal structures, where a 3D array of $[CuO4]^{6-}$ distributed along the c-axis and isolated by the Bi^{3+} ions, is expected to provide long term thermal, moisture, and UV stability without altering the interface at light harvester and transport layer as shown in Fig. 2.8 (Scheme 2). Further, the valence band of CBO has hybrid Bi(6s), Cu(3d), and O(2p) orbitals, which offers a suitable bandgap to harvest visible spectra and result in accelerated mobility of the photogenerated charge carriers within the CBO semiconductors [10, 11]. Moreover, CBO, explored as a photoelectrode material in numerous applications such as photocatalytic dye degradation [12], supercapacitor [13], water splitting [14], CO₂ reduction [15], and antimicrobial applications [16], can easily be synthesized in different morphologies using various synthesis techniques like hydrothermal, sol-gel, electrodeposition, solid-state

reaction, etc. Therefore, it is necessary to assess the applicability of CBO as a light harvester in thin-film solar cells. Hosen et al. [17] investigated CBO-based thin-film solar cells with CdS as an n-type transport layer. However, slightly complex device architecture limits its feasibility in practical application. Therefore, the scrutinization of a suitable, cheap, non-toxic, and easily processible buffer/transport layer is essential to form a p-n junction thin-film solar cells with CBO light harvester. In our previous studies, we have explored the compatibility of various perovskite oxide buffer layers with CBO light harvester to form all oxide solar cells consisting of BaTiO₃, BaSnO₃, SrTiO₃, and SrSnO₃. The optimized ITO/SrSnO₃/CBO/Au solar cells showed a PCE of $\sim 22 \%$ [18]. Further, in a quest to increase efficiency, several metal sulfides, namely CdS, WS_2 , SnS_2 and ZnS_3 , were scrutinized for their application as transport layers with CBO light harvester. The device configuration of ITO/WS₂/CBO/Au yielded a PCE in the range of 22-28 % [19]. The usage of sulfides does not entirely eliminate toxicity in CBO-based solar cells; therefore, the search for a binary metal oxide transport layer is of scientific importance. The n-type large bandgap binary metal oxides (MOs) allow visible light radiation to irradiate light absorbers and are widely used as transport layers in p-n junction photovoltaics [20]. Tungsten oxide (WO₃) [21], tin oxide (SnO₂) [22], zinc oxide (ZnO) [23, 24], and titanium dioxide (TiO₂) [25-27] are stable MOs that can align well with the CBO absorber layer to form a p-n heterojunction, as shown in Fig. 4.1(a). Further, the chosen MO should have high carrier mobility with low trap density and minimal interfacial losses at the MO/CBO heterojunction. Generally, a band offset of 0.2 eV is required for efficient charge transfer at the interface in heterojunctions [28]. The distinct energy level alignment of MOs with CBO absorbers helps smooth transportation of the charge carriers. The intrinsic charge carrier mobility of MOs is sufficiently high to minimize the charge recombination at the heterojunction interface. Thus, high device performance with longterm stability can be achieved by incorporating a suitable n-type MO transport layer. Moreover, MOs are facile, non-toxic, economical, and have excellent physical and chemical stability. Numerous morphological forms of MOs controlling the optoelectronic properties shall be better n-type transport layer of choice than other counterparts.

Numerical simulations predict the performance of solar cells and provide guidelines regarding operational mechanisms and performance. Additionally, the simulation packages

offer guidelines concerning the factors that control the performance of the solar cells before real-time fabrication. In general, any software capable of solving fundamental semiconductor equations can simulate photovoltaic devices. Various simulation packages such as COMSOL, SILVACO ATLAS, AMPS, AFORS-HET, and SCAPS simulate photovoltaic devices. However, here we used SCAPS 1D software to analyze the single heterojunction formed by the n-type MOs transport layer and p-type CBO light absorbers. With indium-doped tin oxide (ITO) as a transparent conducting oxide layer, several MOs, namely, WO₃, SnO₂, ZnO, and TiO₂, are assessed as n-type transport layers. The impact of physical properties, i.e., thickness, carrier density, and bulk defect density, of subsequent MO transport and CBO light absorber layers is analyzed on the performance of all oxide heterostructure solar cells (AOHSC). The effect of work function of rear metal contacts and operating temperature is also studied for real-time application. The well-optimized solid-state device comprising CBO light absorber and Mo/Sn/Zn/Ti oxide transport layer has delivered efficiency close to 22%.

The all oxide planar (n-p) architecture ITO/MO/CuBi₂O₄/Au is considered in this study. The schematics of the band diagram are shown in Fig. 4.1(b). The ITO-coated glass is used as the transparent conducting oxide, which provides the front contact. Various n-type MOs transport layers are scrutinized with the p-type CBO as the light absorber and Au as the rear metal contact.



Fig. 4.1 (a) Absorption coefficient and (b) Schematics of the band diagram of p-type CBO light absorber and various metal oxide transport layers utilized for AOHSC.

4.2 Simulation methodology



Fig. 4.2. Energy band diagram of p-type CBO light absorber and various metal oxide transport layers utilized for AOHSC.

The energy position of CBO with respect to the MO transport layer is shown in Fig. 4.2. The conduction band offsets between CBO absorber film and WO₃, SnO₂, ZnO, and TiO₂ transport layer are 0.18, 0.23, 0.37, and 0.47 eV, respectively, which offers smooth charge transportation at CBO/MO interface [28]. The barrier between the valence band maximum of CBO and WO₃, SnO₂, ZnO, and TiO₂ transport layer is 1.40 eV, 2.35 eV, 2.34 eV, and 2.39 eV, respectively, which is sufficiently high to restrict the flow of positive carriers towards MOs. Also, the high energy barrier minimizes recombination at the CBO/MO interface. The SCAPS 1D program that analyzes heterojunction and multijunction solar cells developed by Marc Burgelman at the Department of Electronics and Information Systems (ELIS), University of Gent, Belgium, is utilized to simulate the

operational parameters of CBO and MO based AOHSCs, which can be comparable with the experimental results [29-31].

The charge carrier transport parameters can be obtained by solving the differential equations that govern the semiconductor material under steady-state conditions. Poisson equation (4.1), which represents the relationship between space charge density (ρ) and electric field E, is given below by,

$$\frac{\rho}{\epsilon} = -\left(\frac{\partial^2 \psi}{\partial x^2}\right) = \frac{q}{\epsilon} \left[-n(x) + p(x) - N_A^-(x) + N_D^+(x) - n_t(x) + p_t(x)\right] = \frac{\partial E}{\partial x}$$
(4.1)

Continuity equations for the electron (Eq. 4.2) and holes (Eq. 4.3) under the steady-state condition, which dictate the charge transport in the semiconductor, are given by,

$$G_n - \frac{n - n_0}{\tau_n} + n\mu_n \frac{\partial E}{\partial x} + \mu_n E \frac{\partial n}{\partial x} + D_n \frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t} \qquad (\text{for electron})$$
(4.2)

$$G_p - \frac{p - p_0}{\tau_p} + p \mu_p \frac{\partial E}{\partial x} + \mu_p E \frac{\partial p}{\partial x} + D_p \frac{\partial^2 p}{\partial x^2} = \frac{\partial p}{\partial t}$$
 (for holes) (4.3)

The charge carrier transport occurring by drift and diffusion for electrons (Eq. 4.4) and holes (Eq. 4.5) are given by,

$$J_n = n\mu_n \frac{\partial E_{Fn}}{\partial x} = q[n\mu_n E + D_n \frac{\partial n}{\partial x}]$$
 (for electron) (4.4)

$$J_p = p\mu_p \frac{\partial E_{Fp}}{x} = q[p\mu_p E - D_p \frac{\partial p}{\partial x}]$$
 (for hole) (4.5)

where ϵ is the permittivity of the material, ψ is the electrostatic potential, q is the electron charge, N_D⁺(N_A⁻) is the density of ionized donors (acceptors), n(p) is the electron (hole) concentration, $n_t(p_t)$ is the trapped electron (hole), G_n (G_p) is the electron (hole) generation rates $\tau_n(\tau_p)$ is the electron (hole) lifetime, D_n (D_p) is the diffusion coefficients for the electron (hole), $\mu_n(\mu_p)$ is the electron (hole) mobilities, E_{Fn} (E_{Fp}) is the quasi-Fermi levels for the electron (hole), $J_n(J_p)$ is the electron (hole) current density, respectively.

The required material properties of each layer of AOHSCs are loaded in the SCAPS-1D software. The detailed physical input parameters used in AOHSC simulations are summarized in Table 4.1. The base value of bulk defect density of 10^{14} cm⁻³ is considered for all the layers. The defect density of 10^{10} cm⁻³ at the CBO/MO interface is also considered along with neutral defects, uniform energy distribution, reference defect energy level (E_t) above E_v, electrons and holes capture cross-section of 1×10^{-19} cm², energy level with reference of 0.6 eV, and characteristic energy of 0.1 eV. The work function of the rear and front electrodes is initially taken as 5.1 eV (Au) and 4.28 eV (ITO),

respectively. The acceptor density of 3.7×10^{18} cm⁻³ is considered for initial optimizations. The simulations are carried out under AM 1.5G spectrum illumination with an incident power of 1000 W/m², series resistance (R_s), and shunt resistance (R_{sh}) of 5 $\Omega \cdot \text{cm}^2$ and $10^5 \Omega \cdot \text{cm}^2$, respectively.

Parameter	ITO	WO ₃	SnO ₂	ZnO	TiO ₂	CuBi ₂ O ₄
Thickness (nm)	350	Optimized (*)				
Bandgap, Eg (eV)	3.50	2.70	3.50	3.30	3.26	1.5
Electron affinity, χ (eV)	4.0	3.8	4	4	4.2	3.72
Dielectric permittivity, ε	9.0	4.8	9	9	10	34
CB DOS, N_c (cm ⁻³)	2.2×10^{18}	2.2×10^{21}	2.2×10^{17}	2.0×10 ¹⁸	2.2×10^{17}	1.2×10^{19}
VB DOS, N_v (cm ⁻³)	1.8×10^{18}	2.2×10^{21}	2.2×10^{17}	1.8×10^{19}	6.0×10 ¹⁷	5.0×10 ¹⁹
e ⁻ /h ⁺ thermal velocity		1.00×10^{7}				
e ⁻ mobility, (cm ² /Vs)	20	30	20	100	100	1.1×10 ⁻³
h ⁺ mobility, (cm ² /Vs)	10	30	10	25	25	1.2×10 ⁻³
Donor density, (cm ⁻³)	1.0×10^{18}	6.3×10^{21} *	$1.0 \times 10^{15*}$	1.0×	10^{18*}	-
Acceptor Density, (cm ⁻³)			-			3.7×10^{18}
Ref.	[32, 33]	[32]	[34]	[35]	[36]	[17]

Table 4.1 Input parameters for different layers used in the simulation.

* Parameters that are being varied to optimize the device.

The simulation parameters for defect present in the MO transport and CBO light absorber layers: Capture cross-section electrons and holes = 1.0×10^{-15} cm²; Energy distribution type is Gaussian; Reference for defect energy level (E_t) is above E_v; Energy level with reference = 0.6 eV, Characteristic energy = 0.1 eV; Bulk defect density (Nt) = 1.0×10^{14} cm⁻³ [17]; Defect type: Single Acceptor of MO transport layer and single donor for CBO absorber layer. DOS – Density of states.

4.3 Results and discussions

4.3.1 Effect of thickness on device performance

A high panchromatic visible light optical absorption coefficient is the most desired property for a light harvester in thin-film photovoltaics. Materials with a high absorption coefficient have high photogeneration and can be modeled into thin-film solar cells that are cost-effective and flexible. The absorption coefficient (α) of a material is governed by Eq. 4.6.

$$\alpha = \left(A + \frac{B}{h\nu}\right)\left(\sqrt{h\nu - E_g}\right) \tag{4.6}$$

where A and B are the optical absorption parameters, h is Planck's constant, v is the frequency of the incident light, and E_g is the bandgap of the material. Fig. 4.1 (left bottom panel) shows the absorption coefficients of the p-type CBO absorber layer and n-type MO transport layers considered in the present study. The CBO shows panchromatic visible light absorption with ~850 nm absorption onset. The absorption coefficient of the CBO layer is ~10⁵ cm⁻¹ at ~600 nm, comparable to the crystalline silicon and lead halide perovskite light absorbers [37]. Therefore, the thickness of the absorber and transport layers is optimized in search of enhanced PCE.



Fig. 4.3. Comparison of solar cell parameters dependent on the variation in thickness of (a) CBO absorber layer and (b) electron transport layer of AOHSCs. The dotted blue line represents the optimized thickness of layers considered for further optimizations.

The thickness of the CBO absorber layer is the critical factor determining the optimum performance of solar cells. For a fair comparison of solar cell parameters, the thickness of n-type MO films is maintained at the constant thickness of 100 nm, given the experimentally feasible thin-film techniques. Moreover, thick films of the MO

transport layer will blind the radiations striking the CBO absorber. Fig. 4.3 (a) shows the variation in solar cell parameters of AOHSC pertaining to the variation in thickness of CBO absorber film. As the thickness of the CBO absorber layer increases, the concentration of photogenerated carriers increases, resulting in high short circuit current density (J_{SC}) and, hence, PCE. The marginal increment in the V_{OC} with respect to thickness is observed due to an increase in the J_{SC}, as given in Eq. 4.7.

$$V_{oc} = V_t \ln \left(\frac{J_{sc}}{J_0} + 1 \right)$$
(4.7)

Moreover, the increase in series resistance with the thickness of the absorber layer resulted in a marginal reduction in the FF. The highest PCE obtained with WO₃, SnO₂, ZnO, and TiO₂ transport layers is 23.01 %, 22.75 %, 22.76 %, and 22.05 %, respectively. However, WO₃ has a relatively lower bandgap, and the highest absorption coefficient produces marginally higher PCE. Accounting for the relatively low charge carrier mobility, TiO₂, among all MOs, delivers lower FF and PCE [38]. However, when the thickness of the CBO absorber layer is further increased than their electrical charge diffusion lengths, it results in increased charge recombination, reducing the PCE. Therefore, the PCE of AOHSCs saturates beyond a thickness of 900 nm for the CBO absorber layer. Consequently, this optimized thickness (900 nm) of the CBO absorber is used to optimize AOHSCs further. Nonetheless, optimizing the thickness of n-type transport layers is also essential to achieve high PCE. The performance of the AOHSCs is analyzed by varying the thickness of the MO films. Fig. 4.3 (b) shows the MO transport layer thickness-dependent variation in the various parameters of the solar cell. The PCE remains almost constant for distinct transport layers as there is no change in band offset between the CBO absorber and MO films with increased transport layer thickness. However, relatively higher PCE and J_{SC} are observed for the WO₃ transport layer than the other three. After all, the increase in PCE and J_{SC} for AOHSCs with WO₃ transport layer is credited to the lower bandgap of WO_3 with the increasing thickness, through which the total charge carriers generated within CBO are aided by WO₃, resulting in higher J_{SC}. Conversely, increasing MO transport layer thickness beyond 400 nm can hamper the effective photogeneration in the CBO light absorber and readily lower PCE. Therefore, the MO layer of 100 nm thickness is considered along with the 900 nm thick CBO absorber layer to analyze the device performance further. Notably,

various thin film techniques ranging from solution processing to vacuum deposition can certainly offer precise control over the CBO absorber and MO transport layer thickness proposed and optimum in this study.



4.3.2 Effect of carrier density on device performance

Fig. 4.4 Effect of variation of (a) acceptor carrier density in the 900 nm thick CBO absorber layer and (b) donor carrier density of 400 nm MO transport layer on the performance of AOHSCs.

Apart from the optimized thickness of the subsequent layers, the electrical properties can be further tuned with doping. Experimentally, several dopants that can replace the metal ion sites can be used to alter the electrical properties of MOs and CBO films. Therefore, the acceptor carrier density in the CBO absorber is varied from 10^{17} to 10^{22} cm⁻³. The PCE of AOHSCs for all MO transport layers is enhanced with increased acceptor carrier density (Fig. 4.4(a)). The maximum PCE possible for AOHSCs consisting of WO₃, SnO₂, ZnO, and TiO₂ transport films is 26.18 %, 25.91 %, 26.13 %, and 26.03 %, respectively. The increase in PCE with doping of the CBO absorber can be ascribed to a corresponding increase in V_{OC} and FF, which mainly

occurred due to the increased band offset at the MO and CBO interface and decreased intrinsic resistance in CBO film [39]. However, the reduction in J_{sc} occurred because of the abrupt junction, which increases charge recombination at the MO/CBO interface. Similarly, the donor carrier density in MO films is also varied from 10¹⁵ to 10¹⁹ cm⁻³, and the overall impact on the device performance parameters is shown in Fig. 4.4(b). The donor density of MO transport layers has altered the overall performance of AOHSCs at higher concentrations, but the PCE remained almost constant irrespective of donor density. The PCE of AOHSCs consisting of 400 nm transport layer of WO₃, SnO₂, ZnO, and TiO₂ is 22.28 %, 21.97 %, 22.01 %, and 21.25 %, respectively, almost constant for all donor densities. However, the PCE was reduced for the TiO₂ transport layer after doping than that of WO₃, SnO₂, and ZnO. Higher resistivity of the TiO₂/CBO interface compared to other MO (i.e., WO₃, SnO₂, ZnO) results in lower FF and PCE for TiO_2 MO films. Though the V_{OC} has not changed with higher donor density in the MO, the improved charge conductivity and higher charge mobility with higher donor density lead to improved J_{SC} , which subsequently improves the PCE. A slight reduction in the FF for all the devices at higher donor density is caused due to the increased resistivity of the MO/CBO interface.

4.3.3 Effect of defect density on device performance

The quality of the light absorber layer is a critical factor that influences the performance of a photovoltaic device. The high defect density light absorbers lead to an increased number of recombination centers, which affect charge carrier collection efficiency, resulting in poor device performance. Due to increased defect density, the localized energy level will act as a recombination site. In general, the Shockley-Read-Hall (SRH) recombination model is used to study the effect of variation in the bulk defect density of CBO layer, and its effect on device performance is given by Eq. 4.8.

$$R_{SRH} = \frac{(np-n_i^2)}{\tau \left(n+p+2n_i \cosh(\frac{E_i-E_t}{k_BT})\right)}$$
(4.8)

where n (p) is the concentration of electrons (holes), n_i is the intrinsic carrier concentration, τ is the lifetime of the charge carrier, E_i is the intrinsic energy level, E_t is the energy level of trap states, k_B is the Boltzmann constant, and T is the operating temperature of the solar cells.



Fig. 4.5. Change in the parameters of AOHSCs with the variation of (a) bulk defect density in the CBO absorber layers and (b) CBO/MOs interfacial defect density.

4.3.4 Effect of parasitic resistance on device performance

The bulk defect density in the CBO absorber is varied from 10^{12} to 10^{16} cm⁻³ to understand its effect on the performance parameters of the AOHSCs (Fig. 4.5(a)). The V_{oC} and J_{SC} decline with the increase in bulk defect density of the CBO absorber layer, irrespective of the oxide transport layer used in AOHSCs, resulting in lower PCE. The maximum PCE for WO₃, SnO₂, ZnO, and TiO₂ is 22.22 %, 21.93 %, 21.94 %, and 21.23 %, respectively, at low defect density in CBO films, which severely decreased with an increase in the bulk density. The decrease in J_{SC} implies the formation of localized recombination centers in the absorber layer, which relatively reduces the effective charge diffusion length, ensuring low charge carrier collection efficiency [40]. The marginal reduction in V_{OC}, with an increase in bulk defect density, can be attributed to the formation of defect energy levels in CBO light absorbers, which alters the effective bandgap of the CBO absorber layer. The effect of changes in J_{SC} and V_{OC} is reflected in the FF of the AOHSCs. Similarly, CBO/MOs interfacial interactions also play an important role in smooth charge extraction. Therefore, the effect of interfacial defect density variation of the CBO/MO interface on the performance parameters is evaluated and shown in Fig. 4.5(b). The increase in interfacial defect density from 10^{10} to 10^{18} cm⁻³ adversely affects the PCE of the device. The maximum PCE of 21.31, 21.84, 20.7, and 18.21 % is achieved at lower interfacial defect density (i.e., 10^{10} cm⁻³) for WO₃, SnO₂, ZnO, and TiO₂ transport layer, respectively. The V_{OC} of the device reduces with increasing interfacial defect density due to the reduced energy band offset level at the CBO/MO interface[18]. The J_{SC} remains stable until the interfacial defect density is 10^{14} cm⁻³ and reduces drastically after further increase. The marginal reduction in FF arises at higher interfacial defect density due to increased parasitic resistance. Overall, the enhancement of the interfacial defect density (> 10^{14} cm⁻³) induces recombination and leads to the decay of photogenerated current, causing a dramatic reduction in PCE and FF.

