MULTIFUNCTIONAL NANO-ARCHITECTURES OF METAL AND METAL OXIDE: SYNTHESIS TO APPLICATIONS

Ph.D. Thesis

By

PARAMESHWAR R. CHIKATE



DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE AUGUST, 2020

MULTIFUNCTIONAL NANO-ARCHITECTURES OF METAL AND METAL OXIDE: SYNTHESIS TO APPLICATIONS

A THESIS

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

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Mr. PARAMESHWAR R. CHIKATE Roll No: PHD1701205005



DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE AUGUST, 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "MULTIFUNCTIONAL NANO-ARCHITECTURES OF METAL AND METAL OXIDE: SYNTHESIS TO APPLICATIONS" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from December, 2017 to August, 2020 under the supervision of Dr. Rupesh S. Devan, Associate Professor, Department of Metallurgy Engineering and Materials Science.

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

> Signature of the student with date (PARAMESHWAR R. CHIKATE)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of Thesis Supervisor with date

(Dr. RUPESH S. DEVAN)

PARAMESHWAR R. CHIKATE has successfully given his Ph.D. Oral Examination held on 29/12/2020.

Signature of Chairperson (OEB) 12/200 Date: 29

Signature of PSPC Member #1

Signature of External Examiner Date: 29.12.2020

ajw Dusane

upesh

Signature of Thesis Supervisor Date: 29/12/2020

Signatury of PSPC Member #2

Date:

Signature of Convener, DPGC Date:

Signature of Head of Department

Date:

Date:

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Date:29/12/2020

Parameshwar R. Chikate

Dedicated

To myparents

Sunanda Chikate and Raysing Chikate





LIST OF PUBLICATIONS

PAPER - 1

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NOMENCLATURE

А	
Ar	Argon
Ag	Silver
Al	Aluminium
Au	Gold
AFM	Atomic Force Microscopy
AIPES	Angle Incident Photoemission
	Spectroscopy
ads	Adsorption
В	
BSE	Back Scattered Electron
С	
С	Carbon
CBD	Chemical Bath Deposition
Cd	Cadmium
CdO	Cadmium Oxide
C ₂ H ₅ OH	Ethanol
C6H6	
C4H6O4Zn.2H2O	Zinc acetate dehydrate
Cr	Chromium
Cr_2O_3	Chromium Oxide
Cu	Copper
CuO	Copper Oxide
СВ	Conduction band
CVD	Chemical vapour deposition
Со	Cobalt
CO	Carbon monoxide
CO ₂	Carbon dioxide
CoO	Cobalt oxide
	Cobalt dioxide
CoTiO ₃	Cobalt Titanate
CoFe ₂ O ₄	Cobalt Ferrite
D	
dc	Direct current
DFT	Density functional theory

dsep	separation	
E		
Ε	Electric field	
Eads	Adsorption energy	
Egas	Isolated gas energy	
Esurf	Isolated oxygen energy	
EDX	Energy dispersive x-ray	
Eg	Energy gap	
Eon	Turn on energy	
Ethr	Threshold energy	
EtOH	Ethanol	
e	Electron charge	
eV	Electron Volt	
F		
Fe	Iron	
FE	Field emission	
F-N	Flower-Nordheim	
FESEM	Field emission scanning electron	
microscopy	C	
FL	Fermi level	
Fe ₂ O ₃	Iron Oxide	
FWHM	Full-Width Half Maximum	
G		
Ge	Germanium	
GGA	Generalized gradient approximation	
GaN	Gallium nitride	
н		
\mathbf{H}^+	Hydrogen ion	
H_2	Hydrogen	
H plasma	Hydrogen plasma	
HDT	Hexadecanethiol	
HER	Hydrogen evolution reaction	
H ₂ S	Hydrogen Sulphide	
HfO ₂	Hafnium oxide	
HAuCl ₄	Chlorouric acid	
hυ	Energy photon	
\mathbf{h}^+	Positron/hole	
L		
I	Intensity	

IUPAC	International Pure and Applied	
Chemistry		
ITO	Indium tin oxide	
In ₂ O ₃	Indium Oxide	
In	Indium	
Ъ		
J	Current density	
J-E	Current vs Field	
ICPDS	Joint Committee for Powder Diffraction	
Standards	Joint Committee for Fowder Dimaction	
	Lonthonum triouido	
	Litnium	
IVI		
M	Molarity	
Mg	Magnesium Matal Orida	
MO Mo	Metal Oxide Molybdenum	
	Molybdenum trioxide	
MnO ₂	Manganese oxide	
MoS ₂	Molybdenum Sulphide	
MoO ₃	Molybdenum Trioxide	
Ν		
N_2	Nitrogen	
Nb	Niobium	
Ni	Nickel	
Na ₂ O ₂	Sodium peroxide	
Na ₃ C ₆ H ₈ O ₇	Trisodium citrate	
Nd	Neodymium	
NiO	Nickel Oxide	
Nb ₂ O ₅	Niobium Pentoxide	
NO ₂	Nitrogen Dioxide	
NH ₃	Ammonia	
NR	Nanorod	
NP	Nanoparticle	
0	1	
	Oxygen	
0.	Oxygen ion	
OFR	Oxygen evolution reaction	
OH.	Hydroxyl ion	
ovd	Ovidation	
UAU	UNIUAUUII	

xxvii

0D	Zero dimension
Р	
PEC	Photoelectrochemical
PL	Photoluminescence
Pt	Platinum
Pd	Palladium
Pd ²⁺	Palladium ion
PLD	Pulse laser deposition
PAW	Project augmented wave
PBE	Perdew-Burke-Ernzernof
PDOS	Partial density of state
ppm	Parts per million
R	
Ra	Resistance in air
Rg	Resistance in gas
Re	rare-earth metal
red	Reduction
RT	Room temperature
RH	Relative Humidity
rGO	Reduced Graphene Oxide
S	
Sn	Tin
Sr	Strontium
Si	Silicon
SiO _x	Silicon oxides
SEM	Scanning electron microscopy
SnO	Tin oxide
SnO ₂	Tin Dioxide
SrTiO ₃	Strontium Titanate
SE	Secondary Electron
S (%)	Sensitivity
sec	Secondary
Т	
Та	Tantalum
Te	Tellurium
TEM	Transmission electron microscopy
Ti	Titanium
t	Time
TiO ₂	Titanium dioxide
ТМО	Transition Metal Oxide

Tres	Response Time	
Trec	Recovery Time	
U		
UV	Ultraviolet	
UPS	Ultra-violet photoelectron spectroscopy	
V		
V	Potential	
VASP	Vienna Ab initio Simulation	
VB	Valence band	
VBS	Valence band spectra	
V_2O_5	Vanadium Pentoxide	
VLS	Vapor liquid solid	
W		
W	Tungsten	
WO ₃	Tungsten Oxide	
Х		
XPS	X-Ray photoelectron spectroscopy	
XRD	X-Ray diffraction	
Z		
Zn	Zinc	
\mathbf{Zn}^{2+}	Zinc ion	
ZnO	Zinc oxide	

Physical Constants and Conversion Factors

Avogadro's number	$N_A\!=6.02\times 10^{23}$ molecules/mole
Boltzmann's constant	$k = 1.38 \times 10^{-23} \text{ J/K}, 8.62 \times 10^{-5} \text{ eV/K}$
Electronic charge (magnitude)	$q = 1.6 \times 10^{-19} \mathrm{C}$
Electronic rest mass	$m_{\rm e} = 9.11 \times 10^{-31} \rm kg$
Planck's constant	$h = 6.63 \times 10^{-34}$ J.s, 4.14×10^{-15} eV.s
Speed of light	$c = 3 \times 10^8 \text{ m/s}, 3 \times 10^{10} \text{ cm/s}$
Gibb's free energy	$\Delta G = 2.37 \text{kJmol}^{-1}$
Field emission constants	$a = 1.54 * 10^{-6} \text{ A eV V}^{-2}$
	$b = 6.83089 * 10^3 \text{ eV}^{-3/2} \text{ Vcm}^{-1}$

Prefixes:

1 Å (angstrom) = 10^{-10} m	milli-, $m- = 10^{-3}$
1 μ m (micron) = 10 ⁻⁶ m	micro-, μ - = 10 ⁻⁶
$1 \text{ nm} (\text{nano}) = 10^{-9} \text{ m}$	nano-, $n-=10^{-9}$
2.54 cm = 1 in.	pico-, $p-=10^{-12}$
$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$	kilo-, $k-=10^3$
	mega-, $M- = 10^6$

Chapter 1 Introduction

This chapter is a brief literature review of current research on metal oxides and metal @ metal oxides, which helped me to understand the research gaps and perform my research on low cost, environmentally friendly ZnO nanostructure and Au@ZnO nano-hetero-architectures for multifunctional applications. It covers an overview of applications such as field electron emission, gas sensing, and photocatalytic watersplitting using nano-hetero-architecture. The motivation and objectives of the research work are briefed at the end of the chapter.

1.1 Significance of metal oxide nanostructures

The emerging nanoscale science and nanotechnology have turned modern research into a new direction for the miniaturization of devices with improved functionality. The nanoscale dimensions control various physicochemical properties of the materials and offer technological advancement along with the miniatured devices structure. Nanotechnology covered numerous research areas, including physics, chemistry, materials science, engineering, and molecular biology, and boomed interdisciplinary research in various fields. Early in the 20th century, various materials with new morphological forms in nanoscale dimensions are widely exploited for the most significant contribution in technological developments.

The materials with either of the dimensions confined in the range of 1-100 nm called 'Nanomaterials' are categorized as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials, which are confined in three, two, one and zero dimensions, respectively. The reduced dimensionality of the nanomaterials alters the configured electronic structures over the bulk and hence tailor various physical and chemical properties. However, among all three categories, 0D nanostructures offer a relatively larger surface area, and 1D nanostructures provided unidirectional electron transfer pathways with reduced contact resistance. Therefore, 1D nanostructures, a computable applicant for the applications in nanoelectronics and electrochemical applications such as field emission (FE), gas sensor, water splitting, smart windows, light-emitting diodes, and supercapacitor, etc. [1] is expected to deliver better performance after forming heteroarchitecture with 0D nanostructures.

The researchers have increasingly engaged in studying metal-oxides for various applications, owing to their flexibility in the nanoscale morphologies and stable properties. The ionic form due to the existence of positive metal and negative oxygen ions and imbalanced valances due to partial and completely filled 's' and 'd' orbitals led metal oxides to deliver a variety of unique physical-chemical properties. The flexibility in electronic distribution and control over dimensionality put insulating, conducting, and metallic properties in single metal oxides system [2], such as wide bandgaps [3-4], high dielectric constant [5-6], reactive electronic transitions [7-8],

good electrical and [9-10] optical [11] properties, superconductivity [12-13], and electrochromic [14-15] and electrochemical [16-17] characteristics, etc. It makes the metal oxides a potentially great use in miniatured devices as fascinating functional materials.

Enormous efforts have been put into the synthesis of Ni, Zn, Cu, Co, Ti, Ta, Nb, W, Mo, and Cd, etc. metal oxides in the form of nanorods [18-20], nanowires [21-22], nanotubes [23-24], nanoneedles [25-26], nanobelts [27-28], nanoribbons [29-30], nanozigzag [31], and nanohelix, [32] etc. However, among all these metal oxides, ZnO nanostructures are found to be most promising for various applications due to low cost, low toxicity, oxidative resistibility, and biocompatibility, etc. [33]. A widely explored ZnO, an n-type semiconductor with a large bandgap (i.e., 3.37 eV), large exciton binding energy (60 meV), near UV emission, piezoelectric nature, greater electric mobility, good conductivity, and ultimate chemical and thermal stability in nanosize are holding good competency for further improvement in electron emission and sensing ability [1, 34-35]. Among all explored ZnO nanostructure morphologies, 1D nanostructure delivers a large surface to volume ratio and continuous pathway for electron transfer [1, 36-38], which promotes electronic transportation in one dimension and facilitates sensing and emission performance. The morphology controlled synthesis of ZnO nanostructures has gained extensive importance in real-time applications. Even though the crystal structure, surface morphology, chemical composition, and operating temperature governs the performance of ZnO nanostructures, the doping/decoration of metals in ZnO was adopted to enhance the electronic properties for improvement in their performance [39].

1.2 Significance of metal @ metal oxide nano-architectures

Morphology controlled synthesis of various metal oxides explored by different synthesis techniques broadly categorized as physical vapor deposition and chemical vapor deposition. However, controlled morphology of pure metal oxides still exhibit some drawbacks and limit the metal oxides for implementation in various commercial applications such as gas sensors, field emission, smart windows, H₂ productions, supercapacitor, etc. [40-41]. The low work function, thermal stability, and high-quality

field electron emission are desirable qualities for improved FE performance. Although most metal oxides satisfy these requirements in the bulk format, their melting point decreases with the reduced dimensions to the nanoscale, and the thermal stability becomes a severe concern even after better field electron emission [42]. Likewise, stability, response, and selectivity have always been one of the most challenging tasks in metal oxide nanostructure. Moreover, poor charge transformation, slow interfacial kinetics, and long-term stability issue limiting the efficiency of photocatalytic water splitting of metal oxides [43]. The fast recombination rate of photo-induce charge carries (e-/h⁺) at the surface of metal oxide photoanode has a prime impediment in achieving high efficiency for photoanode [44-45]. Therefore, alternative synergistic nanostructured materials with excellent properties are explored to meet the required performance [46].

In the quest of the difficulties described above embedded with metal oxide nanostructures, researchers are increasingly engrossed in exploring their nano-heteroarchitectures with metals in the form of doping, decoration, or core-shell structure. The concept of hetero-architecture has been realized in the nanomaterial either to provide more surface area or to overcome the poor surface structure for precisely controlled physicochemical properties [47-48]. Two or more dissimilar materials utilized to form a nano-hetero-architectures offer precise control over synergistic properties [49]. Therefore, various methodologies have been employed to previse controlled over the doping or decorations of different materials. The strategies of doping and decoration metal nanoparticles with metal oxide nanostructures are widely adopted to overcome the limitations of metal oxides and improve the performance in field electron emission, gas sensor, and photoelectrochemical (PEC) water-splitting, etc. The doping alters the electronic structures and may induce an increase in conductivity, but the intercalation of impurities resulted from doping affect adversely on the structural properties. Therefore, the decoration of metal nanoparticles over the surface of metal oxide nanostructures are found to be better alternatives. The alternation in the morphology and stoichiometric of metal oxides after doping of metals can be compromised by employing a decoration strategy to form nano-hetero- architectures of metal and metal oxides.
Owing to the excellent electron affinity, high electronic/chemical stability, and biocompatibility; gold (Au) nanoparticles are increasingly applied in the modification of optoelectronic properties of metal oxides for applications in UV detectors [50], photocatalysis [51], sensors [52], and displays, etc. Despite the larger work function of 5.35 to 5.76 eV, Au nanoparticles were found to perform better because of enhanced electron transfer and surface interactions [51]. Therefore, doping or decoration of Au nanoparticle has been extensively done with various metal oxide, including ZnO nanostructure, to modify optoelectronic properties. The decoration of Au nanoparticles provides high electron density and alters the electronic structure of ZnO. The strong interfacial interaction in the composite of Au and ZnO demonstrated a substantial change in charge transfer between Au and ZnO [53-54] while retaining their chemical stoichiometry and morphology individually. Moreover, the Au decoration assisted in improving light response, the recombination rate of charge carries in the PEC watersplitting and overwhelm the sensitivity, stability, and high operational temperatures issues of metal oxide gas sensors [40]. In this thesis, Chapter 2 is devoted to explaining the synthesis and characterization of ZnO nanowires and Au@ZnO nano-heteroarchitectures. We have demonstrated the use of hierarchical ZnO nanowires for field emission, (Chapter 3) gas sensor, (Chapter 4), and further detailed the effect of controlled decoration of Au nanoparticles over the ZnO nanowires array in the improvement of field emission (Chapter 5) and water splitting (Chapter 6) performance.