The contact resistance of the metal contact and interfacial resistance between HTL/absorber/ETL induces the series resistance in solar cells. The effect of series resistance (i.e., 0 to 5 Ω -cm²) on the performance parameters of the simulated device is shown in Fig. 4.6(a). The maximum PCE of 24.16, 23.82, 23.84, and 23.03% is observed for WO₃, SnO₂, ZnO, and TiO₂ transport layers, respectively, at minimum series resistance (Rs). The Voc and Jsc for all the MO transport layers remained unaffected by variation in R_s. The FF of the device mainly depends on the parasitic resistances, linearly reduced with an increase in the R_s due to increased ohmic power loss, which also contributed to the reduction of PCE. The pinholes, generally pragmatic while film deposition, provide an extra path for charge carriers, lead to leakage current, and reduce the shunt resistance of the device [41]. Therefore, the shunt resistance of the device varied from 10 to $10^6 \Omega$ -cm² to evaluate the performance parameters of solar cells (Fig. 4.6(b)). The maximum PCE of 22.19, 22.31, 22.32, and 21.89 % is observed at resistance $>10^4 \Omega$ -cm² for WO₃, SnO₂, ZnO, and TiO₂ transport layers, respectively. Overall, FF and V_{OC} improved with shunt resistance, resulting in a higher PCE. Even though J_{SC} for ZnO and SnO₂ transport layers improved marginally at higher shunt resistance (>10⁴ Ω -cm²), it does not affect the device performance.



Fig. 4.6. Effect of variation in (a) series resistance and (b) shunt resistance on the performance parameters of AOHSCs.

4.3.5 Effect of work function and operating temperature

The work function of the back metal contact determines the built-in potential of the solar cells. Therefore, in this study, different metals, i.e., Fe, Cu, Au, and Pt, are used as rear contact to assess the performance of the CBO absorber layer and MO transport layer based AOHSCs (Fig. 4.7(a)). With Pt as the counter electrode, the maximum PCE of 23.79 %, 23.55 %, 23.56 %, and 22.84 % is observed for AOHSCs utilizing WO₃, SnO₂, ZnO, and TiO₂ transport layers, respectively. On the other hand, Au shows relatively comparable efficiency with high conductivity and chemical stability to Pt; however, the high cost of Pt and Au will obstruct its application as a back contact for the cost-effective production of AOHSCs. Besides, Fe is the most economical among all the metals tested in this study, but its poor conductivity delivers the least PCE. Nevertheless, Cu delivers reasonably equivalent PCE performance to that of Au, which originated from better charge extraction, showcasing it as a suitable back metal contact. Solar cells are designed to work in all environmental conditions. Therefore, for the
practical implementation of the device, it is critical to study the effect of operating temperature on the performance parameters of the solar cell. Therefore, the operating temperature is varied from 280 to 380 K, and the impact on the solar cell parameters is shown in Fig. 4.7(b).



Fig. 4.7. Effect of variation of (a) work function of rear metal contact and (b) operating temperature on the performance parameters of AOHSCs consisting of CBO absorber and MO transport layer.

The maximum PCE observed for WO₃, SnO₂, ZnO, and TiO₂ is 22.21 %, 21.93 %, 21.94 %, and 21.23 %, respectively, at room temperature. The charge carrier (electron and hole) velocity increases with an increase in operating temperature, resulting in higher excitation, which participates in energy conversion. Therefore, an increment in the Jsc is observed with an increase in operating temperature. However, the FF of the device is reduced due to an increase in internal resistance resulting from higher collisions between charge carriers with increasing operating temperatures. At higher operating temperatures, the reverse saturation current increases, resulting in reduced

Voc. Therefore, a reduction in the PCE is observed with an increase in the operating temperature of the device.



4.3.6 Effect of bias potential and input AC signal

Fig. 4.8. Effect of variation of (a) bias potential and (b) input AC signal frequency on the device capacitance. Inset of (a) is the corresponding Mott-Schottky plot of AOHSCs.

Further, the capacitance-voltage (C-V) characteristic is evaluated to identify the optimistic performance of the device using Eq. 4.9

$$c = \frac{c_0}{\left(1 + \frac{V_r}{V_{bi}}\right)^m} \tag{4.9}$$

Where, C is the junction capacitance, V_r is reverse bias voltage, V_{bi} is built-in potential, C_o is the capacitance at zero bias voltage, and m is the grading coefficient ascertain abrupt (m=1/2) and linearly graded (m=1/3) junction. C-V characteristics provide built-in potential between the CBO and MO layers, the width of the space charge region (SCR), and the apparent doping profile of the CBO absorber layer. The capacitance at different bias potentials is evaluated under AC signal at DC biased p-n junction, considering the device to be a parallel combination of junction capacitance and shunt resistance while neglecting the small series resistance [41]. However, practically, the device comprises different layers, and assuming the whole device is merely single p-n junction diode is an inaccurate estimation. Therefore, the C-V analysis is performed at 1MHz frequency to avoid the contribution of the deep-level defect. The C-V characteristics of AOHSCs simulated at 300K for R_{sh} of 10⁵ Ω -cm² (Fig. 4.8(a)) indicate that the capacitance in all four devices attains maximum values and, after that, decreases sharply with progressing DC bias voltage. At lower biased voltage, the higher capacitance value observed for the ZnO transport layer than other MO indicates the existence of more charged vacancy at the CBO/ZnO interface [42]. However, the reduced capacitance at higher bias voltage is attributed to the increased dielectric dispersion in all devices [43]. The corresponding Mott-Schottky plot (inset of Fig. 4.8(a)) relating capacitance per unit area (C_A) with acceptor carrier density (N_A) at the edge of CBO SCR is evaluated from Eq. 4.10.

$$\frac{1}{(C_A)^2} = \frac{2(V_{b_i} + V)}{q\epsilon_0 \epsilon_s A^2 N_A} \tag{4.10}$$

Where, ϵ_0 is the dielectric permittivity of the space, ϵ_s is the dielectric constant, V_{b_i} is the built potential, *V* is the applied reverse bias voltage, A is the area of the cell, *q* is the electronic charge, and N_A is the acceptor carrier density cm⁻³. The built-in potential of 1.16, 1.13, 1.23, and 0.96 V is observed for WO₃, SnO₂, ZnO, and TiO₂ transport layers, respectively. Similarly, capacitance-frequency (C-f) characteristics of optimized AOHSC are simulated for various frequencies (1 Hz to 10 GHz) under the dark condition at zero bias and 300K (Fig. 4.8(b)). The higher capacitance value below 1 MHz decreases drastically in the range of 1 to 100 MHz and, after that, remains constant. The number of minority carriers increases abruptly above 1MHz frequency, leading to more carrier injection, improving the recombination rate within the junction and, therefore, reducing capacitance across the junction [44].

4.3.7 Recombination rate and intensity variation of AOHSCs

Recombination generally happens at the interface due to differences in charge carrier mobility and band energy, altering the V_{OC} and overall performance of the device. However, The generation and recombination rate (Fig. 4.9 (a)) evaluated for AOHSCs evidences the dominance of SRH recombination. The total generation rate is equal to the recombination rate in the CBO absorber, as all charge carriers recombine at V_{OC} . The recombination rate is given by Eq. 4.11 [45].

$$V_{0c} = \frac{2k_B T}{q} \ln \left[k_1 \left(\sqrt{G_a k_2 + 1} - 1 \right) \right]$$
(4.11)

Where, k_1 and k_2 are given as

$$k_1 = \frac{1}{2} \frac{R_0^d}{(R_0^i + R_0^b)} \tag{4.12}$$

$$k_2 = \frac{4w(R_0^i + R_0^b)}{(R_0^d)^2}$$
(4.13)

The correlation between different recombination coefficients, absorber bandgap (E_g), built-in potential (ϕ_{b_i}) calculated using (C-V) at zero bias is given by Eq. 4.14 [46].

$$E_a = \frac{R_0^i \phi_{b_i} + R_0^b E_g}{R_0^i + R_0^b} \tag{4.14}$$

The V_{OC} of all the devices is estimated under different illuminations at 300 K temperature (Fig. 4.9 (b)) and evaluated values of different recombination coefficients are summarized in Table 4.2.



Fig. 4.9. (a) Generation and recombination rates for all MOs based AOHSCs and (b) Effect of variation of illumination intensity on the V_{OC} of AOHSCs.

Where, R_0^i , R_0^d , and R_0^b are recombination rates at the CBO/MO interface, depletion region and quasi-neutral region, respectively. k_B is the Boltzmann's constant, T is the operating temperature of the device, q is the electronic charge, G_a is the illumination intensity, W is the total width of the device, E_a is the activation energy of recombination, E_g is absorber bandgap, and ϕ_{b_i} is built in potential.

Device	k_1	k ₂	R_0^i (cm ⁻² s ⁻¹)	R_0^d (cm ⁻² s ⁻¹)	R_0^b (cm ⁻² s ⁻¹)
CBO/WO ₃	4.92×10^{5}	2736	96.74	1.35×10^{8}	41.18
CBO/SnO ₂	6.95×10^{5}	5192	25.28	5.01×10 ⁷	10.76
CBO/ZnO	5.14×10^{5}	3236	89.10	1.08×10^{8}	16.04
CBO/TiO ₂	5.87×10^{5}	3942	36.60	7.79×10^{7}	29.76

Table 4.2 Extracted recombination rate and their coefficient of AOHSC.

4.3.8 Optimized J-V characteristics

A high value of incident photon to current efficiency (IPCE) ensures the sufficient availability of charge carriers to take part in the energy conversion process. The effect of the thickness of the CBO absorber layer in the variation of IPCE is shown in Fig. 4.10 (upper panel). The increase in thickness of the absorber layer ensures enhancement in the total number of charge carriers generated, therefore improving the IPCE of the device. However, beyond 900 nm, the limited reach out of incident photons constrains the charge carriers generated and hence saturates the IPCE, as demonstrated in Fig. 4.3(a). Further, the IPCE curves show first and second onset at ~850 nm and < 500 nm wavelength, accounting for the bandgap of the CBO absorber and MO transport layers, respectively. It is also to be noted that the IPCE is a combination of both CBO and MO transport films at higher energy. The optimum solar cell parameters evaluated for the base value of acceptor density, donor density, and defect density of transport land absorber layers offering a series resistance of 5 Ω -cm² are shown in Fig. 4.10 (lower panel). CBO absorber layer based AOHSCs show high Voc, Jsc, FF, and PCE for all transport layers under investigation. The optimum PCE observed for WO₃, SnO₂, ZnO, and TiO₂ transport layers is 22.21, 21.93, 21.94, and 21.23 %, respectively. WO₃ based AOHSC shows a marginally higher value of PCE compared to other MO transport layers., which originates from their lower bandgap and marginally higher photoactivity. Slightly higher photoactivity of the n-type WO₃ transport layer is also one of the reasons behind this higher PCE. The high absorption coefficient of WO_3 in the 350 to 500 nm wavelength range results in the generation of more numbers of charge carriers, which adds up with the CBO absorber. Higher electron mobility of SnO₂ and ZnO than TiO₂ transport layer produced marginally higher PCE for SnO₂ and ZnO based solar cells than TiO₂. Notably, optimized devices of MOs transport layers, which are cost-effective, evinronmently friendly, and easily processible, delivered equivalent performance to that comprising CdS, SrSnO₃, and WS₃ transport layers reported in the literature (Table 4.3).



Fig. 4.10 CBO light absorber effect on IPCE variation of AOHSCs for various MO transport layers without doping. (upper panel). Optimum J-V characteristics of AOHSCs consisting of CBO and MO transport layer without doping (lower panel). **Table 4.3** Comparison of our work with previously reported work.

S.N.	Device Architecture	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)	Ref.
1.	FTO/Al/CdS/CBO/Ni	0.97	31.61	0.846	26.0	[17]
2.	ITO/SrSnO ₃ /CBO/Au	1.32	20.70	0.807	22.19	[18]
3.	ITO/WS ₂ /CBO/Au	1.33	21.08	0.813	22.84	[19]
4.	ITO/MO/CBO/Au	1.33	20.38	0.823	22.21	This Work

4.4 Conclusion

This study reports the p-type kusachiite CBO as a light absorber material for an AOHSC, an alternative for heat, UV, and moisture-sensitive Pb-based organic-inorganic perovskite absorber material. Different n-type MO such as WO₃, SnO₂, ZnO, and TiO₂ are

chosen as transport layers owing to their high charge mobility, efficient charge extraction capabilities, and excellent physical and chemical stability. The simulated AOHSC shows excellent PCE, which can be highly stable due to the nonreactivity of metal oxides to the heat, moisture, and UV radiation altering the interface. Here, we have studied the effect of different parameters like thickness, charge carrier density, bulk defect density, interfacial defect density, parasitic resistance, work function, and operating temperature on our device, which can help researchers to fabricate a practically feasible photovoltaic device. All these MO have shown excellent PCE with high V_{OC} . WO₃ based devices have shown the maximum PCE of 22.21 % among all the MO transport layers, but the higher fabrication cost of WO₃ than other MO limits the advancement of WO₃ as the transport layer. However, without doping, higher charge mobility of SnO₂ and ZnO results in a higher PCE of 21.93 % and 21.94 %, respectively, than TiO₂ based device with PCE of 21.23 %. Nevertheless, all the AOHSCs show excellent PCE of >26 % at high acceptor carrier density of 10²² cm⁻³ for CBO absorber, irrespective of the metal oxide transport layer. C-V and C-f studies performed on the optimized device of CBO absorber and MO transport layer showed the built-in potential of 1.16, 1.13, 1.23, and 0.96V for WO₃, SnO₂, ZnO, and TiO₂, respectively. Therefore, this study proposes stable and economic AOHSCs using SnO₂ and ZnO as the most promising candidate as a transport layer and CBO as an absorber layer. However, one needs to focus on using facile and economical synthesis techniques to obtain the desired SnO₂ and ZnO transport layer and CBO absorber layer, maintaining an optimistic interface to form AOHSCs. Overall, this study provides the guidelines for fabricating high-efficiency AOHSCs using a CBO absorber and SnO₂ or ZnO transport layer, which can be experimentally viable, cheap, stable, and environmentally friendly.

4.5 References

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Chapter 5

1D ZnO nanorods/2D Sb₂Se₃ nanoflakes for light sensing applications

5.1 Introduction

Photodetectors (PDs) play a critical role in converting optical signals into electrical signals. Owing to these signal conversions, PDs have wide range of applications in photoelectric imaging, optical communication, and optical remote sensing; thus, research regarding PDs initially focused on detecting specific wavelength bands or PDs operating only in the narrowband [1-3]. Therefore, to detect various wavelength regions, it is imperative to have different PDs simultaneously operating in particular wavelength regions. However, this would inevitably increase the number of PDs required, data instability, cost, and operational complexity. Therefore, single broadband PDs with photodetection ranging from the ultraviolet (UV) to the terahertz (THz) region are crucial for industrial and scientific applications. For example, broadband imaging has received significant attention owing to its potential applications in environmental and biological research, as well as missile-launch detection technology [4-6]. This indicates that the research, exploration, and development of new PDs with a broad spectral responsivity (R) and high external quantum efficiency (EQE) will intensify, leading to the discovery of new semiconductor materials or their combinations.

Considering the aforementioned, antimony selenide (Sb₂Se₃) is highly promising nontoxic compound with earth-abundant constituents that possesses intrinsically benign grain boundaries that are helpful for the easy transport of charge carriers [7-8]. This compound has been previously reported as a photovoltaic material and is good alternative to cadmium chalcogenides (CdTe, CdSe, CdS, etc.) owing to its sufficient bandgap (1.03 eV) [9], large absorption coefficient (>10⁵ 1/cm in the visible region) [10], decent carrier mobility (10 $cm^2/V \cdot s$ for minority carriers), and long carrier lifetime (60 ns based on the transient absorption spectroscopy) that promise the fabrication of efficient optoelectronic devices [11]. Therefore, in this regard, a thin-film solar cell was fabricated using combinations of CdS/Sb₂Se₃ that indicated a device efficiency of 5.6% [12]. However, owing to the toxic nature of cadmium, researchers have attempted to find alternative compounds that do not contain cadmium. To overcome the aforementioned, a Sb₂Se₃/AgSbSe₂ heterojunction was proposed [13], which was also helpful in solving the intrinsic low electrical conductivity of Sb₂Se₃ and demonstrated photoresponse that was 4.2 times higher than that compared to PDs based on Sb₂Se₃ nanorod (NR) films alone. Furthermore, combining zinc oxide (ZnO) with Sb₂Se₃ was proposed to enhance the optoelectronic properties [14]. ZnO, which is non-toxic material, has high charge-carrier mobility (200-300 cm²/V·s), low-temperature synthesis and stability, and has several optoelectronic applications [15-17]. Therefore, it can be a better alternative to highly toxic CdS when replacing the buffer layer [18]. Although ZnO has a larger bandgap compared to CdS, it has a proper band alignment with respect to Sb₂Se₃. Therefore, it is one of the best options as the buffer layer for Sb₂Se₃ in forming a photovoltaic device.

Furthermore, the doping of nickel (Ni) or bismuth (Bi) in Sb₂Se₃ was proposed, which enhanced the PD properties with the broadband R or demonstrated a good EQE of 1.6×10^6 %, respectively [19-20]. Therefore, finding and developing proper material systems with suitable dopants and band alignments remains a key challenge in developing novel photovoltaic technologies. Furthermore, the formation of suitable interfaces when semiconductor PD device is developed with a combination of different heterostructures defines the functionalities of the device because they provide a potential driving force that facilitates the separation of photoexcited charge carriers, dominates the transfer direction, increases the contact interface, and accelerates the rate of charge transfer within the heterojunction compartment. Regardless, the fabrication of such heterostructures is challenging. In particular, nanostructured p-n heterojunctions between two semiconductors have been reported to be the most challenging. However, if the heterojunctions are appropriately designed, an effective space charge region can be fabricated owing to the depletion of electrons from the n-type semiconductor and holes from the p-type semiconductor near the interface [21]. Therefore, this study proposes a nanostructured p-n heterojunction considering two-dimensional (2D) Sb₂Se₃ nanoflakes (NFs) as p-type semiconductor and one-dimensional (1D) ZnO NRs as an n-type semiconductor, providing an intimate contact area, which may promote the photogenerated charge carriers at the interface of the Sb₂Se₃/ZnO. In addition, ZnO enhances the photoactivity as buffer layer. This provides green and scalable strategy for replacing toxic CdS; most importantly, it operates in the UV region. Conversely, Sb₂Se₃ acts as an effective charge separation layer and operates from approximately 600 nm (in the visible region) to the near-infrared (NIR) region, providing flexibility to tune the electromagnetic (EM) spectrum. In this regard, combination of both can effectively facilitate photoactivity owing to proper band

alignment. Furthermore, the strong interactions between the ZnO crystal facets improve the crystal orientation of Sb₂Se₃. Notably, it provides the broadband operating region necessary for single PD device.

In addition, if these two layers of materials are stacked in nanostructured forms, such as 2D-Sb₂Se₃ NFs/1D-ZnO NRs, they will provide a (a) large surface area, allowing a significant increase in the carrier generation/collection for the PD; (b) well-defined, robust charge transport paths with improved carrier transport properties; and (c) light trapping effects that can result in enhanced light harvesting within the nanostructures. Here, in this study we have developed PDs using coupled ZnO NRs & Sb₂Se₃ NFs which have not been explored in detail. The 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure is novel in terms of synthesis/deposition technique, device architecture, and surface morphology than other reports on ZnO/Sb₂Se₃ based PDs. Present study focuses on investigating the low-intensity light detectivity and stable performance of Sb₂Se₃/ZnO heterostructures. PD showcase an ability to detect even low intensity light at different wavelengths with sufficiently good performance parameters. C-V of Sb₂Se₃/ZnO-based PD exhibits negative capacitance, which helped in improving photo detectivity characteristics; this is discussed, and detailed analysis is provided in this study, which is not provided in earlier reported literatures.

5.2 Experimental Details

5.2.1 Synthesis of ZnO seed layer by spin coating

The seed layer of ZnO NPs was synthesized using a solution-processed spin coating approach. The details of solution process approach along with the schematic are discussed in chapter 2 (section 2.2.1).

5.2.2 Synthesis ZnO NRs by hydrothermal method

A low-temperature hydrothermal technique was used for the growth of ZnO NRs over seed layer coated substrates. The synthesis protocol along with the schematic are discussed in chapter 2 (section 2.2.2).

5.2.3 Preparation of Sb₂Se₃ overs ZnO NRs

The preparation of Sb_2Se_3 precursors by electrodeposition and selenization and after that the growth of Sb_2Se_3 over the ZnO NRs by thermal evaporation is detailed in Chapter 2 (section 2.2.3).