1.3 Application of metal oxides

Metal oxides have attracted considerable scientific and industrial attention for energy storage, energy conversion, displays, semiconductors, sensors, generators, etc. Here we have provided a brief review on the utilization of metal oxides and its heteroarchitectures for field electron emission, gas sensor, and water splitting applications

13.1 Field electron emission

The electron emission process is categorized as (a) Thermionic electron emission, (b) Secondary electron emission, (c) Photoelectric emission, and (d) Field electron emission, etc., based on energy delivered during the extraction of electrons from the materials. In thermionic electron emission, the high temperature produces heat energy in the metal/material, and electrons start tunneling through the surface potential barrier (ϕ), acquiring sufficient kinetic energy. In secondary electron emission, the high energetic particles like electrons or ions or photons incident on the surface of metal/material and knockout electrons from their atoms by creating the vacancy. In photoelectric emission, the electrons are emitted from the surface of metal/material under the influence of electromagnetic radiation. However, in the field electron emission, the electrons are extracted from atoms or molecules of metal/material to the vacuum level under the influence of the intense electrostatic field of the ordered 10^{6} - 10^{7} V/cm. Initially, the field electron emission was examined by quantum tunneling of electrons and considered as one of the triumphs of the emerging quantum mechanics. In 1928, R. H. Flower and L. W. Nordheim proposed field emission theory to understand the clear nature of the electron emission phenomenon from bulk materials. The Flower-Nordheim (F-N) theory for field emission, a family of equations, is named after them. F-N equations strictly applied to the field emission from bulk metals only. However, the same is considered for solid crystalline materials after suitable modifications and frequently used as a rough approximation to explain the FE behavior in various materials. The F-N proposed field emission theory under assumptions of freeelectron approximation and temperature of 0 °K for the metal, using equation

$$V(x) = -eEx - e^{2}$$
 at $x > 0$ --(1.1)

Where, e is the charge of the electron, E is the electric field strength i.e., the total potential experienced by the electrons close to the surface is the resultant of image force potential $(-e^2/4x)$ and external potential due to the applied electric field (-eEx).

However, the electron emission current density (J), the applied electric field (E), and work function (ϕ) are correlated by the modified F-N equation as

$$J = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2))] = 154 \times 10^{-6} \, \beta^2 v^2 \qquad \underbrace{\qquad}_{\phi t^2(y)} exp[-6.83 \times 10^7 \, \phi^2 f(y - \frac{3}{\beta v} -(1.2) \, \phi^2 f$$

Where, $y = {}^{1} (e^{3}E)^{1/2} \phi$



Further, the plot drawn between $\log(J/V^2)$ versus 1/V is known as the F-N plot. Where the slope of the plot (m) is given by

$$m = -\frac{297 \times 10^3 \phi^2}{\beta} \frac{S(y)^3}{(1.3)^3} --(1.3)$$

$$S(y) = f(y) - {y \begin{bmatrix} df(y) \\ - & - \end{bmatrix}} - (1.4)$$

Where ϕ is the work function of the metal, β is a field enhancement factor, J is the current density, and V is applied voltage. S(y) function has a magnitude close to unity.

The morphological aspect ratio and work function are the crucial parameters in field electron emission. The low work function with a high aspect ratio is desirable for stable field electron emission at sufficiently low external applied potential. Moreover, the shape and size of the emitter apex influence the field emission and field enhancement factor. Therefore, various nanostructure morphologies of different materials have been extensively explored to study the field emission behaviors. The carbon nanotubes have been studied commonly for FE due to their 1D morphology, high aspect ratio, high conductivity, high mechanical stability, lower turn-on field, and large emission current density [55]. The sharp tip features of 1D metal oxide nanostructures, analogous to 1D carbon nanotubes, hold the potentials to enhance the field electron emission. Therefore, various metal oxides, such as ZnO, MnO₂, MoO₃, In₂O₃, SnO₂, WO₃, V₂O₅, and TiO_2 [56], are also explored for field emission. The high oxidation resistance in harsh environments, high mechanical stability, and hexagonal morphological form facilitating high aspect ratio has been fascinating researchers to explore the suitability of ZnO nanostructures for field emission. ZnO in the form of nanowires [57], nanopencil [58], multipods [59], and nano-needle [60], thoroughly explored to grain higher field emission current density and larger field enhancement factor. Moreover, Ag and Au metals were employed with the ZnO to form hetero-architectures [61] and nanocomposite [62], which reduced the work function, and enhanced field emission current. The employment of electron-rich metal particles modified the electronic structures and significantly induced the conductivity, thereby delivering additional emitting sites that

improved the electron emission. Nevertheless, a significant discrepancy is observed in the field enhancement factor and the turn-on field reported for various materials in the literature. Therefore, Reichard Forbes [63] has recently developed a simple quantitative test for lack of field emission orthodoxy, particularly for the field enhancement factors evaluated to confirm the suitability of materials for various applications. The field emission studies of the pristine and controlled Au decorated hierarchical ZnO nanowires are systematically discussed in Chapter 3, and Chapter 5.

132 Gas sensing

The exhaust of hazardous gases and chemicals from industries has resulted in global warming and impaired human and environmental health, is demanding to address safety and security concerns on high priority. The explosion of ammonium nitrate recently happened in the Beirut city of Lebanon can be one of the worst examples to cite. Therefore, immediate detection and monitoring are foremost to govern the influence of explosive and highly toxic gases on the environment and health. The gas sensors can serve the purpose of controlled monitoring of harmful gases. However, better sensitivity, optimum selectivity, lower operating temperature, fast responses and recovery, and higher reproducibility are expected with precision from the gas sensor. No single materials have the ability to form an ideal sensor accommodating the above-cited properties. Therefore, researchers across the globe are exploring various materials to invent efficient and reliable gas sensor devices. The environmentally friendly metal oxides with unique intrinsic properties can serve as one of the excellent alternative gas sensor materials.

The surface morphology, crystal structure, defects, or additive impurities influence on sensing performance of metal oxides. The adsorption and desorption of reducing or oxidizing gas molecule/atom/ions on the surface of metal oxide change their conductivity or resistance. This means the sensing mechanism would initiate with adsorption of oxygen molecules over the surface when metal oxides are exposed to the air. The formation of different ionic species such as O^- , Q_-^- , and O^{2-} after chemisorption of ambient air oxygen on the surface of metal oxides play a crucial role in the sensing performance. The O_2^- ionic species exist bellow 100 °C, O^- exit in the temperature range between 100 and 300 °C, and O^2 -appear above 300 °C operational temperature of sensor materials [64]. The generalized reaction mechanisms are,

$O_{2(air)} \rightleftharpoons O_{2(ads)}$					(1.5)
metal oxide +	$O_{2(ads)}$ +	e¯	$\rightleftharpoons O^{-}_{2(ads)}$	at $\leq 100 \ ^{\circ}\text{C}$	(1.6)
metal oxide +	0 ⁻ 2(ads) +	e-	$\rightleftharpoons 20^{-}_{(ads)}$	at 100 < 300 °C	(1.7)
metal oxide +	0 ⁻ (ads) +	e ⁻	$\Rightarrow 0^{2-}_{(ads)}$	above 300 °C	(1.8)

The trapping and releasing of surface electrons/holes after injection of gas molecules control the conduction band electron density and hence the resistance of the material. Therefore, the type of sensor materials (i.e., n-type or p-type metal oxide) and interactive gas (i.e., reducing or oxidizing) alters the gas mechanism. The interaction of reducing gases decreases the resistance of n-type metal oxides, whereas oxidizing gas increases its resistance. On the other hand, the resistance of p-type metal oxide decreases after interaction with oxidizing gases and increases when encountering reducing gases.

The evidence of the space charge layer over the surface of metal oxides and its influence on the conductivity reported by Brattain and Bardeen [65] conceived the idea of consuming metal oxides as a gas sensor. Afterward, Syiyama et al. [66] explored the surface depletion layer over the surface of ZnO due to the interaction of atmospheric air during the gas sensor study. Nevertheless, metal oxides have drawn considerable attention due to their low-cost, high sensitivity, compatible nature, and ease of device fabrication. So far, oxides of various metals such as Sn, Zn, Ti, W, Ni, In, Te, Cd, Fe, and Mo, etc., are remarkably explored as gas sensors [1, 67-69]. Besides the non-toxic nature, thermal and chemical stability, high conductivity, excellent oxidation resistance, and good biocompatibility, n-type ZnO is preferable candidates for gas sensing applications owing to its diverse morphological forms, wide direct band gap (3.37 eV), and large exciton binding energy (60 meV) [70-71]. However, large scale applicability is limited because of high operational temperature, poor selectivity, low sensitivity, narrow lightresponsive range, and high recombination rate [70-71]. The noble metal particles either over the surface or as the dopant in the metal oxide were employed as an alternative to enhance the gas sensitivity and improve the performance [72-78]. The effect of the hierarchical appearance of ZnO nanowires in the detection of various gases within the detection safety limit of 50 ppm at lower operation temperature is discussed in Chapter 4.

133 Photocatalytic water-splitting

The industrial demands for the luxury of society projected to upsurge energy consumption rates enormously are the most significant challenge for the future scientific era. Therefore, the discovery of clean, safe, and sustainable energy sources is the most challenging task. Hydrogen energy is one of the most competitive candidates to fulfill energy requirements. It can serve as an energy device with zero carbon emission and run the vehicles, spacecraft, aircraft, etc. Several techniques based on thermal decomposition, photocatalysis, radiolysis, and PEC processes are employed to extract the hydrogen from water [79-81]. The radiolysis and thermal decomposition required high temperature and are suffering from low hydrogen yield. However, the artificial photocatalytic and PEC splitting of water in to H₂ and O₂ is attracting attention as an easier, cheaper, sustainable, and renewable source to produce energy.