5.2.4 Basic characterization of material property and photodiode testing

The crystallographic properties and planes of the crystalline Sb₂Se₃ phases were investigated via transmission electron microscopy (TEM, ThermoFisher, Talos F200X G2) and X-ray diffraction (XRD, Bruker AXS D8 Discover with a Copper (Cu) Ka radiation source). Morphological investigations of the vertical and horizontal 2D-Sb₂Se₃ NFs and 1D-ZnO NRs crystals were performed by field-emission scanning electron microscopy (FESEM, JSM-6700 F Plus). Chemical element and elemental mapping analyses were performed on the 2D-Sb₂Se₃ NFs and 1D-ZnO NRs using energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, X-Max). The optical bandgaps of the 1D-ZnO NRs and Sb₂Se₃ NFs were analyzed using a UV-visible absorbance spectrophotometer (Shimadzu, UV-2600). UV photoelectron spectroscopy (UPS, AIPES, 40 MeV, $\lambda = 61$ Å, and I = 100 mA) was used to identify the work function and valance band edge of the 1D-ZnO NRs and 2D-Sb₂Se₃ NF films. The time-resolved photoluminescence (TRPL) decay profiles of the 1D-ZnO NRs and 2D-Sb₂Se₃ NF/1D-ZnO NR structure were measured using a single-photon counting method. The samples were illuminated with a laser pulse at 370 nm, which was produced by the second harmonic of a femtosecond Ti:sapphire laser (Tsunami, Spectra Physics) and pumped by a diode laser (Millenia Xs, Spectra Physics). The PL of the samples was dispersed in a spectrometer (G-250 Nikon) and detected using a microchannel-plate photomultiplier (R-3809U-52, Hamamatsu). The chemical compositions and oxidation states were confirmed via X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc., Al-ka). A system source meter (2611 B, Keithley), in conjunction with a computer, was used to record the electrical signals. An optical chopper was used to periodically cut off the light source. The light intensity was measured using a lux meter and laser power meter. For the solar irradiance, while measuring the dynamic response of the PD, the light intensity was varied from 0.25 -1.75 mW/cm². However, for different spectral responses at various wavelengths, the light intensity was 0.15 mW/cm². Capacitance-frequency tests were performed using a 2611B Keithley semiconductor characterization system with a 0 V DC bias and 30 mV AC amplitude ranging from 1 Hz to 1 MHz in the dark.

5.3 Results and Discussion



5.3.1 FESEM, EDS, XRD, TEM and device architecture

Fig. 5.1. (a) Schematics of the heterostructure formed using 2D-Sb₂Se₃ NFs/1D-ZnO NRs, (b) 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure, (c) bare Sb₂Se₃ NFs, and (d) bare ZnO NRs.

Fig. 5.1(a) presents the schematic structure of the 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterojunction PD. Transparent FTO glass was used as the bottom electrode and substrate; n-type ZnO served as the bottom layer; a layer of p-type Sb₂Se₃ thin film functioned as the absorber material; and a point contact of silver (Ag) functioned as the conducting electrode. The device structure was confirmed by the cross-sectional scanning electron microscopy (SEM) image illustrated in Fig. 5.1(b); the effective thickness of the device was approximately 2.5 μm. The FESEM image of the Sb₂Se₃ thin film shown in Fig. 5.1(c) indicates that Sb₂Se₃ with large grains compactly grew on the FTO substrate. Fig. 5.1(d) demonstrates the top view of the FESEM image of the as-grown ZnO NRs, indicating that the ZnO NRs were uniformly and densely grown on the FTO substrates with diameters of approximately 100 nm. Notably, the heterostructure sample clearly revealed that the 2D flake structure of Sb₂Se₃ was

present on the 1D ZnO NRs and conformally coated along the ZnO NRs. Certain porous regions may have developed owing to the combination of the NFs and NRs, which, if considered, can be helpful for light to obtain multiple reflections, indicating that the photoactivity of the heterostructure will be enhanced.

Structural characterization via X-ray diffraction was performed on both ZnO NRs, and the bilayer structure of 1D-ZnO and 2D-Sb₂Se₃ heterostructure, clearly indicating that the Bragg's peaks are related to the ZnO and Sb_2Se_3 materials, with no impurity peaks present. Fig. 5.2(a) demonstrates XRD pattern of the 1D-ZnO NR samples. The peaks observed at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, and 62.9° for (100), (002), (101), (102), (110), and (103) planes, respectively, correspond to the wurtzite crystalline structure of ZnO (JCPDS 65-3411). All other peaks indexed as (*) belongs to the (110), (101), (200), (211), (220), (310), and (301) planes of the tetragonal FTO structure (JCPDS 041–1445), indicating the formation of ZnO without any impurities. Similarly, the diffraction pattern of 1D-ZnO and 2D-Sb₂Se₃ bilayer heterostructure Fig. 5.2(b)shows the diffraction peaks at 24.1°, 28.4°, 31.2°, 34.4°, 35.7°, 39.0°, 45.5°, and 51.8° assigned to (301), (112), (212), (402), (312), (411), (305), and (321) planes of the orthorhombic crystal structure of Sb₂Se₃ NFs (JCPDS 65-2433) along with the characteristics peaks of ZnO NRs and FTO substrates, which confirms the formation of 2D-Sb₂Se₃ NFs /1D-ZnO NRs heterostructure. An optical image of the fabricated heterostructure sample is shown in the inset of Fig. 5.2(b), where the substrate was 1 cm^2 in size and the active area of the PD device was $1 \times 0.5 cm^2$. Furthermore, the 1D ZnO structure facilitated charge transport and provided high electrical performance.



Fig. 5.2. XRD pattern of (a) bare 1D-ZnO NRs and (b) 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure.



Fig. 5.3. Energy dispersive X-ray spectroscopy (EDS) of (a) ZnO NRs film and (b) ZnO/Sb₂Se₃ bilayer with corresponding elemental mapping shown in the inset.

The EDS spectra and corresponding EDS mapping of the ZnO NRs, as well as the 2D-Sb₂Se₃ NFs/1D-ZnO NRs bilayer structure shown in Fig. 5.3, confirm the presence of Zn and O in the ZnO NRs (Fig. 5.3(a)), as well as Sb, Se, Zn, and O in the 2D-Sb₂Se₃ NFs/1D-ZnO NRs bilayer heterostructure (Fig. 5.3(b)) without any foreign elements. The absence of any impurities confirmed the formation of pure ZnO and the 2D-Sb₂Se₃ NFs/1D-ZnO NRs bilayer.

Further, TEM image of the 2D-Sb₂Se₃ NF/1D-ZnO NR bilayer structure is shown in Fig. 5.4(a). A thin film consisting of a compact ZnO seeded layer and ZnO NRs was grown layer-by-layer on an FTO-coated glass substrate. Heavy etching using Ar^+ ions during the thin-film preparation for the TEM analysis resulted in the disappearance of Sb₂Se₃ loaded on the ZnO NRs, as shown in the layer-by-layer form shown in Fig. 5.1. Furthermore, the ZnO NRs with clearly visible textural boundaries remained unaltered after the loading of Sb₂Se₃ (Fig. 5.4(b)), as confirmed by the HRTEM images obtained at the interfacial textural boundaries (Fig. 5.4(c)), the interface of the two consecutive NRs (Fig. 5.4(d)), and the tip (Fig. 5.4(e)). Moreover, the interplanar spacing of 2.81 Å assigned to the (010) plane remained identical throughout the body of the ZnO NRs, confirming that the loading of the Sb₂Se₃ NFs did not alter the crystalline morphology and chemical composition at the interface and offered stable PD performance.



Fig. 5.4. TEM image of the (a) 2D-Sb₂Se₃ NF/1D-ZnO NR bilayer structure and (b) ZnO nanorods in the multilayer structure (dotted regions in the inset are enlarged in (c), (d), and (e)). HRTEM images of the ZnO NRs at the (c) textural boundaries (red region in (b)), (d) two consecutive NRs (orange region in (b)), and (e) tip identified (yellow squares in (b)). The dotted lines indicating the textural boundaries of the ZnO NRs are only visual guidelines. TEM images of the (f, g) 2D-Sb₂Se₃ NFs/1D-ZnO NRs bilayer structure at different magnifications showing stacking of ZnO seed layer, 1D ZnO NRs and 2D Sb₂Se₃ NFs. The EDS spectra collected at (h) 2D Sb₂Se₃ NFs, (i) interface of 2D-Sb₂Se₃ NFs/1D-ZnO NRs, and (j) 1D ZnO NRs are identified with yellow color in Fig. (g).

Furthermore, the TEM image collected at the relatively thicker area (Fig. 5.4(f)) identified during imaging represents the formation of layer-by-layer structure of Glass/FTO/ZnO Seed layer/1D ZnO NRs/2D-Sb₂Se₃ NFs, as observed in Fig. 5.1(b). Moreover, the EDS is collected at high resolution (Fig. 5.4(g)) to trace and precisely identify the existence of Zn, O, Sb, and Se in this layer-by-layer structure. The intensity of peaks identifying Sb and Se, and Zn and O is higher over the nanoflakes (Fig. 5.4(h)) and nanorods (Fig. 5.4(j)) morphologies, respectively, indicating the existence of Sb₂Se₃ and NF ZnO NRs. Moreover, the EDS spectra collected at region (i) (identified in Fig. 5.4(g)) representing the interface of ZnO NR and Sb₂Se₃ indicate the presence of Zn, O, Sb, and Se in the EDS collected at region (j) over ZnO NRs morphology represents the interface formation due to the deposition of Sb₂Se₃ layer long textural boundaries of ZnO NRs depicting a conformal coating over the ZnO NRs.

5.3.2 UV-Visible, UPS, XPS, PL, and energy band diagram

The UV-visible absorbance spectra of the bare ZnO NRs and 2D-Sb₂Se₃ NF/1D-ZnO NR films were recorded between wavelengths of 300 and 1000 nm, as shown in Fig. 5.5(a). The ZnO films demonstrated negligible absorbance in the visible region, allowing the complete transmission of visible light. The ZnO film exhibited an absorption onset at a wavelength of approximately 400 nm and absorbed light in the UV region of the solar spectrum. Similarly, the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure exhibited significant absorbance in the visible region, with an onset at approximately 800 nm. Another onset at approximately 400 nm corresponded to the ZnO film of the 2D-Sb₂Se₃ NF/1D-ZnO NR bilayer. The corresponding Tauc plots of both the ZnO and 2D-Sb₂Se₃ NF/1D-ZnO NR bilayers (Fig. 5.5(b)) indicates bandgaps of approximately 3.24 and 1.63 eV for the ZnO NRs and Sb₂Se₃ NFs, respectively, which are in agreement with the reported literature [14, 19]. The lower bandgap of the Sb₂Se₃ NFs enables the acquisition of the solar spectrum in the visible to NIR region to generate more photoelectrons. Furthermore, UPS were recorded for both the ZnO film and the 2D-Sb₂Se₃ NF/1D-ZnO NR bilayer; the full spectra are shown in Fig. 5.5(c). The work function was evaluated by the difference between the incident UV

photon energy (40 eV) and the secondary onset of the spectrum at 35.79 and 35.70 eV for Sb₂Se₃ and ZnO, respectively, as shown in Fig. 5.5(d). The calculated values of the work functions for Sb₂Se₃ and ZnO were 4.21 and 4.30 eV, respectively, with respect to the vacuum level. The VB onset for both Sb₂Se₃ and ZnO was extrapolated from the long tail of the UPS and is shown in Fig. 5.5(e) [23]. The VB maxima (VBM) values evaluated for both Sb₂Se₃ and ZnO were 0.76 and 3.09 eV, respectively, with respect to the fermi energy level (E_F). By using the optical bandgaps of 1.63 and 3.24 eV for Sb₂Se₃ and ZnO, respectively, the corresponding CB minima (CBM) values were 0.87 and 0.15 eV with respect to E_F . Detailed information regarding the various energy band levels is presented in Table 5.1. The corresponding energy band (EB) diagram of the FTO/ZnO/Sb₂Se₃/Ag device architecture is shown in Fig. 5.5(f). The appropriate band position of ZnO with respect to Sb₂Se₃ provides smooth charge transportation at the interface of the 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure [15]. Similarly, the highenergy barrier of ZnO prevents holes from recombining and enhances the charge separation/extraction process.



Fig. 5.5. (a) UV-visible absorbance, (b) corresponding Tauc's plot, (c) Ultraviolet photoelectron spectra (UPS), (d) secondary cut-off region, (e) VB onset, and (f) Energy band diagram of pristine ZnO NRs and Sb₂Se₃ films.

Sample	Work function,	Valance band	Bandgap,	Conduction band	
	W _F (eV)	maxima, VBM (eV)	EG (eV)	minima, CBM (eV)	
ZnO NRs	4.30	3.09	3.24	0.15	
Sb ₂ Se ₃ NFs	4.21	0.76	1.63	0.87	

Table 5.1. Various energy band levels for ZnO NRs and Sb₂Se₃ NFs.



Fig. 5.6. Time-resolved photoluminescence (TRPL) of 1D-ZnO NRs and 2D-Sb₂Se₃ NFs/1D-ZnO NRs obtained with 370 nm excitation.

Furthermore, the time-resolved photoluminescence (TRPL) (Fig. 5.6) results for the 1D-ZnO NRs and 2D-Sb₂Se₃ NFs/1D-ZnO NRs obtained with an excitation of 370 nm are consistent with the tendency of the defect concentration. The lifetime components represent the fast decay time associated with defect-assisted non-radiative recombination and the slow decay time associated with radiative recombination, respectively [24]. The increase in PL intensity with the deposition of 2D-Sb₂Se₃ NFs represents the suppression of defects [25]. The average carrier lifetime obtained from the TRPL plot increased from 2.23 to 2.63 ns (Table 5.2), which indicates that the defect density decreased with the formation of the 2D-Sb₂Se₃ NFs/1D-ZnO NRs. This implies that there is a reduction in the non-radiative pathways; therefore, after the formation of the 2D-Sb₂Se₃ NFs/1D-ZnO NRs structure, the performance was more stable compared to the individual ZnO or Sb₂Se₃. This implies that there is a reduction in the non-radiative pathways; therefore, after the formation of the 2D-Sb₂Se₃ NF/1D-ZnO NR structure, the performance was more stable compared to the individual ZnO samples (Fig. 5.6).

Sample	$ au_1$ (ns) (A1)	$ au_2$ (ns) (A ₂)	$ au_{av}$ (ns) $(\sum_{i=1}^{2} A_i)$
2D-Sb ₂ Se ₃ NFs/1D-ZnO NRs	2.07 (0.6)	3.43 (0.4)	2.63 (1)
1D-ZnO NRs	1.42 (0.56)	3.26 (0.44)	2.23 (1)

Table 5.2. The lifetime (τ_i) , pre-exponential factor (A_i) , and the average lifetime $(\tau_{an} \equiv \sum_i A_i \tau_i / \sum_i A_i)$ evaluated for 1D ZnO NRs and 2D-Sb₂Se₃ NFs/1D-ZnO NRs.

The XPS spectra of the 2D-Sb₂Se₃ NFs were deconvoluted using the Voigt fitting function with a Shirley background to demonstrate the oxidation state of the elements in the nanostructure (Fig. 5.7). The deconvoluted core-level spectrum of Sb(3d) perfectly fits with the five peaks (Fig. 5.7(a)). The peaks at binding energy (B.E.) values of 530.1 and 539.4 eV correspond to $Sb^{3+}(3d_{5/2})$ and $Sb^{3+}(3d_{3/2})$, respectively, indicating the presence of the Sb³⁺ oxidation state in the nanostructure, and are in good agreement with the literature [26]. Moreover, the spin-orbital energy separation of 9.3 eV in $Sb^{3+}(3d_{5/2})$ and $Sb^{3+}(3d_{3/2})$ signifies the formation of the Sb_2Se_3 nanostructure. The peaks at B.E. values of 528.6 and 537.8 eV with a separation energy of 9.2 eV correspond to $Sb^{0}(3d_{5/2})$ and $Sb^{0}(3d_{3/2})$, respectively, indicating the presence of a negligible amount of unreacted Sb in the metallic form. The peak at a B.E. of 532.0 eV indicates the presence of $SO_4^{2-}(1s)$ sulfate ions. The core-level XPS spectrum of Se(3d) is deconvoluted into three distinct peaks (Fig. 5.7(b)) at B.E. values of 54.5 and 55.5 eV, which correspond to $\text{Se}^{2-}(3d_{5/2})$ and $\text{Se}^{2-}(3d_{3/2})$, respectively, indicating the Se^{2-} oxidation state [19, 27]. However, the peak at 53.1 eV corresponds to $Se^{0}(3d_{5/2})$, which signifies the presence of residual Se in metallic form. Moreover, three different peaks were identified as the auger lines of Sb(MNN) (Fig. 5.7(c)), which were located at B.E. values of 1027.1, 1034.1, and 1036.8 eV, corresponding to the MNN5, MNN4, and MNN3 energy levels of Sb(MNN), respectively. The XPS profiles of the Zn(2p) and O(1s) core levels are shown in Fig. S2(d-e). Deconvolution of the O(1s) XPS spectrum (Fig. 5.7(d)) demonstrated two distinct peaks at B.E. values of 530.0 and 531.5 eV, which involved the presence of $O^{2-}(1s)$ anions and the surface contamination (SC) from the adsorbed hydroxy group, respectively [28, 29]. The core-level XPS spectra of Zn(2p) (Fig. 5.7(e)) demonstrate two distinct peaks with significant intensities located at B.E. values of 1021.1 and 1044.2 eV corresponding to $Zn^{2+}(2p_{3/2})$ and $Zn^{2+}(2p_{1/2})$, respectively. Further, the spin-orbital splitting of the Zn(2p) with a peak separation at a B.E. of 23.0 eV reflects the presence of oxidized Zn and not metallic Zn [16].



level of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure and high resolution XPS spectra of (d) O(1s) and (e) Zn (2p) core level of bare 1D-ZnO NRs.

5.3.3 Light sensing measurements

The rectifying characteristics of the current–voltage (I–V) curves presented in Fig. 5.8(a) indicate the formation of a p-n junction, and the I–V curves of the sample indicate diode characteristics. The nonlinearity and asymmetry of the curves signify a Schottky contact within the heterostructure sample, which was validated by performing Mott–Schottky measurements on the heterostructured 2D-Sb₂Se₃ NF/1D-ZnO NR sample, as shown in Fig. 5.8(b). The co-existence of positive and negative slopes in the Mott–Schottky curve validates the presence of the p–n junction [30]. The negative and positive slopes can be attributed to the p-type Sb₂Se₃ and n-type ZnO, respectively. The time-resolved photoresponse (I–t curves) was measured under a 1 V external bias and illumination with a constant intensity of 1.25 mW/cm² (Fig. 5.8(c)) for the 1D-ZnO NRs, bare 2D-Sb₂Se₃ NFs, and 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure, respectively. This clearly demonstrates that the bare ZnO and 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure, the bare

Sb₂Se₃ NF structures did not exhibit an appropriate response to illumination. Furthermore, it also revealed that the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure demonstrated a fast photoresponse as well as recovery after the light was turned "ON" or "OFF," respectively, whereas this was not observed for the bare ZnO NRs. Conversely, the bare ZnO NRs exhibited a slow photoresponse and no proper recovery. This indicates that the ZnO NRs or Sb₂Se₃ NFs did not individually provide the necessary PD properties; however, when combined to form a heterostructure, they provided the necessary synergetic PD characteristics.



Fig. 5.8. (a) I-V curve of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure, (b) Mott-Schottky plot $(1/c^2 \text{ vs. V})$ for 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure measured at 100 Hz frequency, (c) Time-resolved photoresponse (I-t) curve of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure (upper panel), bare Sb₂Se₃ NFs (middle panel), and bare ZnO NRs (lower panel).

The dynamic photoresponse (I-t) of the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure with different light intensities were measured at an external bias of 1 V, which is shown in Fig. 5.9(a). The photoresponse exhibited an excellent dynamic response after illumination. Additionally, a linear increment in the dark current was observed (Fig. 5.9(a)) as the incident light intensity increased, which may be owing to the localized heating of the sample due to the sample being exposed to longer and continuous light

[31]. The heterostructured sample responded to light intensities ranging between 0.25 mW/cm² and 1.75 mW/cm². A clear photocurrent dependence on the light intensity (Fig. 5.9(b)) was observed, which increased as the power of the light intensity increased and was consistent with the fact that the number of photogenerated charge carriers was proportional to the absorbed photon flux. This correlation can be expressed as $(I \propto p^{\theta})$, where the exponent ' θ ' determines the response of the light intensity. Herein, the linear fitting in the form of a double log plot (not shown) presented a ' θ ' value of 0.9, which was smaller than that of the low-trap state junctions with a ' θ ' value of one. The complex kinetic processes of electron-hole generation, trapping, carrier-carrier interactions, and recombination in the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure can be expected to have an exponent with a value of less than one [32]. The corresponding responsivity (R) as a function of the light intensity is also shown in Fig. 5.9(b), demonstrating that the R value increases as the light intensity decreases and significantly decreases as the light intensity increases. A higher incident light intensity provided a greater number of photogenerated charge carriers. However, the increased carrier concentration leads to an increased charge recombination rate, thus reducing the R value of the device [33].



Fig. 5.9. (a) Dynamic photoresponse (I-t) curve of heterostructure $2D-Sb_2Se_3$ NFs/1D-ZnO NRs measured at different intensities (mW/cm²), (b) Responsivity and photocurrent with light intensity for 2D-Sb_2Se_3 NFs/1D-ZnO NRs heterostructure.

Furthermore, a stability test was performed at two different light intensities, that is, 1.25 mW/cm² and 1.75 mW/cm², at a fixed 1 V external bias, which is shown in Figs. 5.10(a) and 5.10(b), respectively. This indicates that the 2D-Sb₂Se₃ NF/1D-ZnO NR

heterostructure exhibits a stable photoresponse to light intensities and that the sample is relatively stable and produces a stable performance for a longer period of time. Moreover, the dark current continuously increases over time, as shown in in Figs. 5.10(a) and 5.10(b). Continuous light illumination for a prolonged period increases the operating temperature of the device, resulting in a dark current. Owing to the increase in the dark current, the photocurrent also demonstrated similar behavior over time. For comparison, a similar stability test was performed with bare 1D-ZnO NRs, which did not demonstrate proper and long-term stable photodiode performance.



Fig. 5.10. Stability test of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure measured at a light intensity of (a) 1.25 mW/cm² and (b) 1.75 mW/cm².



Fig. 5.11. Photocurrent response of bare 1D ZnO NRs measured at (a) 1.75 mW/cm^2 and (b) 1.00 mW/cm^2 light intensity.

Moreover, despite the good response, recovery was apparently a major issue for the bare 1D-ZnO NRs samples (Fig. 5.11(a-b)). Notably, the heterostructured 2D-Sb₂Se₃

NF/1D-ZnO NR PD device can be controlled through a light-switching mechanism. in Fig. 5.12(a) presents the regular response curve with the light "ON" and "OFF," whereas Fig. 5.12(b) presents the response curve in which the photoresponse can be evidently controlled by increasing or decreasing the light intensity rather than by the ON/OFF process. This indicates that for a longer photorecovery time, the device can recover faster with a gradual decrease in the external light intensity; therefore, it can operate according to the intensity of light and accordingly change its behavior.



Fig. 5.12. (a) Photoresponse curve and (b) light intensity controlled photoresponse curve of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure.

Furthermore, the detection capability of a PD can be calculated using parameters such as R, which is expressed in Eq. 5.1:

$$R = \frac{J_{ph}}{P_{in}} \tag{5.1}$$

where J_{ph} is the photoexcited current generated and P_{in} is the power of the incident light on the effective area of the PD. The corresponding R value as a function of the wavelength is shown in Fig. 5.13(a), which demonstrates that R drastically changes as the wavelength of light changes.

The bare 1D-ZnO NRs demonstrated good R values under UV illumination, whereas the bare 2D-Sb₂Se₃ NFs demonstrated good R values under visible light (628 nm illumination). However, the maximum R value observed for the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructured PD device in this study was obtained at wavelengths ranging from the UV-to-visible region (220, 465, 565, and 628 nm), demonstrating a broad range of detectivity at low light intensities. The EQE is an important parameter related

to the number of e-h pairs excited by one absorbed photon and is defined by Eq. 5.2 as follows:

$$EQE = \frac{R_{\lambda}}{\lambda} \times 1240 \qquad (W \cdot nm/A) \tag{5.2}$$

The EQE (Fig. 5.13(b)) was high for the 1D ZnO nanostructure and the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure under UV illumination. A linear reduction in the EQE was observed for the 1D ZnO nanostructure with an increase in the irradiation wavelength, ranging from UV to visible light. However, for the heterostructured 2D-Sb₂Se₃ NF/1D-ZnO NR PD device, the EQE initially decreased to 465 nm, after which a significant increase was observed for wavelengths in the visible region. To complement the aforementioned calculated parameters of the PD, the specific detectivity (D*) was also calculated with respect to the change in the wavelength, as shown in Fig. 5.13(c). This clearly indicates that the D* value of the heterostructured 2D-Sb₂Se₃ NF/1D-ZnO NR PD device was significantly higher than those of the bare 2D-Sb₂Se₃ NF/1D-ZnO NR S for all the measured wavelengths.

$$D^* = \frac{R}{(2qJ_d)^{1/2}}$$
(5.3)

The maximum values of R and D* were observed in the visible region, which were estimated to be 21.5 mA/W¹ (628 nm) and 5.95×10^{13} Jones (628 nm), respectively, at a light intensity of 0.15 mW/cm². This suggests that the heterostructured 2D-Sb₂Se₃ NF/1D-ZnO NR PD device was extremely sensitive to small optical input signals.



Fig. 5.13. Wavelength dependent variation in the (a) Responsivity, (b) External quantum efficiency (EQE), and (c) Detectivity of the bare 1D-ZnO NRs, 2D-Sb₂Se₃ NFs, and heterostructure 2D-Sb₂Se₃ NFs/1D-ZnO NRs.

In addition, Fig. 5.14 presents the variations in capacitance versus frequency for the 1D-ZnO NRs, bare 2D-Sb₂Se₃ NFs, and the 2D-Sb₂Se₃ NF/1D-ZnO NR

heterostructure, demonstrating a clear variation in the samples studied. Although the bare 2D-Sb₂Se₃ NFs did not demonstrate any proper variation, the 1D-ZnO NRs exhibited a decreased capacitance as the frequency increased. Although the 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure demonstrated similar behavior to the 1D-ZnO NRs, the capacitance sign was notably negative. The measured capacitance (C_m) was a combination of the junction capacitance (C_i) and trap capacitance (C_t) . Importantly, C_i is mostly frequency-independent, whereas C_t is strongly dependent on the frequency, indicating that the main contributor to the variation in the capacitance with the frequency is C_t, which sufficiently agrees with the studies regarding photocurrents with respect to intensity (Fig. 5.9(b)), where the calculated ' θ ' divergence from unity indicates the contribution from the trap/surface states. Furthermore, a negative capacitance (NC) was observed in the bare 2D-Sb₂Se₃ NFs, indicating that the main contributor to the 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure is Sb₂Se₃. Previous studies have reported that NC can be generated owing to a delay in the transient current, which may be caused by interfacial charge trapping/de-trapping or by minority carrier generation-recombination processes [34-38]. Therefore, at certain specific frequencies and applied bias levels, carriers in the trap states can escape from the residing states and contribute to the total current; however, the carriers may be delayed, resulting in the formation of a negative capacitance at the interface, which sufficiently agrees with the TRPL studies (Fig. 5.6). However, the exact origin of NC in several optoelectronic devices remains undetermined and is debatable. The NC has been reported to enhance the overall optoelectronic properties of the heterostructure [39-42], leading to the proposed 2D-Sb₂Se₃ NF/1D-ZnO NR heterostructure to demonstrate the low-intensity detection of light at different wavelengths. Furthermore, a comparative study of similar types of PDs was performed, the results of which are listed in Table 5.3. This clearly indicates that the proposed heterostructured 2D-Sb₂Se₃ NF/1D-ZnO NR PD device has better features in terms of the R and D* values at low light intensities in the measured spectral range. This clearly indicates that the proposed heterostructured 2D-Sb₂Se₃ NFs/1D-ZnO NRs PD device has better features in terms of the R and D* values at low light intensities in the measured spectral range.



Fig. 5.14. C vs frequency spectra of 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructure (upper panel), 1D-ZnO NRs (middle panel), and bare 2D-Sb₂Se₃ NFs (lower panel).

S.N.	Materials system	Intensity	Responsivity	Detectivity	Bias	Ref.
		$(mW/cm^2)(\lambda)$	R (A/W)	D*(Jones)	(V)	
1.	Sb ₂ Se ₃ NWs	1.68(600 nm)	~8.0	-	5	[43]
2.	Sb ₂ Se ₃ nanorod	8.29(850 nm)	~0.015	-	-20	[13]
	Sb ₂ Se ₃ /AgSbSe ₂ hybrid NRs		~0.037	-		
3.	Sb ₂ Se ₃ NRs	5 (808 NM)	0.0051	2.6×10^{14}	3	[20]
4.	$(Sb_{0.40}Bi_{0.60})_2Se_3(Bi^{3+})$	49.3(639 nm)	814.4	-	5	[19]
5.	ZnO/Sb ₂ Se ₃ flexible device	5 (905 nm)	0.078	2.45×10 ¹¹	0	[44]
		5 (520 nm)	-0.011	5.43×10 ¹⁰		
6.	ITO/SnO ₂ /Sb ₂ Se ₃ /Au	(750 nm)	0.312	-	0	[45]
7.	PI/ITO/CdS/Sb ₂ Se ₃ /Au	(625 nm)	0.42	2.4×10^{11}	0	[46]
8.	ITO/Sb ₂ Se ₃ /MoO ₃ /Ag	10 (625)	0.0713	8.08×10^{10}	0	[47]
	B:ZnO/Sb ₂ Se ₃	10 (460)	0.1371	1.33×10 ¹¹	0	
	NRs/MoO3/Ag	10 (625)	0.1728	2.25×10 ¹¹	0	
		10 (930)	0.0740	9.1×10 ¹⁰	0	
9.	ITO/Sb ₂ Se ₃ /ZnO/Ag	14 (450 nm)	-0.000003	-		[48]
		4 (880 nm)	0.000041	-		
10.	Sb ₂ Se ₃ NFs/ZnO NRs	0.25	0.00167	-	1	This
	Sb ₂ Se ₃ NFs/ZnO NRs	0.15(628 nm)	0.0215	5.95×10 ¹³	3	Work

 Table 5.3. Comparative study of similar kinds of photodetectors.

5.4 Conclusion

The 2D-Sb₂Se₃ NFs/1D-ZnO NRs heterostructures were successfully fabricated using simple hydrothermal and thermal transfer processes. The predicted coupling between the two layers of materials in the nanostructured forms of 2D-Sb₂Se₃ NFs/1D-ZnO NRs was confirmed to be helpful in providing robust charge transport paths, light trapping effects, and a negative capacitance, consequently enhancing the light responsivity (R) and specific detectivity (D*). The as-fabricated device provided superior overall performance in terms of a suitable spectral photoresponse ranging from UV to visible light (220–628 nm) at intensities as low as 0.15 mW/cm². The PD yielded a D* value of 3.15×10^{13} Jones (220 nm), which reached up to 5.95×10^{13} Jones in the visible light (628 nm) at a 3 V bias. This study demonstrates that the 2D-Sb₂Se₃ NFs/1D-ZnO NRs PD has excellent potential for low-intensity light detection with a broad bandwidth, which is useful for signal communications and optoelectronic systems.

5.5 References

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Chapter 6

La-doped ZnO nanorods for photoelectrochemical water splitting

6.1 Introduction

Energy has become an indispensable need of modern society, which is often supplied by employing traditional energy sources like coal, petroleum, and natural gas, and emission of greenhouse gases therein leads to severe environmental apprehensions. Besides, the limited disposal of fossil fuel and expanding population are demanding for renewable energy sources at the earliest possible. Subsequently, solar and hydrogen (H_2) energy gathered considerable attention as clean and environmentally sustainable sources of energy [1, 2]. H₂, identified as an ideal alternative fuel, is typically produced from fossil fuel utilization, methane cracking, catalytic steam reformation, gasification, partial oxidation of heavy oil, and water electrolysis [3]. The majority of these techniques are expensive, require complex setups, and have adverse environmental impacts. However, sustainable and eco-friendly photoelectrochemical (PEC) water splitting technique is occupying the desks of various laboratories due to high energy conversion efficiency, carbon-free H₂ generation, scalability, versatility in electrode materials, and the use of abundant water as a feedstock. The photoelectrodes in PEC cells utilize renewable solar energy to generate e⁻ $-h^+$ pairs, which react with H⁺ and OH⁻ ions to produce H₂ and O₂ gas at the counter and working electrode, respectively [4]. Therefore, for efficient harvesting of solar energy and after the gigantic generation of e^-h^+ pairs producing H₂ fuel, the researchers have focused on developing sustainable semiconductor photoelectrode [5].

The eco-friendly and visibly active MOs having excellent optoelectronic properties provide excellent stability as compared to metal sulfide, metal dichalcogenides, and Metal-Organic Framework (MOF) [6]. Owing to stable and efficient photo-performance, MOs (i.e., NiO [7], TiO₂ [8], CuO [9], ZnO [10], BiVO₄ [11], WO₃ [12], etc.) have also been explored for various sustainable energy applications like solar cells [13], PEC water splitting [14], solar steam generation [15], light sensing [16], and photocatalytic dye removal [17]. Among these metal oxides, environmentally benign earth-abundant ZnO is a promising photoanode for PEC water splitting due to superior optoelectronic properties [1]. At room temperature, ZnO possesses direct bandgap of ~3.3 eV and is an attractive candidate to use for applications focusing on the blue-UV region of the electromagnetic spectrum. An exciton binding energy of 60 meV, an affinity towards various dopants, good mechanical stability, the high electronic mobility of ~300 cm²/V·s), and suitable CB edge

potential with H^+/H_2 offered by ZnO make it a promising and versatile candidate for better H_2 evolution activity through advancement in PEC water splitting [18-21].

Additionally, the one-dimensional (1D) morphology significantly enhances its photoelectric performance arises from a blend of factors, including high electron mobility (1D ZnO, 1000 cm²/V·s), a low onset potential, intrinsic stability, and a large surface area. These attributes facilitate visible light activity by multiphoton absorption and scattering effect [22]. The 1D morphology provides continuous pathway for efficient electron transportation with fewer grain boundaries and surface states, allowing better charge extraction at the electrode/electrolyte interface [19]. Therefore, (0002) oriented ZnO NRs exhibited photocurrent of 0.19 mA/cm² at bias potential of 1 V [23]. Similarly, 3D hierarchically branched ZnO nanowires (NWs) structure grown over 1D ZnO NWs using two-step hydrothermal synthesis exhibited photocurrent density of 1.58 mA/cm², which is ~2-fold higher than pristine ZnO NWs [24]. The improved PEC activity in 3D hierarchical ZnO NWs is ascribed to increased light scattering/capturing ability and improved interfacial charge transfer kinetics due to enhanced electrochemically active surface areas. Further, highly porous electrodeposited ZnO nanostructures aminated to form ZnO pin hole (A-ZP) and ZnO rosette sheets (A-ZS) exhibited a photocurrent density of 1.02 mA/cm² and 1.27 mA/cm², respectively [25]. However, its wide optical bandgap limits the absorption in the ultraviolet (UV) region. Therefore, to extend the absorption in the visible light region, the ZnO is subjected to the fabrication of composite and core-shell heterostructures with other visibly active materials [26, 27]. The cathodic shift in flat band potential and lowered onset potential due to synergistic effect of crystalline-amorphous core-shell heterostructure in ZnO-TiO₂ NWs improved the charge separation and allowed fast carrier transportation, which enhanced the photocurrent by ~ 2.5 times than pristine ZnO [8]. The ZnO/BiVO₄ heterojunction photoanode exhibits wide spectral response owing to the narrow bandgap of BiVO₄ and also facilitates efficient charge separation due to better energy band alignment compared to pristine ZnO [11]. The conducting scaffold of multi-walled carbon nanotubes (MWCNT) improved the band-bending and effective interfacial charge transfer/collection when combined with ZnO NPs and delivered 5 times higher photocurrent density of 1.14 mA/cm² compared to pristine ZnO (0.24 mA/cm²) [28]. Further, the hierarchical blend of ZnO nanosheets (ZNS) and Zeolitic Imidazole

Framework 8 (ZIF8) nanocrystals significantly enhanced the photocurrent density from 0.13 mA/cm² (ZNS) to 0.71 mA/cm/⁻². The higher flat-band potential of ZNS@ZIF8 (-0.25 V) compared to ZNS (-0.49 V) exhibited shifting in the Fermi level towards CB, leading to an efficient charge transfer process across the electrolyte [29]. Similarly, CdS QDs have been decorated over ZnO NRs to improve the PEC activity. Likewise, decoration of ZnO NRs to form CdS@ZnO heterostructure delivered high photocurrent of 5.23 mA/cm² by improving charge separation and reducing charge transfer resistance, which further enhanced to 9.16 mA/cm² via thermal treatment. [30]. Several metal NPs Ag, Au, and Pd have been decorated over ZnO to induce surface plasmonic resonance (SPR) for enhanced visible light activity. To improve the PEC activity, Au@ZnO nano-heteroarchitectures were formed by uniformly loading Au NPs over hierarchically grown ZnO NWs. The optimized Au@ZnO photoanode delivered a maximum photocurrent density of 1.04 mA/cm² and an ABPE value of 0.59%, which is 52-fold and 5-fold higher than those of pristine ZnO NWs, respectively [31]. Likewise, the synergistic interaction between Ag NPs and rGO used as co-catalyst over ZnO NRs exhibits a significant improvement in the photocurrent density (~1.3 mA/cm²) compared to that of Ag@ZnO (~0.56 mA/cm²) [32]. Further, bimetallic AuPd NPs hydrothermally grown over ZnO NRs delivered 2.4 times higher photocurrent density (0.98 mA/cm²) than pristine ZnO NRs [33]. The plasmonic effect of Au NPs improved photocurrent to ~1.08 mA/cm² for Au decorated ZnO/CuO heterostructure than that both ZnO/0.5-CuO (~0.7 mA/cm²) and pristine ZnO photoanode $(\sim 0.52 \text{ mA/cm}^2)$ [9]. Further, the surface functionalization of ZnO NRs tailors the electronic structure by shifting the band position, and the band bending at the electrode/electrolyte interface results in fast charge transportation. Therefore, C, N, and S surface functionalized/doped ZnO NRs demonstrated 6.5, 5.5, and 3 times improvement in the photoconversion efficiency [34].

Moreover, the band engineering of ZnO can enhance the electronic conductivity and light harvesting activity, extend the photo-response to visible light, and improve the water splitting performance [35, 36], and hence suitable dopants like Sn, Al, Mg, and Ga are adopted for ZnO. The Al-doped ZnO seed layer provides active nucleation sites for the growth of ZnO and exhibited ~10 times enhancement in the photocurrent (i.e., 0.019 to 0.182 mA/cm^2) [37]. Sn and Al co-doped ZnO NRs exhibited an improved photocurrent of

1.87 mA/cm² @ 1.2 V [38]. Similarly, the incorporation of Mg improved the electronic lifetime and photostability of ZnO photoanode. The 10 % Mg-doped ZnO NRs exhibited photocurrent density of 0.35 mA/cm², which is ~10 times higher than pristine ZnO (0.03) mA/cm²) [36]. The quantum-confinement-tailored band engineering of ZnO QDs/NRs homojunction resulted in the negative shift of the onset potential, which facilitates photogenerated current at small bias potential and enhances the PEC activity [10]. Likewise, Lanthanum (La) has been doped in the ZnO matrix in the search for enhanced optoelectronic properties. The incorporation of La^{3+} ions alters the absorption characteristics and reduces the optical bandgap [39]. The doping of La^{3+} at Zn^{2+} site improves the conductivity of ZnO and improves the charge collection and, hence, PEC activity [40]. The surface defects induced by La doping can also lead to alteration in the surface morphology of ZnO NRs [40]. Moreover, the modification of surface conditions of ZnO due to the incorporation of La³⁺ severely hinders the recombination of photo-induced e^--h^+ pairs, which provides better charge separation and improves photocatalytic properties [41]. Overall, La³⁺ doping can assist in achieving improved PEC activity. To the best of our knowledge, optoelectronic properties and PEC activities of La substituted 1D ZnO NRs have not yet been thoroughly reported in the literature. Therefore, utilizing the La-doped ZnO NRs as photoanode is timely need for sustainable energy applications, including PEC water splitting.

Herein, we propose low-temperature hydrothermal growth of seed-assisted ZnO NRs, which were further doped with La to enhance visible light activity and optoelectronic properties. The tapered morphology of La-doped ZnO nanorods (NRs) with a tip diameter of ~24 nm exhibited reduced optical bandgap of 3.17 eV at 9 % La doping, which is significantly smaller than pristine ZnO NRs (i.e., 3.29). The improved charge transportation with 9 % La doping delivered an excellent photocurrent of ~1.54 mA/cm², which is twice larger than pristine ZnO ~0.81 mA/cm².

6.2 Experimental details

6.2.1 Synthesis of ZnO nanoparticles seed layer

The seed layer of ZnO nanoparticles (NPs) has been synthesized using simple chemical route. The details of solution process approach along with the schematic are discussed in chapter 2 (section 2.2.1).

6.2.2 Synthesis of pristine and La-doped ZnO nanorods

A low-temperature hydrothermal technique was used for the growth of pristine and La-doped ZnO NRs over seed layer coated substrates. The synthesis protocol along with the schematic are discussed in chapter 2 (section 2.2.2).

6.2.3 Structural and chemical analysis

The X-ray diffraction (XRD) pattern of pristine and La-doped ZnO NRs films was recorded (Empyrean, PANalytical, Cu K α) for phase identification and purity. The surface morphology of pristine and La-doped ZnO nanorods and ZnO nanoparticle seed layers was confirmed using field emission scanning electron microscopy (FESEM, JEOL, JSM-7610 F+). Energy dispersive X-ray spectra (EDX, Oxford Instruments, X-Max^N) were analyzed to identify the elements present in various ZnO samples. Absorption and transmission spectra of all these prepared samples were recorded using UV–Visible spectrophotometer (Shimadzu, UV-2600) to evaluate the absorption and band-edge of pristine and La-doped ZnO samples. Raman spectrum (HORIBA-JY LABRAM-HR) was recorded with an excitation wavelength of 633 nm to investigate the crystallinity and interstitial defect level of the pristine and La-doped ZnO samples. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One) was used to identify the functional groups present in pristine and La-doped ZnO samples. The Fermi level and valance band edge of the pristine and La-doped ZnO is identified from Ultraviolet photoelectron spectroscopy (UPS, AIPES, 40 MeV, $\lambda = 61$ Å, and I = 100 mA). The oxidation/electronic state and chemical composition of these samples are confirmed from X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc. Al k_{α}).