Fujishima and Honda first introduced the use of TiO_2 in the PEC water splitting [82]. The PEC cell consisting of photoactive materials (i.e., photoanode/photocathode) as a working electrode and metal as a counter electrode connected by external circuits are immersed in an aqueous electrolyte. The externally applied bias to the electrode drives the reaction at the desired rate. The oxidation and reduction reactions are carried out consuming light radiation of optimum energy and extract oxygen and hydrogen, respectively. The absorption of light photons at the surface of photoelectrode excites the photoelectrons and generates electron-hole pairs through a redox reaction. The water oxidation takes place at photoanode utilizing the photogenerated hole to generate O_2 and H^+ . The photogenerated electron flow towards the photocathode and results in the reduction of H^+ in the form of H₂ production [83]. These processes are known as oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively. This thermodynamically, an endothermic reaction required the potential higher than the minimum essential energy (i.e., 1.23 eV) to subdue the overpotential and expected losses. This reaction mechanism is elucidated as [84],

Semiconductor
$$\rightarrow e_{CB} + h_{VB}^{+}$$
 --(1.9)

Oxidation of water into oxygen gas at photoanode

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$
 E^0_{oxd} 123 V vs RHE --(1.10)

Reduction of water into hydrogen gas at the photocathode

$$2H^+ + 2e^- \rightarrow H_2 \qquad \qquad E^0_{red} \quad 0V \, vs \, RHE \qquad \qquad --(1.11)$$

The overall water-splitting reaction is

$$H_2 0 + 2hv \to H_2 + \frac{1}{2} O_2 \ \Delta E = +1.23 \ V \ vs \ RHE \qquad --(1.12)$$

Where, $\Delta G = +2.37 k mol^{-1}$

For use in a PEC cell, the semiconductor material photocatalytic in nature, demands a wide range of optical absorption, high charge transfer rate at the interface, controlled photo-corrosion, and compatible band alignment for the water redox reaction. To date, several semiconducting materials are explored for PEC water-splitting, but metal oxides are attracting scientific and industrial attention due to good chemical/thermal stability, excellent biocompatible, and environmentally friendly nature [79, 85-86].

The large surface area assisted in driving efficient charge separation and the resultant PEC performance. Therefore, 1D nanostructure morphologies such as nanorods, nanowires, nanotubes, and nanosheets are highly promising for PEC water splitting. The pristine [87], doped (of N, Fe. Mn, and Co, etc.) [88-89], and decorated (of Au) [90] TiO₂ are one of the most explored photoactive materials for PEC water splitting. However, ZnO having a band structure like TiO₂ is competitive enough because of higher electron mobility and higher charge transport rate. Various strategies like nanostructuring, doping [91], modification of morphologies [92], and decoration of metals like Ag, Au, Pt, and Pd, etc. [93-96] are adopted to improve the PEC performance of ZnO. The alteration in the surface and electric properties of ZnO nanostructures after doping or decorating with noble metal particles has improved light absorption and photocurrent density, which resulted in the enhancement of PEC performance [93-96]. The effect of controlled decoration of Au nanoparticles on PEC water splitting performance of ZnO nanowires is elaborated in Chapter 6.

1.4 Motivation

Zinc oxide is one of the most popular materials. It exists in only two forms ZnO and ZnO_2 , [1] with the hexagonal and cubic phases. The hexagonal structure is most stable and hence generally observed. Nevertheless, the cubic structure is stable if grown on the substrate with a cubic crystalline form. It crystallizes in three major structures of rock-salt, zinc-blende, and wurtzite. The existence of largely ionic bonds between Zn^{2+} of atomic radii of 0.074 nm and O^{2-} of 0.140 nm preferentially results in the formation of hexagonal (i.e., wurtzite) phase shown in Figure 1.1. ZnO is typically n-type materials and rarely observed in p-type form. The nonstoichiometry is the common origin of n-type structure, but theoretical studies predicted the unintentional substitution of hydrogen impurities during the synthesis is the source behind n-type characteristics [97]. The direct bandgap of ~ 3.3 eV observed in ZnO can be tuned in the range of 3-4 eV by controlling the surface morphological features and doping concentrations or forming composites [98]. ZnO nanostructures has been synthesized in various forms such as rods [99], wires [100], pencils [101], needles [102], pins [103], bullets [104], ribbons [105], belts [32], tubes [106], combs [105], and helices [32], etc. These 1D nanostructure are found more suitable for applications in biosensors [107], nanogenerators [108], photocatalysis [109], field emission [99], and gas sensing [110], etc.

The growth of the 1D ZnO nanostructures was controlled, either optimizing synthesis conditions or using metal catalysts. The catalyst guided the vertical growth of the ZnO nanostructure with a high aspect ratio, which assisted in improving performance in various applications. Different annealing environments are explored to modify the electronic structure and significantly induce conductivity [59]. Moreover, the doping of various metals such as Al [111], Co [112], Cu [113], and Mg [114], etc., was adopted to improve the functionality of ZnO. However, the hierarchical growth of the sharp tip featured morphologies, and their controlled

decoration with metal nanoparticles are not explored thoroughly. On the other hand, Au nanoparticles are increasingly engrossed in the modification of optoelectronic properties of metal oxides for various in UV detectors [50], photocatalysis [51], sensors [52], and displays, etc. owing to the excellent electron affinity, high electronic/chemical stability and biocompatibility. Therefore, the comprehensive exploration of 1D ZnO nanostructures and tunable nano-heteroarchitectures with metallic 0D Au nanoparticles for utilization as field emission electrode, photoelectrode/photoanode, and the gas sensor is of vital importance in the quest for lower turn-on field, improved field enhancement factor, enhanced photoelectric performance, and gas sensing performance in the detection safety limit of 50 ppm, etc.



Figure 1.1. The schematic representation of the hexagonal wurtzite crystal structure of ZnO [115].

1.5 Aim of the Thesis

The investigations reported in this thesis with the following aims are planned to find answers to the questions pertaining to the methodical literature survey. The aims of this are:

 a) Synthesis of unique 1D ZnO nanostructures morphology in hierarchical form, and investigate the crystalline structure, surface morphology, band alignment, chemical composition, etc. The optimized and controlled synthesis of one 1D ZnO nano-structure employing a simple hydrothermal synthesis technique.

- b) To form controlled hetero-architectures by decorating 0D Au nanoparticles along the surface of 1D ZnO nanowires and investigate their crystalline nature, surface morphology, band alignment, and chemical properties.
- c) Study the effect of sharp-tip features on the field emission performance of pristine ZnO nanostructure in terms of turn-on field and stability
- d) Study the sensing behavior and mechanism of hierarchically connected ZnO nanowires in the detection safety limit at the lower operating temperatures.
- e) Investigate the role of controlled hetero-architecture of 0D Au nanoparticles decorated 1D ZnO nanowires in the field electron emission displays.
- f) Study the effect of Au nanoparticle loading on the photoelectrochemical activities of Au@ZnO nano-hetero-architectures.

1.6 Reference

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Chapter 2 Experimental Techniques

This chapter explains the synthesis protocol of 1D ZnO nanowires and Au@ZnO nano-heteroarchitectures and their various characterization techniques.

2.1 Introduction

The ZnO nanostructures have shown potentials to use pigment, UV absorber, corrosion prevention in a nuclear reactor, food additive, biomedical applications, including field emission, gas sensing, nanogenerators, nanoelectronics, water splitting, etc. [1-4] The large aspect ratio and micrometer length of 1D nanostructures providing better contact at the microscopic level, and hence found more suitable for the application in nanoelectronic among all other morphologies [5]. Therefore, the scientific community has explored various synthesis techniques to obtain a wide variety of 1D nanostructure morphologies.

2.2 Synthesis of ZnO and Au@ZnO nanostructures

Nanomaterials are usually synthesized top-down and bottom-up approaches. In these approaches, the bulk material is lowered down to nano dimensions, and separate entities like atomic/molecular species bring together to obtain nano dimensions, respectively, by utilizing chemical or physical methods. The chemical processes are known for their cost-effectiveness, ease of synthesis, and well-controlled nanostructure growth. Therefore, the hydrothermal and citrate reduction method is employed to synthesize ZnO nanowires and Au nanoparticles. The fundamental aspects of these synthesis methods are briefly discussed below.