6.2.4 Photoelectrochemical measurements

Photoelectrochemical (PEC) water splitting measurements were performed in 0.1 M Na₂SO₄ (AR, 98%, SRL Chem) electrolyte solution using three-electrode electrochemical setup where pristine and La-doped ZnO NRs films (1 cm²), Platinum (Pt) mesh, and saturated calomel electrode (SCE) are used as working photoanode, counter electrode (CE) and reference electrode (RE), respectively. The I-V characteristics under dark and illumination were recorded with a Potentiostat (Metrohm Autolab: PGSTAT302N) equipped with a 150 W Xenon lamp (PEC-L01) of 100 mW/cm² (AM 1.5G) intensity. Electrochemical impedance spectra (EIS) were also

recorded at a biased potential of 0.4 V in the frequency range of 0.1 Hz to 100 kHz. Mott-Schottky (MS) plot of the pristine and La doped ZnO films ($1/C^2$ vs. bias potential) was evaluated under dark conditions at a frequency of 1000 Hz. Finally, the Chronoamperometry (CA) measurements were recorded at a fixed biased potential of 0.4 V up to 500 sec with an ON/OFF cycle of 40 sec.

6.3 Results and discussions



6.3.1 XRD analysis

Fig. 6.1. Reitveld refined XRD spectra of (a) pristine, (b) 1 % (1LZO), (c) 5 % (5LZO), and (d) 9 % (9LZO) La-doped ZnO NRs.

The XRD profiles of the pristine and La-doped ZnO NRs were Rietveld refined by FullProf suite to determine lattice parameters and hexagonal wurtzite crystal structure as shown in Fig. 6.1. The observed peaks at 31.77°, 34.42°, 36.25°, 47.54°, 56.58°, and 62.86° for (100), (002), (101), (102), (110), and (103) planes, respectively, (Fig. 6.1(a)) correspond to the wurtzite crystalline structure of ZnO (JCPDS 65-3411). All other

peaks indexed as (*) are the characteristic peaks of FTO, confirming the absence of impurity in the ZnO film [42]. Moreover, the highest intense (002) characteristic peak signifies well-oriented growth of ZnO NRs along the c-axis. Similarly, the XRD spectra of 1LZO, 3LZO, and 5LZO samples represent the c-axis oriented growth of hexagonal wurtzite crystalline La-doped ZnO NRs (Fig. 6.1(b-d)). Moreover, the absence of any impurity peak of La₂O₃ in the XRD pattern of La-doped samples confirms the successful substitution of La³⁺ at Zn²⁺ site. The unit cell and fitting parameters of pristine and La-doped ZnO samples are provided in Table 6.1. The refined spectra demonstrate considerably good fit with the experimental data.

Table 6.1: Rietveld refined parameters, optical bandgap (E_g), and Urbach energy (E_U) of pristine and La-doped ZnO NRs films.

Sample	Lattice parameter (Å)			Rp	Rwp	Rexp	GOF	Eg (eV)	Eu (eV)
code	а	b	c						
ZnO	3.2495	3.2495	5.2006	11.1	14.5	7.42	3.81	3.29	0.362
1LZO	3.2486	3.2486	5.2007	11.3	14.8	7.44	3.94	3.24	0.387
5LZO	3.2476	3.2476	5.2004	11.0	14.5	7.41	3.82	3.22	0.414
9LZO	3.2472	3.2490	5.1996	11.6	15.7	7.25	4.69	3.17	0.435

6.3.2 FESEM and EDS analysis

The uniformity of the ZnO seed layer and the effect of La doping on surface morphology and thickness of ZnO NRs were analyzed from top and cross-sectional FESEM micrographs. Uniform deposition of ZnO seeds formed compact layer (~50 nm) without any pinholes over the FTO substrate (Fig. 6.2(a,b)). These distinct individual seeds act as a nucleation site and assist in the growth of ZnO NRs. The uniformly distributed pristine ZnO NRs of hexagonal shape and average diameter of ~44 nm were vertically grown over seed layer coated FTO glass substrate (Fig. 6.2(c,d)). Similar vertical growth of hexagonal shaped NRs was observed for 1LZO (Fig. 6.2(e,f)), 5LZO (Fig. 6.2(g,h)) and 9LZO (Fig. 6.2(I,j)) samples. However, increase in the La doping concentration reduced the diameter at the tip of uniformly distributed ZnO NRs, leading to more tapered morphology for the 9LZO sample (inset of Fig. 6.2(i)).



Fig. 6.2. Low and high magnification FESEM images of (a, b) seed layer of ZnO NPs, (c, d) pristine ZnO, (e, f) 1LZO, (g, h) 5LZO, (i, j) 9LZO samples, respectively, and (k) cross-sectional view of ZnO NRs grown over seed layer deposited FTO substrate.



Fig. 6.3. Cross-sectional FESEM micrographs of (a) 1LZO, (b) 5LZO, and (c) 9LZO films.

The vertically aligned pristine ZnO NRs of length ~800 nm were grown over compact, thin seed layer of ZnO (Fig. 6.2(k)). Likewise, ~934, ~1028, and ~1100 nm long NRs were observed for 1LZO, 5LZO, and 9LZO samples, respectively (Fig. 6.3). Slight increment in the NRs length has been observed with La doping, which is possibly due to the reduction in tip diameter with La doping. The average diameter evaluated for 1LZO, 5LZO, and 9LZO NRs is ~41, ~32, and ~25 nm, respectively (Fig. 6.4). The difference in the electronegativity of La³⁺ (1.10) and Zn²⁺ (1.65) causes a decrease in the Zn–O bond length and, therefore, results in reduced size of ZnO with La doping

[39]. The reduced diameter shall provide more space for visible light to penetrate and increase the multiphoton absorption. Further, the oxygen vacancies created due to the substitution of La^{3+} at the Zn^{2+} site might have resulted in the formation of tapered morphology of ZnO NRs, which is akin to report on tapered morphology evaluation after UV illumination induced oxygen vacancies [43]. Further, the EDS spectra and elemental mapping of ZnO NPs seed layer and pristine ZnO NRs confirm the uniform existence of Zn and O elements. Whereas the existence of La in the 9LZO sample confirmed its doping in ZnO. The presence of F, Sn, and Si corresponds to FTO coated silica glass substrate in all the samples (Fig. 6.5).



Fig. 6.4. Average diameter distribution of NRs observed in the FESEM images (a) pristine, (b) 1LZO, (c) 5LZO, and (d) 9LZO.



Fig. 6.5. EDS of (a) ZnO NPs seed layer, (b) pristine ZnO NRs, and (c) 9LZO films.

6.3.3 UV-Visible analysis

Fig. 6.6(a) shows UV-visible absorbance spectra of pristine and La-doped ZnO samples, and corresponding bandgaps were calculated using Tauc's Eq. 6.1 [44]. $(\alpha h\nu)^n = B(h\nu - E_g)$ (6.1)

Where, α is absorption coefficient of the material, $h\nu$ is energy of incident photon, B is constant, E_g is bandgap of material, and n is factor that depends on the electron transition (1/2 or 2) for direct and indirect transition bandgaps, respectively. The bandgap of pristine ZnO NRs (i.e., 3.29 eV) has reduced with increase in La doping concentration, and lowest bandgap of 3.17 eV is observed for 9LZO sample (Fig. 6.6(b)). Reduced bandgap of La-doped ZnO NRs representing enhancement in light absorption is attributed to strong orbital coupling between La and O [39, 45]. Moreover, to analyze the change in the defect level of ZnO NRs with La doping we have evaluated the Urbach energy (E_U) of pristine and La-doped ZnO samples. The exponentially decaying Urbach tails in the absorption spectra below the bandgap corresponds to the lattice vibrations and defect present in the crystal [46]. The relation between E_U and absorption spectra of pristine and La-doped ZnO photoanode is given by Eq. 2,

$$E_U = \frac{h\nu - E_g}{\ln\left(\frac{\alpha_E}{\alpha_0}\right)} \tag{2}$$

The change in E_U with La doping is provided in Fig. 6.6(b) and Table 6.1. The increase in E_U with increasing La doping concentration indicates rise in the defect level in ZnO crystal, which corresponds to increase in oxygen vacancies with La doping. This also patronages the creation of surficial defects due to morphological alterations, i.e., tapering NRs observed in FESEM images. These observations enunciate the reports in the literature [47]. Moreover, the generation of more oxygen vacancies by doping La³⁺ at the Zn²⁺ site can govern the optoelectronic properties [44].



Fig. 6.6. (a) UV-Vis absorbance spectra with corresponding Tauc's plot in the inset and (b) variation in optical bandgap and Urbach energy with La doping in ZnO NRs films.

6.3.4 Raman and FTIR analysis

Further, Raman spectroscopy was performed in the range of $50-1300 \text{ cm}^{-1}$ to confirm the lattice and vibrational modes of pristine and La doped ZnO crystal structure (Fig 6.7(a)). The optical phonon mode at the center of the Brillouin zone (τ) is quantified by summation of A₁, E₁, 2E₂, and 2B₁ modes [48]. Where A₁ and E₁ represent the Raman and IR active polar modes, which further split into transverse (TO) and longitudinal (LO) optical modes, respectively. E₂ mode comprises of E_{2H} and E_{2L}, represents Raman active non-polar mode. Raman modes observed at 95, 117, and 240 cm⁻¹ correspond to the interstitial defects of the Zn ion, and their enhanced intensity with increasing La doping concentration represents the substitution of La within the ZnO crystal [49]. Raman mode at ~333 cm⁻¹ in pristine ZnO corresponds to E_{2H}–E_{2L},

typically arises due to A_{1T} symmetry and multi-phonon vibrational mode, represents the highly crystalline nature of ZnO [50]. The characteristic peak of the wurtzite hexagonal phase of ZnO observed at 434 cm⁻¹ is the E_{2H} mode associated with Oxygen vibrations [48]. The increase in its intensity can be attributed to the increase in oxygen vacancies with doping of La in ZnO. Furthermore, the Raman modes $A_{1(LO)}$ and $E_{1(LO)}$ obtained at 577 and 580 cm⁻¹, respectively, in La-doped ZnO reflects oxygen vacancy [49, 51], which can enhance electronic mobility to achieve superior optoelectronic properties. Single broad asymmetric peak at 1092 cm⁻¹ exhibits the dominating $2_{A1(LO)}$ and $2_{E1(LO)}$ modes [48]. The absence of additional Raman modes in La-doped ZnO confirms its phase purity [52]. Overall, these observations reflect the formation of Wurtzite crystal structure of ZnO with hexagonal P63mc space group and are analogous to XRD analysis. Further, pristine and La-doped ZnO samples were characterized using FTIR Spectra in the range of 400-4000 cm⁻¹ (Fig 6.7(b)). The characteristic vibrational bands of ZnO are observed at 532 and 889 cm⁻¹ in pristine ZnO samples, which are slightly shifted with different extents of La-doping, corresponding to the microstructural changes in the ZnO lattice [53]. Additionally, two weak bands observed at 1416 and 1562 cm⁻¹ are attributed to stretching vibrations of C-O and C-H bonds, respectively, reflecting the presence of moieties of acetate ions onto the surface of ZnO, which fainted on La doping [54].



Fig. 6.7. Room temperature (a) Raman spectra and (b) Fourier transform infrared (FTIR) spectra of pristine and La-doped ZnO NRs.

6.3.5 XPS and UPS analysis



Fig. 6.8. Core level XPS spectra (a) Zn(2p), (b) O(1s), and (c) La(3d), (d) complete UPS spectra, (e) secondary cut-off spectra, and (f) VB onset spectra of ZnO and 9LZO.

The XPS spectra of the ZnO and 9LZO samples were evaluated to demonstrate the effect of La doping on the chemical and electronic states of ZnO. The Zn(2p) core level of pristine ZnO NRs showed two distinct peaks at binding energy of 1021.0 (\equiv a) and 1044.1 (\equiv b) eV are attributed to Zn²⁺(2p_{3/2}) and Zn²⁺(2p_{1/2}), respectively (Fig. 6.8(a) lower panel) [31]. However, peak shift of 0.5 eV observed in Zn²⁺(2p_{3/2}) and Zn²⁺(2p_{1/2}) core levels of 9LZO ((Fig. 6.8(a) upper panel)) is assigned to the difference in the electronegativity of the Zn and La and also the alteration in bond length due to larger ionic radii of La [55]. Similarly, core level XPS spectra of O(1s) for pristine ZnO (Fig. 6.8(b), lower panel) and 9LZO (Fig. 6.8(b), lower panel) samples are deconvoluted in to two peaks located at B.E. of 529.9 (\equiv a) and 531.5 (\equiv b) eV corresponding to the lattice oxygen (O_L) bound to Zn and oxygen vacancies (O_V), respectively [56]. The increase in the intensity of the O_V peak of 9LZO indicates the creation of more oxygen vacancies is evaluated from the ratio of integrated intensities of O_V to O_L. The increase in the O_V/O_L from ~0.65 (\equiv ZnO NRs) to ~0.93 (\equiv 9LZO) indicates the rise in

oxygen vacancies in the ZnO crystal with La doping. The XPS spectra of La(3d) core level for 9LZO are deconvoluted into two peaks located at the B.E. of 836.6 and 853.3 eV, corresponding to $La^{3+}(3d_{5/2})$ and $La^{3+}(3d_{3/2})$, respectively (Fig. 6.8(c)) [57]. The peak separation of 16.7 eV confirms the successful substitution of La³⁺ ions at the Zn²⁺ site [58]. Thereafter, ultraviolet photoelectron spectra (UPS) were recorded for ZnO and 9LZO film to understand the effect of La doping on energy band level of ZnO films (Fig. 6.8(d-f)). The energy difference between the incident ultraviolet photon energy (40 eV) and the secondary electron onset of the spectrum gives the work function (W_F) level of 4.31 and 4.26 eV for the ZnO and 9LZO samples, respectively, with respect to the vacuum level (Fig. 6(e)). The VB onset for both pristine and 9LZO samples is extrapolated from the long tail of the UPS and is shown in Fig. 6(f) [59]. The evaluated values of various energy band levels are provided in Table 6.2. The VB and CB energy levels of ZnO and 9LZO samples were then converted to the NHE scale to correlate with hydrogen evolution (H^+/H_2) energy level. The energy band diagram of ZnO and 9LZO photoanode (Fig. 6.9). Confirms that the lower energy difference of 0.32 eV for La doped ZnO than pristine ZnO photoanode (0.74 eV) provided an easier path for eto reduce H^+ and evolve H_2 at counter PT electrode.



Fig. 6.9. Energy band diagram of ZnO and 9LZO samples.

Sample	Work function,	Valance Band	Bandgap,	Conduction Band	
	W _F (eV)	Maxima, VBM (eV)	EG (eV)	Minima, CBM (eV)	
ZnO	4.31	2.07	3.29	1.22	
9LZO	4.26	2.39	3.17	0.78	

Table 6.2. Evaluated values of various band levels for pristine ZnO and 9LZO NRs.





Fig. 6.10. (a) Linear sweep voltammetry (LSV) curve under dark and illuminating conditions and (b) applied bias to photon efficiency (ABPE) of pristine and La-doped ZnO NRs photoanode.

Linear sweep voltammetry (LSV) was performed to analyze the photocatalytic activity of pristine and La-doped ZnO films. The I-V characteristics of all the samples were recorded in a voltage range of -0.5 to +1.0 V under dark and illuminating conditions to evaluate the effect of La doping on the PEC performance (Fig. 6.10(a)). The high photocurrent density of ~0.81 mA/cm² at bias potential of +1.0 V (vs. SCE) is observed for pristine ZnO NRs, which is ~10³ higher than the dark current density of 0.6 μ A/cm². Whereas the 1LZO, 5LZO, and 9LZO samples exhibited higher photocurrent densities of 0.84, 0.96, and 1.54 mA/cm², respectively. The significant enhancement in the photocurrent density with La doping concentration is mainly attributed to increased light absorption and electronic conductivity of ZnO with La doping. Moreover, the reduced dimension of tapered nanorod morphology of La-doped ZnO provides maximum surface area for visible light scattering and allows multiphoton absorption for more favorable charge transfer kinetics at the electrode/electrolyte interface [24]. Notably, the 9LZO samples have delivered ~2 times higher photocurrent

density than pristine ZnO samples. After that, to get an idea about the photo-response efficiency of this photoanode, the applied-bias-photon to current conversion efficiency (ABPE) is evaluated from Eq. 6.2.

$$ABPE (\%) = \frac{J_{ph} \times (E_{rev} - |V_b|) \times \eta_f}{P_{in}} \times 100$$
(6.2)

Where, J_{ph} is the photocurrent density of photoanode, E_{rev} is the standard reversible potential (1.23 V), V_b is the applied bias potential, η_f is the faradaic efficiency (~1), and P_{in} is the power of incident light (100 mW/cm²).

The ABPE curves of pristine and La-doped ZnO photoanode were plotted and represented in Fig. 6.10(b). The maximum ABPE of 0.58 % was achieved at a bias potential of 0.4 V for pristine ZnO films. The maximum ABPE of 0.83, 0.91, and 1.14 % was observed at bias potential of 0.3 V for 1LZO, 5LZO, and 9LZO films, respectively. The enhancement in ABPE corresponds to the improved photoactivity and better charge extraction of La-doped ZnO photoanode, which is supported by UV-visible and UPS analysis of pristine and La-doped ZnO films.



Fig. 6.11. (a) Electrochemical impedance spectroscopy (EIS) with equivalent circuit in the inset and (b) Mott-Schottky (MS) plot of pristine and La-doped ZnO NRs photoanode.

The EIS measurements of the pristine and La-doped ZnO films were recorded at a fixed bias potential of 0.4 V with frequency ranging from 0.1 Hz to 100 kHz for better understanding of the charge transfer kinetics at the ZnO/electrolyte interface. The Nyquist plot of the pristine and La-doped ZnO samples is shown in Fig. 6.11(a) with an equivalent electrical circuit. Fig. 6.11(a) depicts only single semicircular curve that

signifies the involvement of the electrode/electrolyte interface in the charge transfer process and also confirms the absence of any diffusion process [60]. The charge transfer resistance (R_{Ct}) of 6.91, 5.79, 3.75, and 1.67 k Ω between electrolyte and photoanode has been observed for ZnO, 1LZO, 5LZO, and 9LZO, respectively. The lower R_{Ct} indicates improved charge extraction at the ZnO/electrolyte interface with increasing doping concentration. The generation of an electrical double layer at the ZnO/electrolyte interface has been observed as expected. Therefore, Mott-Schottky (MS) analysis was performed to investigate the effect of applied potential on the capacitance (C_P). The in-depth analysis of the MS plot enables us to understand the effect of La-doping on the carrier concentration (N_D), flat band potential (V_{fb}), and width of space charge region (SCR) or depletion layer (W) of different ZnO films. d The positive slope of the MS plot confirms the n-type nature of the pristine and doped ZnO photoanode (Fig. 6.11(b)) [32]. Further, MS draws the relation between C_P and applied bias potential as given in Eq. 6.3.

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r A^2 q N_D} \left[V - V_{fb} - \frac{k_B T}{q} \right]$$
(6.3)

Where, ϵ_0 and ϵ_r represents the dielectric permittivity of the space and semiconductor, respectively, k_B is the Boltzmann's constant, A is the surface area of the photoanode, T is the operating room temperature, and q is the electronic charge. The V_{fb} of the photoanode is calculated by extrapolating the MS plot. The slope (S) of the extrapolated line gives the N_D of the photocatalyst material. Similarly, the relation between W with N_D is also evaluated from Eq. 6.4-6.5 [28].

$$N_D = \frac{2}{\epsilon_0 \epsilon_r A^2 q S} \tag{6.4}$$

$$W = \sqrt{\frac{2\epsilon_0 \epsilon_r}{qN_D} \left(V_{applied} - V_{fb} \right)} \tag{6.5}$$

The values of V_{fb} , N_D, and W for all the samples are provided in Table 6.3. The V_{fb} has increased from -0.49 V (pristine ZnO) to -0.16 V (9LZO) with increase in La doping concentration. The positive shift in the V_{fb} Indicate the decrease in band bending, i.e., shift in the fermi level towards CB, thus facilitating the charge transfer at the ZnO/electrolyte interface [28]. Moreover, the higher V_{fb} initiate charge transfer process at lower overpotential, insuring the smooth charge extraction with reduced

recombination rate [61]. Similarly, with increase in the doping concentration, the N_D of the ZnO film increases from 3.08×10^{20} (pristine ZnO) to 1.24×10^{21} cm⁻³ (9LZO), resulting in higher number of free charge carriers available to participate in the redox reaction. The width of the depletion layer also reduces from 7.68 to 2.88 nm with an increase in doping concentration. The lower width of the 9LZO photoanode facilitates the diffusion of photogenerated charge carriers, [29] thus enhancing the PEC activity of the La-doped ZnO samples.

Sample Flat band potential,		Charge carrier	Depletion region	
code	V _{fb} (V)	density, N _D (cm ⁻³)	width, W (nm)	
ZnO	-0.49	3.08×10^{20}	7.68	
1LZO	-0.32	6.27×10^{20}	4.88	
5LZO	-0.27	9.31×10 ²⁰	3.9	
9LZO	-0.16	1.24×10^{21}	2.88	

Table 6.3. The V_{fb} , N_D, and W for the pristine and La-doped ZnO photoanodes.