2.2.1 Synthesis of ZnO nanowires

The hydrothermal synthesis involves the heterogeneous chemical reaction in the presence of aqueous or non-aqueous solvents above room temperature and at a pressure greater than 1 atm in closed conditions to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions [6]. The hydrothermal synthesis is cost-effective and environmentally friendly to provides a variety of high-quality nanostructure morphology. The hydrothermal setup includes an Autoclave and a Teflon liner. An ideal hydrothermal autoclave (Figure 2.1 (a)) that encompasses Teflon liner (Figure 2.1 (b)) (i) should be inert to acids, bases, and oxidizing agents, and (ii) must withstand high pressure and temperature for a long duration of time without the leakage.

The ZnO nanowires were synthesized on the conducting glass substrates through this approach. The analytical grade reagents, Zinc Acetate dehydrates (C₄H₆O₄Zn.2H₂O, 98 %, Sigma Aldrich), and Sodium peroxide (Na₂O₂, 97 %, Sigma Aldrich), and absolute ethanol (Thomas Baker Pvt. Ltd) along with Deionized (DI) water were used throughout the experimentation. Initially, all the glasswares utilized in the reaction were cleaned using acetone and DI water. The appropriate amount of Zinc Acetate dehydrates (C₄H₆O₄Zn.2H₂O, 98 %, Sigma Aldrich) and Sodium peroxide (Na₂O₂, 97 %, Sigma Aldrich) were stirred separately at room temperature to dissolved in water. Later, these solutions were mixed in 1:1 promotion at its 30 mM/L and 100 mM/L concentration at room temperature for 30 min under constant stirring to ensure a homogenous mixture. This solution was then transferred to an autoclave containing well-aligned ITO coated glass substrates. The hydrothermal reactions were carried out at various temperatures and times to observe desirable hierarchical ZnO nanowire growth. The hierarchical growth of ZnO nanowires over the ITO coated glass substrate was obtained at an optimized temperature of 85 °C for an optimized reaction time of 12 hr. The synthesis details are briefly discussed in Chapter 2. Thus, obtained ZnO nanowires were further subjected to the decoration of Au nanoparticles synthesized by the citrate reduction method.



Figure 2.1. Photograph of (a) stainless still autoclave and (b) Teflon liner.

2.2.2 Synthesis of Au nanoparticles.

Various methods are explored for the synthesis of Au nanoparticles [7]. However, the Au nanoparticle of uniform dimensions in the range of 10-150 nm can be gained from the synthetic route known as the citrate reduction method. This method is well explored for various applications and investigated the nanoparticles formation mechanism when the tetrachloroauric acid solution precursor reacts with the reducing agent (a trisodium citrate solution). However, this method is cursed with the irreproducible production of polydisperse nanoparticles. Therefore, we have a well-optimized reaction parameter to reduce the polydispersity.

In this citrate reduction method, the metal salt is reduced in the proper agent at optimized conditions [8]. The analytical grade reagents, Chloroauric acid (HAuCl₄), and Trisodium citrate (Na₃C₆H₅O₇), and Deionized (DI) water were used for the synthesis of Au nanoparticle. The 0.1 gm of Trisodium citrate (Na₃C₆H₅O₇) solution prepared in 15 ml deionized water was continuously added to Chloroauric acid (HAuCl₄; 12 mM/L) dissolved in 25 mL deionized water for 30 min under a controlled temperature of 98 °C. As the reaction progresses, a change in the color of HAuCl₄ from light yellow to violet and finally turning to wine-red was observed, indicating the formation of Au nanoparticles. Au atoms are formed by nucleation and condensation and grow bigger in size by reducing more Au⁺ ions on the surfaces (Figure 2.2). The reaction was continued for 15 min to obtain an Au nanoparticle of uniform dimensions.



Figure 2.2. Schematic representation of the formation of Au nanoparticles.

2.2.3 Synthesis of Au@ZnO nano-hetero-architecture.

Various studies reported that the decoration of conducting metal nanoparticles over the metal oxide nanostructure to form nano-heteroarchitectures shows a significant enhancement in their properties and, specifically, electronic properties, such as field emission. [9,10] Therefore, in the present study, the reaction time was controlled to decorate the Au nanoparticles over the ZnO nanorods. The independently synthesized ZnO nanowires and Au nanoparticles were subjected to the formation of Au@ZnO nano-hetero-architectures. As-synthesized ZnO nanowires arrays were transferred to the mobilized solution of Au nanoparticles. The Hexadecanethiol (HDT, 20 pmol/L) was added to the solution to conform the functionalization of Au nanoparticles along the ZnO nanowires. As-synthesized ZnO nanowires arrays were immersed in the mobilized solution of Au nanoparticles. The Au concentration, reaction temperature, and stirring conditions were well maintained to ensure the reliable decoration of Au nanoparticles at various reaction times. The Au nanoparticles were allowed to react with ZnO nanowires at room temperature for 4, 8, 12, 24, and 48 hr to ensure the distinctive decoration of Au nanoparticles. The loading of Au nanoparticles has increased with reaction time and reached saturation after 24 hr. The amount of Au nanoparticle decoration is confirmed from XPS and FESEM analysis. More details are discussed in Chapter 5.

2.3 Characterization techniques

The structural and morphological features of the well-optimized nanostructures were confirmed from the X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), and Transmission Electron Microscopy (TEM). The elemental analysis and chemical compositions were explored from Energy Dispersive Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). These characterization techniques are well-known, therefore, not discussed in this thesis. However, related experimental details are discussed briefly in the experimental section of each chapter. Further, the field emission, gas sensing, and water splitting performance of ZnO nanowires and Au@ZnO nano-hetero-architectures were explored using laboratory built experimental setups. The experimental design and rationale behind the optimization of various parameters are discussed here. The details on the optimized experimental conditions for field emission, gas sensing, and water splitting performance are briefed in the respective chapters.

2.3.1 Field Emission Measurements

A good electron source is much required and always hunted for simple domestic gadgets (i.e., television) to highly sophisticated instruments (i.e., FESEM, SEM, and TEM). The electron emission, obtained from the cathode by means of an energy supply of external agencies in a suitable form, is categorized as thermionic emission, photoelectric emission, secondary electron emission, and field electron emission. The field electron emission has attracted the scientific and industrial community due to the emission of the electron by quantum tunneling through the potential barrier at the surface of the material under the influence of a high electrostatic field. R.W. Wood [11] first reported the field emission while was attempting to produce intense x-rays in 1897. Further, it was described theoretically in 1928 by Ralph H. Fowler and Lothar W. Nordheim [12], assuming the temperature of 0 °K, the free-electron approximation, smooth and planar surface for the metals. This theory is called Fowler-Nordheim theory by their name, which still serves as the basis for modern field emission analysis.

The field emission performance of ZnO nanowires and Au@ZnO nanohetero-architectures was deliberated from a lab-based field emission microscope system. The photograph and schematic of the general configuration for the field emission setup are shown in Figure 2.3. The material under investigation acts as the cathode, and the subsequent anode is a semitransparent ITO coated circular conducting phosphor screen of 65 mm diameter. The spacing between cathode and anode (\equiv d) typically has hundreds of micrometers range. The applied potential typically in the kV range is optimized to acquire a high electric field, and thus, to observe the field electron emission from the sample. The electrons tunnel through the potential barrier and get attracted towards the anode under the influence of a high electric field. The emission phenomenon is evaluated from the emission current density as a function of the applied voltage. The ultra-high vacuum (UHV) is essential to reduce the possibility of breakdown across the micron size interelectrode spacing. A thin film consisting of 1D or 0D nanostructures act as multi emitters (number of emitters grown on the flat substrate). Therefore, the parallel plate diode configuration is considered for the field electron emission studies. This is also termed as close proximity due to the interelectrode separation of 250 μ m to a few mm.



Figure 2.3. (a) The photograph (b) schematic of the parallel plate configuration of the field electron emission measurement system [13].

In the present study, the measurement system was maintained at a base pressure of ~ 7.5×10^{-9} Torr. During the field emission measurements, the leakage current was ditched using shielded cables and ensuring proper grounding. Samples were preconditioned at a voltage of ~ 3 kV for 30 min. to avoid the influence of contamination and loosely bound nanostructures in the field emission. The three different cathode-anode separations of 1500, 2000, and 2500 µm were considered to gain the best optimized stable field emission from ZnO nanowires. The optimized distance of 2000 µm for ZnO nanowires was established further for field emission studies on Au@ZnO nano-heteroarchitectures. The effect of these separations on the field emission behavior is detailed in Chapters 3 and 5. The emission current was measured on Keithley Electrometer (6514) at direct current (dc) voltage (V) applied to the cathode with a step of 40 V using high voltage dc power supply (0-40 kV, Spellman, U. S.). The instantaneous emission current fluctuation supervene even at constantly applied bias due to various processes occur at the emitter surface. Therefore, error in the emission current is crucial, and it is recorded over several sets of the field emission measurements. The averaged emission measurements were accounted for the J-E and F-N plots and long-term stability study.

2.3.2 Gas Sensing Measurements

Gas sensing is a process of detecting various flammable, combustible, and toxic gases as part of a safety system. The gas sensing device used to detect leaks or emissions of gases can be interfaced with a control system to signify the gases through a series of audible or visible indicators (i.e., alarms, lights, etc.) and shut down the process automatically. The gas detector units were fabricated initially to detect single gas, but the modern multifunctional sensing devices can detect several gases at a time. The various basic terms, such as sensor response, selectivity, optimal operating temperature, response and recovery time, long-term stability, detection limit, etc., are briefly discussed in Chapter 4. Herein, details of the experimental setup employed for gas sensing measurements are presented. Sensing performance is investigated on the asprepared of ZnO nanowires samples with Pt interdigitated electrodes and a Pt heater located on the backside. Figure 2.4 shows the schematic representation of the laboratory built sensing setup utilized in the present study [14].

This measurement was done by Keithley 2401 source meter. The current was varied according to the resistance of the sample from $0.1 - 1\mu$ A. The Keithley instrument was interfaced to a PC using LABVIEW[®] software and GPIB USB interface from National instruments. All the test gases were procured from Ultra-Pure Gases Pvt. Ltd., Gujarat, India (99.9 % purity). The gas flow was controlled using digital mass flow controllers with flow rate 0-200 mL/min (Dakota Instruments, USA), out of which one is dedicated to zero air, and the other one was calibrated for the use of various test gases like CO,

NH₃, C₂H₅OH, etc. Synthetic air (zero air) was used to take care of the humidity effect on the gas sensing measurements. The sensing behavior was studied at different operation temperatures ranging from 30 (R.T.) to 150 °C for various gas concentrations (i.e., 10, 20, 50, 100 ppm) controlled by DigiFlow® software interfaced through PC. The sensing performance of ZnO nanowires is estimated by measuring the change in the resistance in the air and gas environment. The response and recovery time are estimated at 90 % of the maximum and minimum resistance value observed for ZnO nanowires, respectively, during gas sensing studies. Other details on the gas sensing measurements are detailed in Chapter 4.



Figure 2.4. Schematic of the gas sensing setup used for the detection of ethanol (C₂H₅OH), ammonia (NH₃), and carbon monoxide (CO) gas.

2.3.3 Photoelectrochemical (PEC) Measurements

The photoelectrochemical experiments were performed in a threeelectrode home-made cell wired to a typical potentiostat/galvanostat (Parstat 3000A, Princeton Applied Research), operated by Versa Studio software shown in Figure 2.5 [15]. The as-synthesized sample was mounted onto a Teflon chamber cell having a size of $16 \times 9 \times 10$ cm³ (L×W×H). The photoelectrochemical behaviors were tested under ambient conditions using a

three-electrode cell containing 0.5 M Na₂SO₄ electrolyte (pH of 6.8). The semiconductor material (ZnO nanowires, photoanode), a Pt wire, and an Ag/AgCl electrode (sodium-chloride-saturated silver chloride electrode) were used as the working, counter, and reference electrodes, respectively. The photo-anode was mounted onto the Teflon chamber, where the sample surface was directly in contact with the electrolyte through a hole with a diameter of approximately 0.5 cm. A conductive Cu wire was bonded to the photoanode surface using indium contact and wired to the counter electrode for hole transport. The sample was irradiated through a transparent quartz window using simulated sunlight provided by a 300 W Xe lamp set with 1.5 AM (Newport 66902). The light irradiance was kept constant at 500 mW/cm^2 during the measurement and illuminated surface area 0.30 cm². The chronoamperometry and linear scan voltammetry (LSV) (10 mV/s) experiments were performed using a single-channel potentiostat. The photoanode performance was assessed based on the photocurrent density-voltage (J-V) curves evaluated both in the dark and under illumination. Other related details are discussed in Chapter 6.



Figure 2.5. The photograph of the laboratory-made photoelectrochemical cell for water splitting studies [15].

2.4 References

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Chapter 3 Field emission of ZnOnanostructures

This chapter presents the synthesis of 1D ZnO nanowires using a simple hydrothermal method. The structural, chemical, and electronic properties of ZnO nanowires are examined using FESEM, XPS, UPS, etc. The effect of morphology on the field emission performance of ZnO nanowires is discussed in this chapter.

3.1 Abstract

We observed enhanced field emission (FE) behavior for spitzer shaped ZnO nanowires synthesized via hydrothermal approaches. The spitzer shaped and pointed tipped 1D ZnO nanowires of average diameter 120 nm and length ~ 5-6 µm were randomly grown over the ITO coated glass substrate. The turn-on field (E_{on}) of 1.56 V/µm required to draw the current density of 10 µA/cm² from spitzer shaped ZnO nanowires is significantly lower than that of pristine and doped ZnO nanostructures and MoS₂@TiO₂ heterostructure based FE devices. The orthodoxy test was performed to confirms the feasibility of the field enhancement factor (β_{FE}) of 3924 for ZnO/ITO emitters. The enhancement in FE behavior can be attributed to the spitzer shaped nanotips, sharply pointed nanotips, and individual dispersion of ZnO nanowires. The ZnO/ITO emitters exhibited considerably stable electron emissions, with average current fluctuations of ± 5 %. Our investigations suggest that the spitzer shaped ZnO nanowires holds the potentials for further improvement in electron emission and other functionalities after forming their tunable nano-hetero-architectures with metal or conducting materials.

3.2 Introduction

Among the various 1D nanostructure morphologies, nanowires and nanorods offering the advantages of the large surface area are found to improve the field electron emission. Carbon nanotubes are of great interest to field emission (FE) because of their high aspect ratio, better electrical and thermal conductivity, and robust mechanical and chemical stability. However, the difficulties in the density controlled vertical growth of nanotubes at lower cost have significantly impeded the practical execution of carbon nanotubes in field emission devices. Wide bandgap transitions metal oxides such as NbO₂, TiO₂, CuO, and SnO are known for their stability are found suitable for field emission in their 1D forms such as wire, rods, tubes, needles, etc.[1-4] Even though ZnO is fascinating for the diverse applications in solar cell, catalysis, sensing, photocatalysis, smart windows, photoluminescence, supercapacitor, and generators, etc., and also found more suitable for ultraviolet light emitters or laser diodes [4,5], is moderately considered for FE displays because of the larger work function in the range

of 5.3 to 5.6 eV, limited morphological forms, and field screening effect from uncontrolled dispersion [6-9]. Therefore, emerging practices to tailor the work function and improve the electron emission are modifications of emitter geometry, induction of impurities decoration of metals, and vertical alignment of the structures [2,10]. Implantation of elements in ZnO nanowires was found to produce nanoscale protuberances and surface-related defects, which turns out to reduce turn-on field (E_{on}) from 3.1 to 2.4 V/µm (at 0.1 µA/cm²) [11]. However, the Cu doping in ZnO through direct current magnetron sputtering in the Ar and O₂ environment deteriorated the crystalline quality by reducing Zn interstitials and formed electron traps, which weaken the field emission and hence leads to the E_{on} of 9 to 22.5 V/µm [12]. Even though, doping of elements like Ga [13], Al [14], Mg [15], C [16], and In [17], etc., lead to the favorable alternation in electronic properties of ZnO. Which might have assisted in the lower possible E_{on} of 2.4, 2.8, 5.99, 18, and 193 V/µm, respectively, for field emission, but one cannot neglect that these values are defined at a lower current density ranging from 0.1 to 1 µA/cm².