Fig. 6.12. (a) Chronoamperometry plot with 40 sec ON/OFF cycle for pristine and Ladoped ZnO NRs photoanode and (b) schematic representation of solar-driven PEC water splitting mechanism.

Stable photoanodes with higher lifetime and recyclability are also important for practical PEC water-splitting applications. Therefore, chronoamperometry (CA) measurements were performed at bias potential of 0.4 V for the duration of 500 sec with an ON/OFF cycle of 40 sec (Fig. 6.12(a)) to analyze the stability of the pristine and La-doped ZnO films. All films deliver stable photocurrent for 500 sec. Moreover, the PEC performance of pristine and La-doped ZnO is either better or comparable with the various ZnO-based materials reported in the literature (Table 6.4). The charge generation and transportation mechanism can be understood by the schematic

illustrated in Fig. 6.12(b). When light (AM 1.5G) is illuminated on the ZnO photoanode, the absorption of photon energy > E_g excites the e^- from VB to CB and results in the formation of $e^- - h^+$ exciton (Eq. 6.6). The holes (h^+) migrates towards the photoanode/electrolyte interface and are available for the reaction with water. The h^+ dissociates the water molecules by liberating the O₂ gas and hydrogen (H^+) ion (Eq. 6.7). These H⁺ ions will move towards the negatively charged Platinum (Pt) counter electrode through electrolyte medium. Concurrently, the photoelectrons (e^-) travel to Pt electrode via external circuit, react with the available H⁺ ions, and release the H₂ gas (Eq. 6.8). The complete cell reaction of photo-electrochemically generated O₂ and H₂ at Pt and ZnO, respectively, under illumination is given by (Eq. 6.9).

$$ZnO + h\nu \to ZnO (e^- + h^+) \quad (\text{at anode}) \tag{6.6}$$

 $H_2O + h^+ \rightarrow H^+ + O_2\uparrow \qquad (at anode) \qquad (6.7)$

 $\mathrm{H}^+ + e^- \to \mathrm{H}_2 \uparrow$ (at cathode) (6.8)

 $2H_2O \rightarrow 2H_2 + O_2$

(complete cell reaction) (6.9)



Fig. 6.13. (a) FESEM micrograph, (b) EDS spectra of ZnO NRs films, (c) FESEM micrograph, and (d) EDS spectra of 9LZO NRs films after stability study of PEC measurements.

Furthermore, the FESEM micrograph and EDS spectra, along with the elemental mapping after PEC measurements, were analyzed to ensure the physicochemical stability and recyclability of the ZnO and best-performing 9LZO photoanode. Both ZnO and 9LZO NRs remain well intact with uniform distribution over the FTO substrate after PEC measurement but are partially covered by some flakes, probably due to the reaction of Na₂SO₄ electrolytes (Fig. 6.13(a,c)). Similarly, the EDS spectra and elemental mapping (inset of Fig. 6.13(b,d)) show the presence of Na and S elements corresponding to Na₂SO₄ electrolyte along with the Zn, Sn, and O for the ZnO NRs and La, Zn, Sn and O for 9LZO over FTO substrates. Overall, these observations confirm the morphological and chemical stability of the 9LZO electrodes even after longer exposed PEC measurements.

S.	Photoanode	Electrolyte	Photo-	Donor	Flat band	Ref.
N.			current	density ND,	potential	
			(mA/cm ²)	(cm ⁻³)	V _{fb} , (V)	
1.	10 % Mg ZnO NRs	0.1 M NaOH	0.35	4.4×10^{21}	1.341	[36]
2.	ZnO pin hole (ZP)	0.5 M Na ₂ SO ₄	0.62	1.1×10^{20}	-0.50	[25]
	Aminated ZP (A-ZP)		1.02	1.7×10^{20}	-0.55	
	ZnO rosette sheets (ZS)		0.76	1.4×10^{20}	-0.50	
	Aminated ZS (A-ZS)		1.27	3.4×10^{20}	-0.55	
3.	ZnO rods	0.5 M Na ₂ SO ₄	0.019	1.8×10^{18}	-0.22	[37]
	ZnO-0.04 AZO flower		0.18	9.0×10 ²⁰	-0.32	
4.	SILAR ZnO NRs	0.5 M Na ₂ SO ₄	0.19	2.2×10^{21}	-0.29	[23]
5.	ZnO NRs	0.1 M KOH	0.17	2.3×10^{20}	-0.11	[38]
	Sn0.05Al0.03Zn0.92O		1.87	4.4×10^{21}	-0.69	
6.	ZnO NPs	0.5 M Na ₂ SO ₄	0.24	7.2×10^{18}	-0.66	[28]
	ZnO/CNT		1.14	2.0×10^{19}	-0.25	
7.	ZnO NRs	0.5 M Na ₂ SO ₄	0.41	-	-	[33]
	Au-Pd/ZnO		0.98			
8.	Z-NRs	0.5 M Na ₂ SO ₄	0.26	1.7×10^{18}	-	[32]
	Z-NRs-Ag		0.56	1.8×10^{19}		
	Z-NRs-Ag@rGO		1.30	9.3×10 ¹⁹		
9.	ZnO NRs/CuO NPts	0.1 M Na ₂ SO ₄	0.70	4.0×10^{19}	-0.81	[9]
	ZnO/CuO/Au		1.08	5.1×10 ¹⁹	-0.74	
10.	ZnO NRs	0.1 M Na ₂ SO ₄	0.81	3.08×10 ²⁰	-0.49	This
	9LZO tapered NRs		1.54	1.24×10^{21}	-0.16	Work

Table 6.4. Comparison of PEC performance of various ZnO-based photoelectrodes.

6.4 Conclusion

In conclusion, pristine and La-doped ZnO NRs have been successfully grown over FTO substrates using a low-temperature hydrothermal technique. The XRD pattern indicates a slight shift towards the lower Bragg's angle with La doping, which confirms the substitution of higher ionic radii La³⁺ ion at the Zn²⁺ site. The FESEM micrograph reveals the tapered morphology for the La-doped ZnO samples with reduced diameter of the NRs. The EDS and XPS spectra also confirm the presence of La^{3+} ions in doped ZnO samples. The UV-Vis and UPS spectra depict the improved light activity and better charge extraction process by shifting the CB edge towards H^+/H_2 potential, which enhances the charge transportation and results in improved PEC activity for La doping. The 9LZO photoanode exhibits a higher photocurrent density of ~1.54 mA/cm² over pristine ZnO photoanode $(\sim 0.81 \text{ mA/cm}^2)$. Nyquist analysis reveals the lower charge transfer resistance for 9LZO sample at the electrode/electrolyte interface. The Mott-Schottky analysis provides a higher flatband potential (V_{fb}) potential of -0.16 V for 9LZO photoanode than pristine ZnO photoanode (-0.49 V), which indicates that charge transfer will initiate at lower overpotential for 9LZO photoanode. Chronoamperometry data shows the high stability of the pristine and doped ZnO samples. The 9LZO photoanode exhibits 2 times higher photocurrent than that of pristine ZnO. Overall, this study suggests that La-doped ZnO NRs can be utilized as a photoanode for effective and improved PEC water-splitting applications.

6.5 References

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Chapter 7

BaSnO₃ nanoparticles for bifunctional photocatalytic applications

7.1 Introduction

The new era of industrialization with a continuously increasing population creates a scarcity of energy and fresh water. Currently, billions of people do not have access to drinkable water, and thousands die annually from diseases spread via contaminated water. Over the last two decades, various treatments, such as nanofiltration, water oxidation, reverse osmosis, ion exchange membranes, and biological methods, have been investigated for wastewater purification [1]. However, the photocatalytic process has the potential to overcome limitations of above-cited treatments and cost-effectively reduce the level of contaminants in water to meet environmental regulations [2]. Furthermore, an effective energy conversion with minimum environmental pollution is one of the prerequisites of the rapidly emerging technology in demand. The production of hydrogen, an environmentally friendly renewable energy source providing high combustion efficiency, has been considered a promising route to produce clean energy [3]. Numerous methods involving fossil fuel, direct cracking using methane, catalytic steam reforming, partial oxidation of heavy oil, gasification, and electrolysis of water, etc., have been studied for hydrogen generation [4]. Most of these are costly, include complex setups, or have detrimental environmental effects. Nevertheless, photoelectrochemical (PEC) water splitting is an ideal approach that has potential to achieve the objectives of converting water into hydrogen and/or oxygen using solar energy [5]. Therefore, researchers are engrossed in hunting for different photoelectrodes to efficiently produce hydrogen by harvesting solar energy.

The various photoelectrode materials, such as metal oxides (MO), metal sulfide (MS), dichalcogenides, metal-organic frameworks (MOF), etc., have a wide bandgap of ~1-4 eV, are able to harvest a wide range of solar spectrum, and therefore, extensively engaged for multifunctional photocatalytic applications through utilization of solar energy [6-8]. However, MOs are given priority due to their environmentally friendly and thermally stable nature and tunable bandgap [9] to harvest solar energy via photovoltaic cells, solar thermal, and PEC water splitting [10-13]. Moreover, MOs can efficiently degrade organic waste and desalinate seawater in the presence of photons [8, 14]. Among the class of MOs, perovskite oxides having a chemical composition of $A^{2+}B^{4+}O_3$ or $A^{3+}B^{3+}O_3$ are more striking for hydrogen and oxygen evolution due to their unique structural and
compositional flexibility, offering controlled charge transfer at the interface [15]. The greater charge carrier mobility, lower charge recombination, and higher thermal stability of the ABO₃ materials also make them an ideal contender for photocatalytic water splitting and dye degradation [15-17]. BaTiO₃, one of the more explored perovskites ABO_3 compounds for a variety of applications, has attracted attention for photocatalytic electrochemical water splitting [18, 19]. Qiao et al. [20] investigated the synergistic effect of Pyro-photo-electric and oxygen vacancies on the PEC water splitting performance of the BaTiO₃ electrode. The BaTiO_{3-x} photoanode carrying ~5% oxygen deficiency exhibited a photocurrent density of 0.68 mA/cm^2 , which is ~3.7 times higher than that of the pristine BaTiO₃ photoanode. Furthermore, the improved separation of photogenerated charge carriers (electrons and holes) in the heterojunction of nanostructured Cu₂O and BaTiO₃ photocatalyst delivered a higher photocurrent density of 1.44 mA/cm² compared to pristine BaTiO₃ electrode (0.02 mA/cm^2) [21]. The ferroelectric polarization-endowed band engineering in the core-shell TiO₂/BaTiO₃ nanowires (NWs) resulted in 67 % enhancement in the photocurrent density (i.e., from 0.78 to 1.30 mA/cm²) [22]. Likewise, various such perovskite oxides of BaTaO₂N, [23] SrTiO₃, [24] ZnSnO₃ [25] have also been investigated for efficient photocatalytic and PEC water splitting. The enhanced visible light activity and charge transportation at the interface of heterojunction formed by ZnSnO₃ with ZnO nanowires improved the photocurrent density to 0.4 mA/cm² than the pristine ZnO nanowires (i.e., 0.25 mA/cm²) [25]. However, hardly any reports explain the methodical utilization of BaSnO₃ perovskite for both PEC water splitting and wastewater treatment. In the cubic crystalline n-type BaSnO₃ (BSO) nanostructure, the smaller Sn⁴⁺ cation sits at the center of the octahedra formed by the coordination of Sn with face centered O²⁻ anions with bigger Ba^{2+} cations occupy the voids surrounded by the oxygen (O²⁻ anions) octahedron, which provide an optical bandgap of $\sim 3.0-3.4$ eV with high thermal stability. On the other hand, BSO has high charge mobility of ~ 320 and ~ 150 cm²/V·s for single crystal and thin film structures, respectively, due to the Sn(5s) orbitals on the bottom of the conduction band [26] and its optoelectronic properties, i.e., bandgap and electronic mobility can be engineered through suitable doping [27, 28]. Therefore, BSO is employed in several optoelectronic applications [29-31]. The BSO perovskite has conduction band (CB) edge potential ~0.69 V (vs. NHE) more negative than H^+/H_2 potential, which

facilitates the smooth electron extraction from $BaSnO_3$ for efficient water splitting [32]. The creation of oxygen vacancies within the BSO crystal (i.e., BaSnO_{3-δ}) capable of tailoring the band edges has improved H_2 evolution activity [33]; nonetheless, researchers explored suitable dopants and composites of BSO to enhance photocatalytic activity. The electrical conductivity of BSO is enhanced by substituting La onto the Ba sites. The optimized Ba_{0.98}La_{0.02}SnO₃ photoanodes showed a photocurrent density of ~0.34 mA/cm² at a bias potential of 1.1 V [34]. Moreover, in the quest for enhanced PEC performance, the oxide based QDs have been decorated as surface modifiers over the perovskite oxides. The decoration of CdS quantum dots (QDs) yielded ~9 times enhancement in the photogenerated current from the BSO nanowires (NWs) photoanodes during PEC water splitting [32]. The higher electronic conductivity of rGO facilitates the electron transfer from BSO to rGO at the interface, effectively suppressing the recombination of $e^- - h^+$ pair and resulting in higher photocatalytic activity [35]. Likewise, the TiO₂ [36] and BiVO₄ [37] infused with BSO to induce the carrier or $e^- - h^+$ pair separation and then improve the photocatalytic dye degradation. Besides, oxygen vacancies were induced in the BSO crystal (BaSnO_{3- δ}) to tailor the band structure for enhancing light absorption and gaining higher photoactivity [33, 38]. Several elements such as La, [27] Zn, [39] Nd, [40] and Cr [28] are adopted in the BSO to enhance the optoelectronic properties for multifunctional applications. However, despite of suitable energy bandgap to harvest solar energy, high electronic mobility, and structural stability, the literature focusing on the photocatalytic application of BSO perovskite are very limited. Furthermore, most of the previous reports deal with the larger surface morphological forms, resulting in the small surface area offering limited active sites and hence shrinking the photocatalytic activity [33-35, 41-43]. Therefore, BSO nanoparticles (NPs) with larger surface areas providing more active sites for efficient interactions with photons are desirable photocatalysts for application in PEC water splitting and organic dye removal. Moreover, the BSO catalyst is mostly used for the photocatalytic degradation of Remazol golden yellow (RNL) and methylene blue (MB) dyes [35-37, 41, 42] and none of the reports focused on crystal violet (CV). The reaction kinetic and plausible degradation pathway for the photocatalytic degradation of organic azo dyes using BSO catalyst is also not explained in any of the previously reported work.

Therefore, the removal of multiple organic dyes using a single BSO catalyst is also essential for efficient wastewater purification.

Herein, we proposed an economical co-precipitation route for the synthesis of highly crystalline BSO NPs with a diameter of ~30 nm, surface area of ~15.11 m²/g, and bandgap of ~3.24 eV. The BSO NPs with a charge carrier concentration of 2.56×10^{18} cm⁻³ with a flat band potential of -0.82 V show a photocurrent density of 20 μ A/cm² at a forward bias potential of 0.6 V under illumination. The BSO catalyst delivers an outstanding degradation performance of ~96 % for CV and MB dyes after constant illumination for 240 min.

7.2 Experimental details

7.2.1 Synthesis of BaSnO₃ NPs

The BSO NPs were synthesized using co-precipitation process in hydrogen peroxide solvent. The schematic representing the steps involved in the synthesis of the BSO NPs are shown in the chapter 2 (section 2.2.5(a)) and Fig. 2.4.

7.2.2 Synthesis of BSO thin films

Thin film of BSO NPs were deposited over FTO substrate using spin coating technique. The schematic representing the steps involved in the synthesis of the BSO NPs are shown in the chapter 2 (section 2.2.5(b)).

7.2.3 Characterization

The morphological and physicochemical properties of BSO NPs were examined before they were subjected to photocatalytic studies. X-ray diffraction (XRD, PANalytical, Empyrean-DY2528) analysis was performed to identify the crystal structure and phase purity of BSO NPs. The surface morphology and chemical elementals of BSO were analyzed using Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-7610 F+) and energy dispersive X-ray spectra (EDX, Oxford Instruments, X-Max^N), respectively. The bandgap of BSO NPs was evaluated from the Diffuse Reflectance Spectra (DRS) recorded using UV–Vis. spectrophotometer (Shimadzu, UV-2600). X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc. Al-k α) was used to identify the chemical composition and electronic/oxidation states of BSO NPs. The surface area and pore size distribution of BSO NPs were evaluated from Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis with N₂ adsorption-desorption isotherm. The presence of several functional groups in BSO NPs was examined from FTIR spectroscopy (Perkin Elmer, FTIR Spectrum One).

7.2.4 Photocatalytic studies

The PEC water splitting measurements were performed in 0.1M Na₂SO₄ (AR, 98%, SRL Chem) electrolyte of pH ~6.8 using a three-electrode electrochemical cell assembly of BSO NPs photoanode, platinum (Pt), and saturated calomel electrode (SCE) as working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. The schematic of the photoelectrochemical cell is shown in Fig. 2.9(a). The photoanode was irradiated with a 150 W Xenon lamp (PEC-L01) of 100 mW/cm² (1 sun) intensity through a quartz window. Potentiostat (Metrohm Autolab: PGSTAT302N) was used to measure the I-V characteristics under dark and illumination conditions. Chronoamperometry (CA) measurements were performed with an ON/OFF cycle of 40 sec. at fixed biased potential of 0.3 V. Electrochemical impedance spectra (EIS) were recorded at biased potential of 0.3 V in the frequency range of 0.1 Hz to 100 kHz, and Mott-Schottky (MS) plot (1/C² vs. bias potential) was evaluated under dark at 1 kHz.

The photocatalytic dye degradation activity of BSO NPs was evaluated for the MB and CV dyes under Xenon lamp (300 W) in photochem reactor. The schematic of the photochem reactor is shown in Fig. 2.9(b). More experimental details are provided in our earlier published articles [44]. To achieve adsorption-desorption equilibrium, the catalyst was mixed with dye solution and stirred constantly for 60 min. under dark and then exposed for photocatalytic reaction. Moreover, the adsorption-desorption equilibrium for all the dye degradation measurements and is tabulated in Table 7.2. The catalyst dose was first optimized for 10 ppm MB dye and further reacted with 20 and 30 ppm dyes. The degradation performance was approximated at regular intervals by examining the changes in UV-visible absorbance spectra of the dye solution. The scavenging study was performed to identify the role of active radicals like photogenerated holes (h^+), hydroxyl radicals ($\cdot OH^-$), and superoxide radicals ($\cdot O_2^-$) on the photocatalytic degradation performance. Further, plausible degradation pathway for

the MB dye was proposed from the byproducts examined at various stages of degradation using Liquid Chromatography Mass Spectrometry (LCMS, micrOTOF-Q II, Bruker Daltonik).

7.3 Results and discussion

7.3.1 XRD and SAXS analysis



Fig. 7.1. (a) Rietveld refined XRD spectra and (b) Small angle X-ray scattering (SAXS) spectra of the BSO NPs. The corresponding inset shows the crystal structure and average particle size distribution of BSO NPs.

The XRD spectra were evaluated to confirm the formation of crystalline perovskite BSO NPs. The obtained XRD spectra were further Rietveld refined by FullProf software to determine lattice parameters, crystallinity, and phase purity of BSO NPs. The refined spectra (Fig. 7.1(a)) indicated a good fit between the experimental and fitted XRD patterns with fitting parameters such as R_P, R_{WP}, R_{EXP}, and χ^2 of 11.3, 16.7, 11.36, and 2.16, respectively. The diffraction spectra of BSO NPs show peaks at 30.76°, 37.91°, 44.04°, 54.63°, 63.96°, and 72.62° correspond to the (110), (111), (200), (211), (220), and (310) planes of the cubic crystal of *Pm*3*m* space group (JCPDS: 15-0780). The lattice parameters of a=b=c=4.11 Å and $\alpha=\beta=\gamma=90°$ are observed for BSO NPs. The simulated packing of cubic crystalline BSO NPS drawn from atom positions of Ba, Sn, and O and Rietveld refined lattice parameters using VESTA software (inset of Fig. 7.1(a)) represents the estimated bond length of 2.054 Å, (\equiv Ba-O) and 2.905 Å (\equiv Sn-O), and corresponding bond angle of 60° (\equiv O-Ba-O) and 90° (\equiv O-Sn-O). Furthermore, the small angle X-ray scattering (SAXS) profile was measured in 2 θ range of 0-5° to calculate the particle size distribution. The plot shows the best fit for type-I Gaussian function with the most frequent diameter of ~31 nm and average diameter of ~37 nm representing the formation of uniform BSO NPs (Fig. 7.1(b)). The BSO NPs exhibited a high surface-to-volume ratio (S/V) of 0.216 nm⁻¹, which might have contributed to improving photocatalytic activity.





Fig. 7.2. (a) FESEM images, (b) statistical histogram of the particle size distribution evaluated from FESEM image in (a), (c) N_2 adsorption-desorption isotherm and corresponding, (d) BJH pore size distribution, (e) EDS spectra, and (f) diffuse reflectance UV-Vis spectra (DRS) and corresponding Kubelka-Munk plot (in the inset) of the BSO NPs.