The modification of critical surface bonding length at the nano regime can tailor the ZnO nanostructure morphologies of the pyramid-, pencil-, rod-, and wire-, etc., forms [18]. However, metals as catalysts were employed in the growth process for control over random alignment and density of structures, which unfavorably tailored field emission properties. The density controlled growth of ZnO nanopillars using self-assembled Ag nano-islands/layers provided the E_{on} of 2.39 V/µm [19]. Catalysts guided the vertical alignment of ZnO nanowires on an insulating substrate such as sapphire, which limited their applications in photonic/electronic devices like field emitters [20]. On the other hand, it has been demonstrated that needle morphological forms can emit electrons more efficiently [21]. Many growth methods have been utilized to explore various 1D morphologies [4], but very few known to provide tip features are cursed with post-treatments such as annealing or in-situ heating. The air annealed tip-morphology of ZnO nanorods exhibited the E_{on} of 3.5 $V/\mu m$ owing to the large rod-body diameter and shortened tips [21]. C-axis oriented ZnO nanocones in-situ heated at 580 °C in the O₂ atmosphere to grow on Si substrate conceived E_{on} of 2.57 V/µm defined at a very low current density of 0.1 µA/cm² [22].

Zhao et al. [23] thermally annealed ZnO nanorods in oxygen, air, and NH₃ to improve the E_{on} (at 0.1 μ A/cm²) from 8.8 V/ μ m to 4.1 V/ μ m. Ghosh et al. [24] observed enhancement in the FE performance after capping the tips of randomly oriented and highly oxygen defective ZnO nanostructures with metal nanoparticles despite their larger work function (i.e., 5.04-4.7 eV). Therefore, for promising field emission performance, efforts on size reduction, uniform morphology, sharp tip features, and periodic growth of pristine ZnO nanowires appear to be of scientific and technological importance.

In this work, we present the synthesis of large-area arrays of randomly oriented spitzer shaped truncated/pointed ZnO nanowires grown periodically like Christmas tree using hydrothermal methods as excellent field emitters. The influence of spitzer shaped tip morphologies of 1D ZnO nanowires on field electron emission properties was studied methodically. The surface morphological features, chemical and electronic structure of pristine ZnO nanowires were revealed using field-emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). The FE behaviors of pristine 1D ZnO nanowires were studied at optimized anode-cathode separation and observed that at the separation of 2000 µm, the 1D spitzer shaped hexagonal ZnO nanowires exhibited excellent FE properties.

3.3 Experimental section

The large area arrays of ZnO nanowires were synthesized on ITO coated glass substrates utilizing the hydrothermal approach. The Zinc Acetate dehydrates (C₄H₆O₄Zn.2H₂O, 98 %, Sigma Aldrich) and Sodium peroxide (Na₂O₂, 97 %, Sigma Aldrich) were mixed in 1:1 promotion at its 30 mM/L and 100 mM/L concentration, respectively. This solution was stirred at room temperature for 30 min. and then transferred to an autoclave containing well-aligned ITO coated glass substrates. The hydrothermal reaction was carried out at 85 °C for 12 hr to grow 1D ZnO nanowires over the ITO coated glass substrate. After that, the surface morphology of pristine ZnO nanowires was confirmed using a field emission scanning electron microscopy (FESEM, Carl Zeiss, Merlin 6073). The chemical states of ZnO nanowires were analyzed utilizing an X-ray photoelectron spectrometer (XPS, Thermo Scientific Inc.

 K_{α}) with a microfocus monochromated Al K_{α} X-ray. The valence band spectra (VBS) was measured using the Omicron energy analyzer (EA-125, Germany) at angle incidence photoemission spectroscopy (AIPES) beamline on Indus-1 synchrotron source at RRCAT, Indore, India. The FE studies of pristine ZnO nanowires were carried out in a vacuum chamber maintained at a base pressure of ~ 7.5×10^{-9} Torr. The anode, semi-transparent phosphor screen was maintained at various distances of 1500, 2000, and 2500 µm from pristine ZnO nanowires (\equiv ZnO/ITO emitter). Samples were preconditioned at a voltage of ~ 3 kV for 30 min to avoid the influence of contamination and loosely bound nanowires in field emission. Field emission current (I) was measured with an electrometer (Keithley 6514) at direct current (dc) voltage (V) applied using a high-voltage dc power supply (0-40 kV, Spellman). The long-term stability of the field emission current was recorded for ZnO/ITO emitters.

3.4 Field Emission Scanning Electron Microscopy

The FESEM images in Figure 1 show the surface morphology of a large area array of ZnO nanowires grown over ITO coated conducting glass substrates. The hexagonal ZnO nanowires are confined to the limited range of diameter (< 180 nm). The well-separated nanowires with clearly visible textural boundaries were of average body diameter of ~ 120 nm and ~ 5-6 μ m long (Figure 3.1(a). These distinct ZnO nanowires were well arranged in the hierarchical form, which appeared like the forest of well separated and periodically arranged trees (Figure 3.1(a)), to deliver the highly porous thin films of thickness ~ 1300 nm (Figure 3.1(b)). The close examination of the ZnO nanowires array revealed the curtailing of the hexagonal facets at its tip, which resulted in the formation of spitzer shaped truncated/pointed tips (Figure 3.1(c)). Utmost spitzer shaped ZnO nanowires with truncated tips were of a diameter of less than ~ 30 nm (Figure 3.1(c)). The spitzer shaped truncated tip construction of ZnO nanowires are expected to govern the enhanced FE behaviors. The electronic structure and chemical properties of spitzer shaped ZnO nanowires were confirmed from XPS investigations.



Figure 3.1 FESEM images are showing (a) top view, and (b) side view of a large area array of ZnO nanowires with (c) spitzer shaped morphologies grown on ITO coated glass substrate.

3.5 X-ray Photoelectron Spectroscopy

Figure 3.2 shows the high-resolution XPS spectra of the Zn(2p) core level of ZnO nanowires. The perceptible double peaks feature of Zn(2p_{3/2}) and Zn(2p_{1/2}) located at a binding energy of 1020.88 (\pm 0.1) and 1043.98 (\pm 0.05) eV, respectively, represents the core level of Zn²⁺ cations [5,25]. The estimated energy separation of

23.1 eV assigned to ZnO and not metallic Zn [26] was maintained between Zn(2p) core levels of spitzer shaped nanowires.



Figure 3.2 High-resolution XPS spectra of the Zn(2p)) core levels of spitzer shaped ZnO nanowires.

3.6 Field emission measurements

The FE measurements of the spitzer shaped 1D ZnO nanowires (\equiv 1D ZnO/ITO) were performed in the planer diode configuration. The emitting device with an emission area of ~ 0.30 cm² was maintained with the anode-cathode separation of 1500, 2000, and 2500 µm. The applied electric field (E) dependent variation in the electron emission current density (J) (i.e., J-E plot) of ZnO/ITO emitters is shown in Figure 3.3(a). Although spitzer shaped ZnO nanowires are periodically arranged in the form of trees, their random orientation leads to treating the applied electric field (E = V/d_{sep}) as the average field and not a uniform field between the electrodes separated by the distance d_{sep} . The spitzer shaped ZnO nanowires (\equiv ZnO/ITO) were subjected to electron field emission at the separation of 1500, 2000, and 2500 μ m to confirm the optimized field emission behavior. The large emission current density of $572 \,\mu \text{A/cm}^2$, lower threshold field (E_{thr}) of 1.9 V/µm, and lower E_{on} of 1.56 V/µm were observed at 2000 μ m. Although the lowest E_{on} (1.16 V/ μ m) was observed at the separation of 2500 μ m, the emission current density was decreased significantly to 198 μ A/cm². The E_{on} observed for these spitzer shaped truncated tips ZnO nanowires array is much lower than that reported for ZnO nanorods grown on Si substrate using PLD (i.e., 2 V/µm)