The morphological aspects of the perovskite BSO are shown in Fig. 7.2(a). The FESEM indicates the NPs like morphology of BSO with uniform size distribution in the range of 10 to 50 nm and an average diameter of ~30 nm (Fig. 7.2(b)). The Nitrogen (N₂) adsorption-desorption isotherm in Fig. 7.2(c) depicts a characteristic hysteresis loop with relative pressure (P/P₀) ranging from 0.05 to 0.98, representing type IV isotherm and indicating highly porous arrangement of BSO NPs. The BSO NPs delivered a surface area of 15.11 m²/g and pore volume of 0.29 cc/g. The corresponding BJH pore size distribution curve (Fig. 7.2(d)) shows the average pore diameter of 3.06

nm. Thus, the evaluated surface area and pore size distribution of the BSO represent the enhanced surface area due to nanoparticulate morphology than that of bulk size, which might be the asset behind the higher photocatalytic activity. The EDS spectra show the presence of Ba, Sn, and O elements without any other elements (Fig. 7.2(e)), representing the absence of impurity in the BSO NPs. The C is observed due to the use of carbon tape during the FESEM/EDS analysis of BSO NPs powder. Furthermore, the diffuse reflectance spectroscopy (DRS) spectrum of BSO NPs was measured in the visible range, and the bandgap was evaluated (Fig. 7.2(f)) using the Kubelka-Munk function in Eq. 7.1.

$$F(R) = \frac{(1-R)^2}{2R}$$
(7.1)

Where, R is measured reflectance, *h* is the plank's constant, and ν is the frequency. The absorption coefficient of the material is directly related to the F(R). The bandgap of 3.24 eV was evaluated for BSO nanoparticles, which is analogous to the literature [45].



Fig. 7.3. High-resolution XPS spectra of (a) Ba(3d), (b) Sn(3d), and (c) O(1S) core level of the BSO NPs.

The core level XPS spectra of Ba(3d), Sn(3d), and O(1s) for BSO NPs are analyzed to understand the elemental composition and oxidation state. The deconvoluted spectrum of the Ba(3d) core level shows a perfect fit for four distinct peaks at binding energy (B.E.) of 779.3 (\equiv a), 780.6 (\equiv a'), 794.6 (\equiv b), and 795.9 (\equiv b') eV corresponds to the Ba²⁺(3d_{5/2}), Ba³⁺(3d_{5/2}), Ba²⁺(3d_{3/2}), and Ba³⁺(3d_{3/2}), respectively (Fig. 7.3(a)). The highly intense peak of Ba(3d_{5/2}) and Ba(3d_{3/2}) with peak separation energy of 15.3 eV represents the majority existence of Ba²⁺ in the BSO NPs. However, the relatively much lesser intense peaks observed at 1.3 eV higher B.E. represent the minor existence of Ba³⁺, assigned to the carbonate group on the surface of NPs, assisting Ba to move in higher oxidation states [46, 47]. Similarly, the deconvolution spectra of the Sn(3d) core level show a perfect fit with four distinct peaks (Fig. 7.3(b)) at B.E. of 486.0 (\equiv a) and 494.4 (\equiv b) eV with peak separation energy of 8.4 eV, corresponding to Sn⁴⁺(3d_{5/2}) and Sn⁴⁺(3d_{3/2}), respectively, Whereas, minor peaks at B.E. of 487.1 (\equiv a') and 495.5 (\equiv b') eV representing Sn²⁺(3d_{5/2}) and Sn²⁺(3d_{3/2}) core levels, respectively, The much larger intensity of Sn⁴⁺(3d_{5/2}) over the Sn²⁺(3d_{5/2}) represent the majority presence of Sn⁴⁺ accompanied by negligible existence of Sn²⁺ ions in the BSO NPs [48]. The broad peak of O(1s) is deconvoluted perfectly with two distinct peaks at B.E. of 529.4 (\equiv a) and 530.9 (\equiv b) eV (Fig. 7.3(c)) corresponding to the lattice oxygen of the core level of the O²⁻ anions of the BSO NPs, and a surface hydroxyl group, respectively [49]. Overall, the XPS and EDS represent the formation of BSO NPs.





Fig. 7.4. (a) I-V characteristics of BSO photoanode film under dark and illuminating conditions. (b) Applied bias photon to current efficiency (ABPE), (c) Nyquist (d) Bode plot, (e) Mott-Schottky plot, and (f) chronoamperometry (*i-t*) plot with ON/OFF cycle of every 40 sec. time in 0.1 M Na₂SO₄ electrolyte of the BSO photoanode films.

Linear sweep voltammetry (LSV) was performed to evaluate the PEC activity of BSO photoanode. Fig. 7.4(a) shows the I-V characteristics of BSO films under dark and illuminating conditions. The twenty-fold increment in current density under

illumination to that of dark indicates the excellent photoactivity of BSO NPs. The suitable CB edge potential of BSO with H⁺/H₂ provides efficient charge separation with reduced recombination, which results in high photogenerated current [32]. The maximum photogenerated current density of ~21 μ A/cm² was observed at a small bias potential of 0.6 V (vs. SCE). To analyze the effective use of the photogenerated $e^- - h^+$ pair, the applied bias photon to current efficiency (ABPE) of the BSO photoanode (Fig. 7.4(b)) was calculated from Eq. 7.2 [50],

$$ABPE(\%) = \frac{J_{ph} \times (1.23 - |V_b|) \times \eta_f}{P_{in}}$$
(7.2)

Where, J_{ph} is the photogenerated current density of BSO NPs (mA/cm²), V_b is the applied bias potential (V), η_f is the faradaic efficiency (~1), and P_{in} is the power of incident light (mW/cm²). The BSO photoanode shows a maximum ABPE of 0.0013 % at 0.6 V biased potential. Further, to analyze the charge transport characteristics at the BSO photoanode/electrolyte interface, EIS was performed at 0.3 V (Fig. 7.4(c)), from where current density significantly increased. The perfect fitting of the equivalent electrical circuit to observed EIS provided the electrolyte resistance (R_S) of 26.56 $\Omega \cdot \text{cm}^2$, charge transfer resistance (R_{Ct}) of 181 k $\Omega \cdot \text{cm}^2$ at the BSO/electrolyte interface, and constant phase element (Q_P) of 5.65 µF. The Bode plot extracted from the EIS measurement is shown in Fig. 7.4(d). The maximum phase angle at the frequency (f_{max}) gives an insight into the lifetime (τ) of free charge carriers calculated by Eq. 7.3.

$$\tau = \frac{1}{2\Pi f_{\text{max}}} \tag{7.3}$$

The lifetime of the free charge carrier is 71.4 ms for BSO NPs, which is relatively higher and, therefore, results in lower recombination rate and better charge extraction [50]. The Mott-Schottky (MS) plot shown in Fig. 7.4(e) was also analyzed to evaluate the intrinsic properties, namely space charge region (W), flat band potential (V_{fb}), and donor carrier concentration (N_D) of BSO NPs using Eq. 7.4 to 7.6 [51],

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r A^2 q N_D} \left[V - V_{fb} - \frac{k_B T}{q} \right]$$
(7.4)

$$Slope\left(S\right) = \frac{2}{\epsilon_0 \epsilon_r A^2 q N_D} \tag{7.5}$$

$$W = \sqrt{\frac{2\epsilon_0 \epsilon_r}{q N_D} \left(V - V_{fb} \right)} \tag{7.6}$$

Where, C is the capacitance at the electrolyte/photoanode interface, V is the biasing potential, ϵ_0 is the dielectric permittivity of space, ϵ_r is the relative permittivity, A is the surface area of the photoanode, k_B is the Boltzmann's constant, q is the electronic charge, and T is the operating temperature. The BSO NPs have V_{fb}, N_D, and W of -0.82 V, 2.56×10^{18} cm⁻³, and 12.6 nm, respectively. The positive slope of the MS plot (Fig. 7.4(e)) shows the n-type nature of the photoanode. The more negative flat band potential indicates reduced recombination at the BSO/electrolyte interface, leading to better charge extraction. The N_D of 2.56×10^{18} cm⁻³ indicates the high electronic conductivity of BSO, thus having low width of space charge region (SCR) [50, 52]. Furthermore, we analyzed the transient response of BSO NPs at bias potential of 0.4 V with an ON/OFF cycle of 40 s. The corresponding i-t plot of BSO NPs for 240 sec. (Fig. 7.4(f)), representing the stable transformation in the current for each ON/OFF cycle despite of slight reduction in photocurrent density with the progression of cycles, indicating good stability of BSO NPs for PEC water splitting. Moreover, the PEC water splitting performances of various pristine and/or doped/composite BSO photocatalysts reported in the literature are compared with the BSO NPs (Table 7.1).



Fig. 7.5. Schematic of the PEC water splitting mechanism for the BSO photoanode.

With these observations, the schematic of the proposed PEC water splitting mechanism is shown in Fig. 7.5. The BSO NPs at photoanode generate electron-hole $(e^- - h^+)$ pairs under illumination (Eq. 7.7). The holes (h^+) react with water molecules at the BSO/electrolyte interface and release the O₂ gas along with the dissociation of hydrogen ion (H⁺) (Eq. 7.8). The photogenerated e^- , simultaneously traveled to the counter electrode through an external circuit, attract the H⁺ ions via an electrolyte medium, and liberate the H₂ gas (Eq. 7.9). Overall, the O₂ and H₂ are electrochemically

generated at the BSO NPs photoanode and counter electrode under illumination (Eq. 7.10) as represented below.

$BSO + h_V \rightarrow BSO (e^- + h^+)$	(at anode)	(7.7)
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$H_2O + h^+ \rightarrow H^+ + O_2\uparrow$	(at anode)	(7.8)
$\mathrm{H^{+}}+e^{-}\rightarrow\mathrm{H_{2}}\uparrow$	(at cathode)	(7.9)
$2H_2O \rightarrow 2H_2 + O_2$	(complete reaction)	(7.10)

Table 7.1. Comparison of PEC water splitting performance of the various pristine and doped/composite Ba and Sn based perovskite photoanode.

S.	Photoanode	Electrolyte	Photocurrent	Photocurrent Donor		Ref.
N.			(mA/cm ²)	density	Potential	
				(cm ⁻³)	(V)	
1.	BaSnO ₃ NPs	1 M K ₃ BO ₃	0.81 @ 1.23 V	2.16×10 ¹⁸	-0.52	[38]
	BaSnO _{3-δ}		7.86 @ 1.23 V	8.47×10^{18}	-0.24	
2.	BaSnO ₃ NWs	0.25 M Na ₂ S +	0.5 @ 0 V	-	-	[32]
	BaSnO ₃ -CdS QD	0.35 M Na ₂ SO ₃	4.8 @ 0 V	-	-	
3.	Ba _{0.98} La _{0.02} SnO ₃	1M KOH	0.339 @ 1.1 V	7.24×10^{20}	0.05	[34]
	(Bulk)					
4.	ZnO NW/ZnSnO ₃	0.25 M Na ₂ S +	0.4 @ 1.2 V	-	-	[25]
		0.35 M Na ₂ SO ₃				
5.	TiO ₂ /BaTiO ₃ NWs	1 M Na ₂ SO ₃	1.30 @ 1.5 V	-	-	[22]
6.	BaTiO ₃ NRs	0.5 M Na ₂ SO ₄	0.17 @ 1.2 V	6.26×10 ¹⁷	0.0712	[20]
	BaTiO _{3-x} (5%)		0.68 @ 1.2 V	9.6×10 ¹⁸	-0.0937	
7.	BaTiO ₃	0.1 M NaOH	0.02 @ 0.95 V	-	-0.37	[21]
	BaTiO ₃ /Cu ₂ O		1.44 @ 0.95 V	-	-0.71	
8.	BaSnO _{3-δ} (Bulk)	0.5 M KOH	0.024 @ 0.5 V	1.2×10^{20}	-0.87	[33]
	DCO ND-		$0.021 \oplus 0.031$	256.1018	0.92	T1.:
9.	B20 NPS	0.1 M Na ₂ SO ₄	0.021 @ 0.6 V	2.36×10 ¹⁰	-0.82	Inis
						Work

7.3.5 Photocatalytic dye degradation

To explore the potential of BSO NPs towards photocatalytic degradation of organic dye, we have performed MB and CV dye degradation studies using BSO NPs as catalysts. Initially, the 20, 30, and 40 mg BSO NPs catalyst was reacted with 10 ppm MB dye under a Xenon lamp (300 W) for photocatalytic dye degradation, and corresponding UV-Vis spectra were recorded at 30 min. interval, as shown in Fig. 7.6.

The MB dye has a highly intense characteristics band at 664 nm along with small shoulder peaks at 615 nm and 290 nm in the visible and UV region corresponding to the aromatic rings with N and S dye dimmer absorbance functional group (-C=S and - C=N), $\pi - \pi^*$ transition of unsaturated conjugate aromatic rings, respectively [53, 54]. With increased exposure time, the intensity of these absorption peaks decreases drastically for all the catalyst doses and reaches the minimum (or saturation) after 240 min. irradiation, indicates the demolition of the conjugate structure and fragmentation of the aromatic ring of the MB molecule. The degradation efficiency of the dye was calculated from the UV-visible spectra using Eq. 7.11,

Dye degradation (%) =
$$\frac{c_0 - c_t}{c_0} \times 100$$
 (7.11)

Where, C_0 is the initial dye concentration before light irradiation and C_t is the dye concentration after continuous light irradiation for 240 min. The histogram of degradation efficiency is shown in Fig. 7.7(a). The 5.86, 76.84, 96.49, and 92.80 % degradation of MB dye in the presence of 0, 20, 30, and 40 mg BSO catalyst, respectively, indicate the active participation of BSO in the dye degradation. Their respective lower values of adsorption capacity, provided in Table 7.2, confirm the effective photon-dependent degradation of the MB dye. The Langmuir-Hinshelwood kinetics (Eq. 7.12) model utilized for better comparison of dye degradation signifies pseudo-first-order reaction kinetics for photocatalytic dye degradation (Fig. 7.7(b, c)).

$$\ln(\frac{\sigma_i}{c_0}) = -k_{obs} t \tag{7.12}$$

Where, k_{obs} is the rate constant of pseudo-first-order reaction kinetics, and t is irradiation time.

The estimated rate constant (*k*) and correlation coefficient (\mathbb{R}^2) values are 0.006, 0.013, and 0.011 min⁻¹ and 0.96, 0.93, and 0.97 for the 20, 30, and 40 mg BSO catalyst, respectively. This interprets that more active sites for the adsorption of dye molecules were offered with an increased amount of catalyst (i.e., 30 mg). However, further increase in the catalyst (> 30 mg) increases the opacity of the dye solution and inhibits the penetration of light deep inside the catalyst, resulting in the decay of degradation efficiency. Consequently, the 30 mg BSO catalyst delivered better degradation efficiency for 10 ppm MB dye and hence continued for further optimization.



Fig. 7.6. Time-dependent UV-Visible absorption spectra of 10 ppm MB dye solution collected at different intervals during photocatalytic irradiation (a) without, i.e., 0 mg, and with (b) 20, (c) 30, and (d) 40 mg BSO catalyst.

S. N.	Dye	Catalyst (mg)	Dye concentration (ppm)	Adsorption capacity (%)
1.	MB	20	10	12.33
2.	MB	30	10	7.07
3.	MB	40	10	8.76
4.	MB	30	20	6.41
5.	MB	30	30	10.07
6.	CV	30	10	21.87

Table 7.2. Adsorption capacity of various degradation reactions for BSO photocatalyst.

Further, 30 mg BSO was irradiated in increased concentrations (i.e., 20 and 30 ppm) of MB dye. The histogram of degradation efficiency evaluated from the absorption spectra recorded at regular time intervals (Fig. 7.8(a, b)) is shown in Fig. 7.7(d). The 97.49, 75.12, and 53.35 % degradation with adsorption capacity (Table 7.2) of 7.07, 6.41, and 10.07 % was observed for 10, 20, and 30 ppm MB dye with the pseudo-first-

order reaction kinetics. The corresponding k and \mathbb{R}^2 of 0.013, 0.005, and 0.003 min⁻¹ and 0.93, 0.95, and 0.98 were observed for 10, 20, and 30 ppm MB dye, respectively (Fig. 7.7(e, f)). This inverse relation between dye concentration and degradation efficiency might be observed due to the adsorption of the large number of dye molecules over the catalyst surface, inhibiting better infiltration of light inside the catalyst and diminishing the exciton pair formation, which turned out in reduced photocatalytic dye degradation efficiency.



Fig. 7.7. (a) Histogram of degradation efficiency, (b) kinetic curves, and (c) pseudo first order kinetic plot of 10 ppm MB dye solution reacted with different doses of BSO catalyst. (d) Histogram of degradation efficiency, (e) kinetic curves, and (f) pseudo first order kinetic plot of optimized 30 mg BSO catalyst reacted with various concentrations of MB dye, collected at 60 min. intervals during the degradation process.

Furthermore, the photocatalytic degradation performance was analyzed for 10 ppm CV dye at the optimized dose of 30 mg BSO. The characteristics peak for CV dye at 590 nm accompanied by another peak at 550 nm represents the $\pi - \pi^*$ transition of regular and distorted propeller monomers, respectively [14]. The peak intensity of CV dye decreased with irradiation time (Fig. 7.9), which is the onset of the photocatalytic dye degradation process. The histogram in Fig. 7.10(a) shows 96.49 and 95.38 % degradation of the MB and CV dye after 240 min. of irradiation. The Langmuir-Hinshelwood model suggests the pseudo-first-order reaction kinetics for CV dye

degradation as well. The *k* and R^2 of 0.013 and 0.013 min⁻¹ and 0.93 and 0.99 were obtained for MB and CV dye, respectively (Fig. 7.10(b, c)). The real-time images of the MB (Fig. 7.10(d)) and CV (Fig. 7.10(e)) dyes were captured at regular intervals of 60 min. under light irradiation during the degradation process indicates the conversion of blue and violet color into transparent solution, representing the thorough degradation of MB and CV dyes.



Fig. 7.8. Time-dependent UV-Visible absorption spectra of (a) 20 and (b) 30 ppm MB dye solution collected at different intervals during photocatalytic irradiation in the presence of 30 mg BSO catalyst.



Fig. 7.9. Time-dependent UV-Visible absorption spectra of 10 ppm (a) MB and (b) CV dye solution collected at different intervals during photocatalytic irradiation in the presence of 30 mg BSO catalyst.



Fig. 7.10 (a) Histogram of degradation efficiency, (b) kinetic curves, and (c) pseudo first order kinetic plot of 10 ppm MB and CV dyes in the presence of 30 mg BSO NPs. Photographs of (d) MB and (e) CV dyes collected at 60 min intervals during the degradation process.



Fig. 7.11. (a) Effect of different scavengers and (b) Cyclic stability performance of BSO catalyst on photocatalytic degradation of MB dye, (c) FESEM image and (d) EDS spectra of BSO catalyst after cyclic stability performance, and (e) FTIR, and (f) XRD spectra of BSO catalyst before and after the degradation study.

To investigate the active radicals responsible for the photodegradation, the scavenger study was performed on 10 ppm MB dye solution. Herein, benzoquinone

(BQ), isopropyl alcohol (IPA), and ammonium oxalate (AO) are used as a scavenger of superoxide radicals ($\cdot O_2^-$), super hydroxide radical ($\cdot OH^-$), and photogenerated holes (h^+) , respectively. The histogram in Fig. 7.11(a) demonstrates the influence of scavengers on dye degradation efficiency, and corresponding UV-visible spectra are provided in Fig. 7.12(a-c) of supporting information. The significantly reduced efficiency in AO indicates the dominance of h^+ radicals, moderately decayed efficiency in IPA suggests the considerable role of $\cdot OH^{-}$, and reasonably reduced efficiency in BQ indicates a marginal role of $\cdot O_2^-$ in the degradation process. Overall, the h^+ and $\cdot OH^-$ plays a significant role in the photocatalytic degradation of MB dye, whereas $\cdot O_2^-$ plays an insignificant role. Further, the stability study of BSO NPs performed for three consecutive degradation cycles is shown in Fig. 7.11(b). The timedependent UV-Vis spectra recorded for all three cycles (Fig. 7.13) represent excellent stability with negligible reduction in the degradation efficiency (i.e., 96.49 to 89.45 %) after the third cycle. The ~7 % reduction is ascribed to the loss of BSO NPs during the recycling process. To check the morphological and chemical stability of the BSO catalyst, the FESEM and EDS analysis were performed after three cycles of degradation. Even after three cycles of degradation, the nanoparticle like morphology of the BSO remained intact (Fig. 7.11(c)) without the interference of any elemental impurity (Fig. 7.11(d)). The C is observed due to the use of carbon tape during the FESEM/EDS analysis of BSO NPs powder. Likewise, to check the structural and compositional stability, the FTIR and XRD of the BSO catalyst were analyzed before and after the degradation process. The FTIR spectra of BSO NPs before and after the stability study remained identical without adding or removing any function group, indicating its stable cyclic degradation performance (Fig. 7.11(e)). The strong characteristic peak at 626 cm⁻¹ is ascribed to the Sn-O symmetrical stretching vibration contributing to the [SnO₆] octahedron. The peak at 1452 cm⁻¹ is of the (O-H) group and characteristic of the proton in the BSO. The low intense absorption bands at 855 and 1018 cm⁻¹ correspond to C-O and C=O bonds, respectively [35, 43, 55]. The XRD spectra of BSO NPs before and after degradation studies are akin to each other, without hoist of other impurities peaks after degradation studies (Fig. 7.11(f)), exhibiting their structural stability in the degradation process. Moreover, the degradation performance

of BSO NPs reported here is either better or comparable to the various pristine and/or doped/composite BSO reported in the literature (Table 7.3).



Fig. 7.12. Time-dependent UV-Visible absorption spectra of 10 ppm MB dye solution collected at different intervals in presence of (a) BQ, (b) IPA, and (c) AO scavengers



Fig. 7.13. Time-dependent UV-Visible spectra collected at regular intervals during (a) 1^{st,} (b) 2^{nd,} and (c) 3rd cycle of MB dye degradation of BSO catalyst.

Table 7.3. Comparison of degradation performance of the pristine anddoped/composite BSO catalysts.

S.N.	Photocatalysts	Dose	Dye	Dye Conc.	Degradation		Ref.
		(mg)		(ppm)	Time (min)	(%)	
1.	BaSnO ₃ (Bulk)	10	RNL	10	300	74	[41]
2.	$BaSn_{0.9}Fe_{0.1}O_3$ (Bulk)	10	RNL	10	240	93	[42]
3.	BaSnO ₃ /TiO ₂ @HNTs		MB	40	300	92	[36]
3.	BaSnO ₃ rods	100	MB	-	180	46	[35]
	rGO/BaSnO ₃					94	
4.	BaSnO ₃ @HNT	50	MB	10	180	60.2	[43]
	Bi/BaSnO ₃ @HNT					90.2	
6.	BiVO ₄ /BaSnO ₃ @HNT spheres	50	MB	20	120	94.1	[37]
7.	BaSnO ₃ NPs	30	MB	10	240	96.5	This
			CV			95.4	work



Fig. 7.14. LCMS data collected (a) before and (b) after 240 min irradiation time of MB dye degradation for BSO catalyst.



Fig. 7.15. Proposed photocatalytic degradation pathway of MB dye and identification of intermediates by LCMS.

To identify various byproducts produced during the photocatalytic degradation of MB dye, LCMS analysis was performed before and after the MB dye degradation (Fig. 7.14). The proposed dye degradation mechanism for MB dye is shown in Fig. 7.15. The MB dye molecule initially identified at m/z = 284.12 is fragmented via attack of super hydroxide radicals on the methyl group of molecules. The auxochromic alkylamine groups in the dye play a significant part in photocatalytic dye degradation. The methyl group cleavage on amine nitrogen produces the intermediates identified by the m/z ratio of 270.11, 256.10, and 228.07, which are considered the de-methylated byproducts [44]. The subtraction of sulfur from the relative parent compound produces the intermediate with m/z of 279.16.[56] Other intermediates with m/z = 167, 126.5,

and 111.04 may arise due to the breaking of benzene rings by the attack of hydroxyl radicals [57]. Moreover, the breaking of the benzene ring results in the intermediate pentanoic acid (m/z = 102.12).[58] Finally, another identified intermediate, viz. m/z = 135.01 and 114.04, mineralizes the MB molecule into non-toxic and eco-friendly compounds like CO₂ and H₂O [59].

To analyze the degradation mechanism of organic dyes using BSO photocatalyst, the conduction (E_{CB}) and valence (E_{VB}) band edges are calculated from the Mulliken electro-negativity theory using Eq. 7.13 and Eq. 7.14.

$$E_{CB} = \chi - E_e - 0.5 E_g \tag{7.13}$$

$$E_{VB} = \chi - E_e - 0.5 E_g \tag{7.14}$$

Where E_g is the band gap of BSO (3.24 eV, Fig. 7.2(f)), E_e is the energy of free electron on the NHE scale (~4.5 eV), and χ is the absolute electro negativity of BSO (3.04 eV) [35]. The E_{CB} and E_{VB} values calculated for BSO are -3.08 and 0.16 eV, respectively. The schematic of the generalized degradation mechanism is shown in Fig. 7.16. Generally, two degradation pathways are feasible, viz. oxidative path (combination of OH^-/H_2O with h^+) and reductive path (combination of O_2/H^+ with e⁻). However, the redox potential of OH^{-}/OH^{-} (i.e., 1.89 eV) is more positive to E_{VB} of BSO (i.e., 0.16 eV); hence, from the thermodynamic point of view h⁺ can react with the OH⁻ rather than H₂O for the formation of \cdot OH⁻ radicals. Similarly, the redox potential of O_2/O_2^- (-0.13 eV), positive to E_{CB} of LFO, assists the e⁻ to react with O_2 and produce $\cdot O_2^{-}$. When light is incident on the surface of the BSO catalyst, $e^{-} h^{+}$ pair is generated and responsible for the effective degradation via oxidation and reduction (Eq. 7.15). Furthermore, h^+ from the VB react with OH⁻ to produce \cdot OH⁻ radicals as this pathway is more thermodynamically feasible (Eq. 7.16). Similarly, the e⁻ from the CB combined with adsorbed O_2^- and generate O_2^- radicals (Eq. 7.17). The active involvement of $\cdot OH^-$ and $\cdot O_2^-$ radicals then convert the organic dye molecule into less harmful byproducts like CO_2 and H_2O (Eq. 7.18). Overall, above stated reactions that occurred at the surface of the BSO catalyst during the photocatalytic dye degradation process are as follows,

$$BSO + h\nu \rightarrow BSO (e^- + h^+)$$
(7.15)

$$BSO(h^+) + OH^- \rightarrow OH^-$$
(7.16)

BSO
$$(e^{-}) + 0_{2}^{-} \rightarrow 0_{2}^{-}$$
 (7.17)

$$\cdot 0 \text{H}^{-} / \cdot 0_{2}^{-} + (\text{MB}) \rightarrow \text{CO}_{2} + \text{H}_{2} 0$$
 (7.18)



Fig. 7.16. Schematic of generalized photocatalytic degradation mechanism for organic dyes using BSO catalyst.

7.4 Conclusion

In conclusion, the cost-effective co-precipitation synthesis route resulted in cubic crystalline pure perovskite BaSnO₃ phase with a particle size of ~30 nm providing a surface area of 15.11 m²/g and, therefore, more active sites to participate in solar-driven water splitting and organic dye degradation. The BSO nanoparticles, spin-coated to form films as photoanode, showed ~20 times higher photogenerated current density ($20 \mu A/cm^2$) than that of dark current and good stability. The lower interfacial charger transfer resistance enhanced the simultaneous interaction of electron-hole ($e^- - h^+$) pairs, and improved charge carrier lifetime resulting in the lower recombination rate are found to regulate the water splitting capabilities of BSO photoanode. Furthermore, BSO NPs exhibited excellent photocatalytic degradation performance for MB and CV dyes. The kinetic study revealed the 96.49 and 95.38 % degradation of MB and CV dyes under 240 min. of continuous irradiation, respectively, which is the highest degradation efficiency reported so far for the MB and CV dyes with pristine BSO photocatalyst. Scavenger trapping study reveals the

active participation of the h^+ and $\cdot OH^-$ radicles in photocatalytic degradation of MB dye at rate constant and correlation coefficient of 0.013 min⁻¹ and 0.93, respectively. The EIS-LCMS study confirmed the fragmentation of MB dye molecules via the attack of super hydroxide radicals on the methyl group of molecules. The methyl group cleavage on amine nitrogen produced intermediates and finally converted into less toxic byproducts such as CO₂ and H₂O. Overall, BSO NPs are found to be effective photocatalysts for bifunctional photoactive applications in water splitting and remediation.

7.5 References

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Chapter 8

Summary and conclusion

8.1 Summary and conclusion

The rapid industrialization and population growth project global energy requirements to reach ~46 terawatts (TW) by the year 2100. With continuously increasing energy demands coupled with the dwindling supply of fossil fuels, it is inevitable to develop a sustainable future without alternate energy sources. Therefore, extensive investigation of various sustainable and renewable energy sources is prerequisite to meet future energy needs. Among various available renewable energy sources, harvesting solar energy by PV cells and PEC water splitting has gained significant attention. The direct conversion of sunlight into electricity and the generation of green H_2 for use in fuel cells are the most viable approaches for increasing renewable energy production. Likewise, the p-n junction PDs, akin to solar cells, transform incident light energy into electrical output signals and attract significant attention for utilization in various modern applications. These PDs can be used in combination with PV panels in self-powered mode for space applications. On the other hand, the difficulties confronting civilization in the current scenario are associated with the quality and supply of water. 80% of the industrial and agricultural waste is directly disposed into freshwater bodies. Photocatalytic wastewater purification provides complete mineralization of toxic organic dye molecules under sunlight and is highly essential to fulfill freshwater requirements. Overall, solar cells, PDs, PEC water splitting, and photocatalytic wastewater purification will be efficient approaches in the development of self-sustainable future.

Oxides of transition metals, namely Sn, Ti, W, Zn, Ba, and Ni, have been investigated for applications in light sensing, solar cells, PEC water splitting, and wastewater purification, owing to their well-controlled structural, chemical, and optoelectronic properties. Additionally, the 1D morphology significantly enhances its photoelectric performance arising from a blend of factors, including high electron mobility and enhanced charge transfer characteristics. Several dopants and composite nanostructures are explored to tailor the optoelectronic and physicochemical properties benefiting these applications. The synergistic effect of p-n junction heterostructure allows to achieve higher photodetection ability. Various MOs have been explored to transport charge carriers from perovskite absorbers to metal contacts for solar cells. MOs/perovskite interface and band energy of MOs with perovskite light absorber are crucial to achieving highly efficient PV cells. Among various MOs, ZnO attracts researchers to explore it as a potential charge transport layer to improve photovoltaic and light sensing performance. Band engineering via suitable dopants can enhance the electronic conductivity and light harvesting activity, extend the photo-response to visible light, and improve the water-splitting performance. Therefore, several dopants, like Al, N, Mg, and Sn, have been explored to enhance the PEC performance of ZnO. Similarly, perovskite oxides having a chemical composition of $A^{2+}B^{4+}O_3$ or $A^{3+}B^{3+}O_3$ are also striking for hydrogen and oxygen evolution due to their unique structural and compositional flexibility offering controlled charge transfer at the interface. The greater charge carrier mobility, lower charge recombination, and higher thermal stability of the ABO₃ materials also make them an ideal contender for photocatalytic water splitting and dye degradation. In these connections, we have addressed the following objectives in this thesis work:

- Low-temperature synthesis of pristine and La-doped ZnO NRs and perovskite BaSnO₃ NPs by cost-effective hydrothermal and co-precipitation methods and further explore their physicochemical, morphological, and optoelectronic properties.
- Investigation on the photovoltaic performance of ZnO NRs with CH₃NH₃PbI₃ absorber layer in FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au device configuration. Further, numerical investigations are performed on ZnO/Cs₂SnI₆ double perovskite and ZnO/CBO all oxide heterostructure solar cells to avoid the degradation of the absorber layer and hence device efficiency by introducing alternative absorber layers to CH₃NH₃PbI₃.
- Formation of heterostructured p-n junction diode using 1D ZnO NRs and 2D Sb₂Se₃ nanosheets and evaluate their light sensing performance.
- Band engineering to probe the physicochemical properties through La doping in ZnO NRs photoanode for PEC water splitting performance.
- Investigations on the PEC performance of BaSnO₃ photoanode for green H₂ and photocatalytic degradation of azo dyes for wastewater purification.

8.1.1 ZnO NRs as charge transport layer for perovskite solar cells

Hydrothermally grown 1D ZnO NRs film was utilized as electron transport layer (ETL) for PSC. The device architecture of FTO/c-ZnO/ZnO NRs/CH₃NH₃PbI₃/Au

delivered a PCE of 3.13%. Poor film quality due to ambient processing and instability of lead halide perovskite results in poor device performance. Therefore, non-toxic and air-stable Cesium tin (IV) halide (Cs₂SnI₆) is explored as promising alternative to Lead halide perovskite for photovoltaic applications. Extensive analysis is performed on the vacancy-ordered Cs₂SnI₆ perovskite as an efficient light harvester sandwiched between the n-ZnO electron transport layer (ETL) and different p-type metal oxides, namely CuBi₂O₄, Cu₂O, CuAlO₂, and NiO, hole transport layers (HTL), using SCAPS-1D software (Fig. 8.1). Various physical parameters, viz. thickness, defect density (bulk and interfacial), and charge carrier concentration of different layers for the device architecture of FTO/ZnO/Cs₂SnI₆/HTL/Au, are systematically investigated along with the effect of parasitic resistance, work function, and operating temperature in the quest for best device performance in terms of photoconversion efficiency (PCE). The effect of DC biasing voltage is analyzed using C-V characteristics to understand the spatial charge distribution, absorber doping profile, and junction built-in potential. The frequency-dependent admittance was studied using simulated C-f characteristics to give an insight into the defect and the conductance. The Cesium tin (IV) halide (Cs₂SnI₆) based device optimized with CuBi₂O₄, Cu₂O, CuAlO₂, and NiO HTLs has shown PCE of 28.18 %, 29.72 %, 29.43 %, and 29.33 %, respectively.



Fig. 8.1. Device architecture of FTO/ZnO/CSI/HTL/Au for highly efficient DPSCs with corresponding energy level alignments of CSI and ETL/HTLs layer.

8.1.2 Theoretical investigation of all oxide heterostructure solar cell

The ambient sensitivity and toxicity of CH₃NH₃PbX₃ perovskite limit the advancement of perovskite solar cell technology. Therefore, we have explored highly stable and non-toxic kusachiite CuBi₂O₄ (CBO) as an excellent light harvester for thin-film photovoltaics. All oxide solar cells (AOSC) of p-type CBO light absorber and n-type metal oxides (MOs), namely, WO₃, SnO₂, ZnO, and TiO₂, are engineered, compared, and optimized using SCAPS 1D (Fig. 8.2). The effect of thickness, doping density, and defect density of various MOs and CBO light absorbers are varied, and device performance is comprehensively analyzed. The impact of operating temperature and the work function of rear metal contact on the device performance of CBO-based solar cells is also assessed for real-time application. At high doping density of CBO absorber, the AOSCs show excellent power conversion efficiency (PCE) of 26.18 %, 25.93 %, 26.13 %, and 26.03 % for WO₃, SnO₂, ZnO, and TiO₂ buffer layers, respectively.



Fig. 8.2. Influence of external factors on perovskite (Scheme 1) and all oxide (Scheme 2) solar cells.

8.1.3 1D ZnO/2D Sb₂Se₃ heterostructure for low-intense light detection

The multifunctional photodetectors (PDs) having broadband responsivity (R) and specific detectivity (D*) at low light intensity are attracting much attention. Hence, we report the creatively designed two-dimensional (2D) Sb₂Se₃ nanoflakes (NFs) over

one-dimensional (1D) ZnO nanorods (NRs) bilayer PD fabricated using simple hydrothermal and thermal transfer processes (Fig. 8.3, Upper panel). The unique coupling of these two layers of materials in nanostructure forms, such as 2D-Sb₂Se₃ NFs/1D-ZnO NRs, provided an effective large surface area, robust charge transport paths, and light trapping effects that help in enhancing light harvesting. Further, the combination of both can help effectively facilitate photoactivity because of proper band alignment. The as-fabricated device has superior overall performance in terms of suitable bandwidth, good R, and high D* at low intense light, unlike the single-layered 1D-ZnO NRs and 2D-Sbe₂Se₃ NFs structures with poor detectivity or response for the measured spectral range. The PD shows a spectral photoresponse range from ultraviolet (UV) to visible (220-628 nm) at an intensity as low as 0.15 mW/cm². The PD yields a D* of 3.15×10^{13} Jones (220 nm) and as high as 5.95×10^{13} Jones in the visible light (628 nm) at 3 V bias (Fig. 8.3, Lower panel). This study shows that the 2D-Sb₂Se₃ NFs/1D-ZnO NRs PD has excellent potential towards low light detectivity with broad bandwidth useful for signal communications and optoelectronic systems.



Fig. 8.3. Schematic and cross-sectional FESEM image of 2D Sb₂Se₃ NFs/1D ZnO NRs heterostructure (top panel). The synergistic coupling between Sb₂Se₃ and ZnO delivered highly responsive PD with low intense light detection ability (bottom panel).
8.1.4 La-doped ZnO NRs photoanode for PEC water splitting.

In the quest to improve photoelectrochemical water splitting performance, we have doped lanthanum (La) in highly crystalline zinc oxide (ZnO) nanorods using a facile and low-temperature hydrothermal route and successful substitution of La^{3+} at the Zn^{2+} site is confirmed from structural and chemical analysis. The tapered nanorods morphology gained after La doping resulted in lower optical bandgap of 3.17 eV and enhanced visible light trapping and multiphoton absorption, which assist to achieve good PEC activity. The La doping also offered higher Urbach energy (E_U) , subsidizing the number of oxygen vacancies. The UPS spectra show that La doping reduces conduction band energy level and endorses smooth charge transportation (Fig. 8.4 (left panel)). The La-doped ZnO exhibits two times enhancement in photocurrent (1.54 mA/cm²) compared to pristine ZnO (0.81 mA/cm²) (Fig. 8.4 (right panel)). The higher applied bias to the photon conversion efficiency of ~1.14 % for La-doped ZnO confirms the efficient utilization of solar energy. The EIS measurements demonstrated reduction in charge transfer resistance with La-doping (Fig. 8.4 (middle panel)). Mott-Schottky analysis shows that La doping lowers the flat band potential and enhances charge transportation, making it potential photoanode for PEC water-splitting applications.



Fig. 8.4. Band engineering of La-doped ZnO NRs photoanode provides better charge transportation (left panel), which results in lower charge transfer resistance (middle panel) for enhanced PEC water splitting activity (right panel).

8.1.5 BaSnO₃ NPs for bifunctional photocatalytic application

The highly crystalline n-type BaSnO₃ (BSO) nanoparticles (NPs) with size ~30 nm, a larger surface area of 15.11 m²/g, and a wide optical bandgap of 3.24 eV have been synthesized using a co-precipitation route for applications in photoelectrochemical (PEC) water splitting and organic dye degradation. The spin-coated films of BSO NPs

photoanodes exhibited a photocurrent density of 20 μ A/cm² at a bias potential of 0.6 V, a donor carrier density (N_D) of 2.56×10¹⁸ 1/cm³ with a flat band potential (V_{fb}) of -0.82 V, and four-fold increment in the photocurrent density at a small bias voltage of 0.3 V, under AM 1.5 illumination (100 mW/cm²). Pseudo-first-order kinetic study showed 96.49 and 95.38 % photocatalytic degradation of Methylene Blue (MB) and Crystal Violet (CV) dyes at rate constant (k) of 0.0128 and 0.0127 min⁻¹, respectively, under constant irradiation for 240 min in the presence of BSO NPs, which is the highest degradation efficiency reported so far for BSO photocatalyst. The scavenger study revealed the significant role of $\cdot OH^-$ and h^+ radicals in the photocatalytic degradation of dyes. This study delivered insight into the BSO NPs as potential candidates for bifunctional applications in photocatalytic water splitting and dye degradation (Fig. 8.5).



Fig. 8.5. Highly crystalline BaSnO₃ NPs with excellent optoelectronic properties, namely high electron mobility, low charge recombination, wide bandgap, and high surface area (middle panel), show outstanding performance for solar driven bifunctional applications in PEC water splitting (left panel) and photocatalytic degradation of organic dyes (right panel).

8.2 Future work

Industrialization and economic development require continuous supply of energy and freshwater. However, non-renewable energy sources will give rise to greenhouse gas emissions and other environmental issues. The water bodies get polluted due to industrial and agricultural waste. Therefore, renewable energy applications are the only way toward

a sustainable future. Solar light dependent applications such as solar cells, PEC water splitting, and PDs can help to move towards zero carbon footprint. Nowadays, gridconnected PV systems are widely used to supply excess power to the grid, thus moving towards high-quality flexible power systems. The PDs can also be coupled with solar panels to monitor the power output at remote locations. Photoelectrochemically generated green H₂ can be utilized as fuel with minimum pollution. Similarly, photocatalytic wastewater purification utilizing the abundantly available sunlight is a cost-effective approach to fulfill freshwater requirements. Thus, it is imperative to enhance the total efficacy of materials either by doping or forming heterostructures for these environmentally friendly green energy applications. In this connection, our present study demonstrates that 1D ZnO thin films are excellent multifunctional materials for solardriven water splitting, light sensing, and solar cell applications. Likewise, BaSnO₃ perovskite was found to deliver excellent photocatalytic activity towards wastewater purification and H₂ production. With these key findings, some of the possible further work shall be focused on,

- 1. Explore various core-shell and nanocomposite heterostructures of 1D ZnO with other semiconductor materials for PEC water splitting application.
- Experimental investigation on the theoretically well-performing all-inorganic and alloxide solar cells with device architecture of FTO/ZnO/CSI/HTL/Au and FTO/ZnO/CuBi₂O₄/Au, respectively.
- Doping and/or composite formation of BaSnO₃ nanostructures for enhanced photocatalytic and H₂ generation activity.
- Investigating the light sensing performance of CuBi₂O₄/ZnO p-n junction heterostructure.
- 5. Decoration of noble plasmonic NPs such as Au, Pt, and Ag over ZnO nanostructures to induce surface plasmonic effect for enhanced photoactivity.