[6], ZnO nanopillers grew by vapor transport deposition (i.e., 3.15 V/ μ m) [27], ZnO nanorods and nanodisk network (i.e., 4.8 and 2.6 V/ μ m, respectively, reported at 1 μ A/cm²) [7], ZnO nanoneedles (i.e., 2.4 V/ μ m) and bottle like nanorods (i.e., 4.6 $V/\mu m$) fabricated using vapor phase growth [8], ZnO agave like (i.e., 2.4 V/ μm) and pencil-like (i.e., $3.7 \text{ V/}\mu\text{m}$) nanostructures grown on amorphous carbon [9], nitrogen implanted ZnO nanowires (i.e., 2.4 V/ μ m at the current density of 0.1 μ A/cm²) [11], metal (Ag/Pt/Au) loaded ZnO nanorods (i.e., 1.9 and 2.6 V/ μ m, respectively) [28], CuO nanoplates (i.e., 6.7 V/ μ m) [3], ZnO nanotetrapods scree-printed on carbon nanofiber buffered Ag (i.e., 6.7 V/ μ m defined at 0.1 μ A/cm²) [29], and brookite TiO₂ [2,30]. C-axis oriented ZnO nanocones were expected to deliver better field emission because of the tapered cone-like morphology. Nevertheless, the E_{on} obtained at a very low current density of 0.1 μ A/cm² was restricted to 2.57 V/ μ m might be due to the very low areal density of ZnO nanocones [22]. Dense morphology reported as hexagonal flowerlike ZnO nanowhiskers delivered E_{on} of 2.2 V/µm (at a current density of 0.1 μ A/cm²) might be due to the diameter of whiskers limited to 300 nm [31]. The n-type Nitrogen [32] or H-plasma [33] treated ZnO nanowires did not improve the E_{on} beyond 2.1 V/µm. Furthermore, Sugavaneshwar et al. [34] have reported enhancement in the field emission of branched ZnO nanostructures than simpler nanostructures such as nanowire, nanorods, etc., but the actual values of E_{on} were not stated. Although, Chang et al. [27] have reported enhancement in the FE properties of ZnO nanopillars after decorating Au nanoparticle along the surface, the minimum E_{on} of ZnO nanopillars limited to the 3.15 V/µm was further reduced to 2.65 $V/\mu m$ (after Au decoration) owing to the larger diameter and flat top of the ZnO nanopillars (i.e., ~ 200 nm). Additionally, the selective patterning of ZnO nanorods achieved E_{on} of 2.85 V/µm [35]. The possible reasons behind such higher turn-on values are the flat tips, nonuniform morphologies, uneven distribution, and the larger diameter of the 1D ZnO structures. Moreover, emission current density of 572 μ A/cm² attained at lower applied field of 2.34 V/µm for ZnO nanowires (\equiv ZnO/ITO) is reasonably higher than that reported for pristine and Al-doped ZnO nanostructures (i.e., ~ $4 \mu A/cm^2$, ~ $3 \mu A/cm^2$, respectively) [14], C (i.e., 16 $\mu A/cm^2$) [16], and In (i.e. 1.5 µA/cm²) [17]. On the contrary, pristine ZnO and Mg-doped ZnO nanostructures

have drawn slightly better emission current (i.e., 0.8 to 3.2 mA/cm²) at the pretty higher applied field of 9.2 V/ μ m [15].

The reduction in the work function enhances the FE properties. Therefore, Ultraviolet Photoelectron Spectroscopy (UPS) was utilized to estimate the work function of ZnO/ITO emitters. The UPS spectra recorded for the ZnO nanowires array at an energy of 23 eV is shown in figure 3.3(b). Two distinct peaks in the VBS of ZnO nanowires, located at higher and lower binding energy, are assigned to the hybridization of the O(2p) and Zn(4s) orbitals and nonbonding O(2p) orbitals, respectively [36]. Moreover, the work functions of ZnO emitters is estimated from the equation [37]

Where, h ω is the energy of the source utilized (= 23 eV), E_{sec} is the onset of the secondary emission, and E_{FE} is the Fermi edge. The spitzer shaped truncated tip appearance of ZnO nanowires resulted in reduced work-function of 4.9 eV (i.e., Φ_{ZnO}) than that of ZnO nanostructures such as nanorods and nanowires [10,14], oxygen plasma-treated ZnO (i.e., 5.5 eV) [33], Ag decorated ZnO nanorods (i.e., 4.7 eV) [10], and Au faceted oxygen-deficient ZnO nanostructures [24]. In the present case, the reduction in the work-functions believes to have come from the spitzer shaped truncated tip enhanced FE behavior of ZnO nanowires.

A modified Fowler–Nordheim (F–N) equation (i.e., Eq. 3.2) is used to substantiate the variation in the emission current density of ZnO/ITO emitters subject to the applied field,

$$J = \alpha \, a \Phi^{-1} E^2 \beta^2 \exp\left(-\frac{b\Phi}{FE} - \frac{3/2}{\beta_{FE} E^F} \nu\right) --(3.2)$$

Where, *J* is the average FE current density of the device, α_f is a macroscopic preexponential correction factor, *a* and *b* are constants ($a = 1.54 \times 10^{-6} \text{ AeV/V}^2$, $b = 6.83089 \times 10^3 \text{ eV}^{-3/2} \text{ V/}\mu\text{m}$), Φ is the work function of the emitter (i.e., $\Phi_{ZnO} = 4.9 \text{ eV}$), *E* is the average applied electric field, β_{FE} is the local electric field enhancement factor, and v_F is the correction factor also known as a specific value of the principal Schottky-Nordheim barrier function *v*. Due to the random alignment of ZnO nanowires confirmed from FESEM images (Figure 3.1), the emission surface of ZnO/ITO emitters is treated to be rough.



Figure 3.3 Field emission (a) J–E curves and (c) F-N plots obtained from J–E curves, and (b) UPS valence bands spectra, measured for spitzer shaped ZnO nanowires. The inset in figure (b) shows magnified valence bands spectra at a higher binding energy

Therefore, applied and local electric fields at emission sites (i.e., ZnO) differ from each other, and their ratio is identified as the β_{FE} . A plot of $\ln\{J/E^2\}$ versus (1/E), accepted as F-N plot, is illustrated using equation (3.3), and the field enhancement factor (β_{FE}) is estimated from equation

$$\beta_{FE} = \frac{-sb\phi^{3/2}}{s} ---(3.3)$$

Where, s (= 0.95), the slope correction factor for the Schottky-Nordheim barrier is 1 in the present case, for simplicity.

The F-N plots for pristine ZnO/ITO emitters determined at various anodecathode separations are shown in Figure 3.3(c). The distinct F-N plots as ascribed to the well-defined band alignment of nanowires morphology of ZnO. The optimized anode-cathode separations in pristine ZnO/ITO emitters have tailored the values of β_{FE} . The β_{FE} values estimated for ZnO/ITO emitters at the anode-cathode separation of 1500, 2000, and 2500 µm are 3089, 3924, and 4760, respectively. These estimated values of β_{FE} for ZnO/ITO emitters are more significant than the reported values of ZnO nanostructure array with nanoneedle, nanocavity, and bottle-shaped morphologies [8], hierarchical and pencil-like ZnO nanostructures self-assembled on amorphous carbon [9], ZnO branched nanostructures [34], density controlled ZnO nanopillar arrays [19], tapered ZnO nanorods growth on Fe and Cu electrode [38], metal-doped ZnO nanowires [14,15,17] composites of Carbon-ZnO [39], and MoS₂@ZnO nano-heterojunctions [40]. Bae et al. [22] revealed a field enhancement factor of 2216 for ZnO nanocones, which was not improved after tailoring the density of nanocones in the emission area. Sugavaneshwar et al. [34] tailored vapor phase transport to synthesize ZnO nanostructures in the form of wires and branches, but their larger diameter restricted the β_{FE} values in the range of 1129 to 3985. Although, Naik et al. [41] and Xiao et al. [42] have reported larger values of β_{FE} for ZnO nanosheets and nanotowers, respectively, the orthodoxy test knows to authenticate such values was not performed in support of it. The practicality of the FE measurements and β_{FE} of ZnO/ITO emitters was confirmed by performing the orthodoxy test utilizing the spreadsheet provided by Forbes in the reference [43]. The scaled-barrier-field (f)values estimated for all cathode-anode separations in ZnO/ITO emitters are given in Table. 3.1

Materials	Separation (µm)	flow	fhigh	Orthodoxy test result
	1500	0.29	0.47	Pass
ZnO nanowires	2000	0.24	0.44	Pass
	2500	0.26	0.50	Pass

Table 3.1. Scaled-Barrier-Field (*f*) values estimated from F-N plots for ZnO nanowires

 (i.e., ZnO/ITO) emitters using the spreadsheet from Reference [43]

The emission situation is orthodox throughout all cathode-anode separations of ZnO/ITO emitters for the lower (f_{low}) as well as higher (f_{high}) Scaled-Barrier-Field (f) values. The hexagonal ZnO nanowires with clearly visible textural boundaries revealed reasonable emission behavior for all maintained anode-cathode separations. The unique morphological features of ZnO nanowires, such as hexagonal morphology, individual dispersion, spitzer shaped truncated tips, and very sharp pointed tips, have resulted in low E_{on} and large β_{FE} values for ZnO/ITO emitters.

This emission behavior can be more detailed from the band alignment of ZnO (Figure 3.4(a)). In the present case, owing to the unique morphological features, the work function of ZnO nanowires (i.e., 4.9 eV) has been reduced than that of reported values (i.e., 5.5 to 5.2 eV) [6-9]. The reduced Φ_{ZnO} provides a significantly smaller barrier for the emission of an electron. Therefore, the FE behavior enhancement is expected along with lower E_{on} and higher values of β_{FE} . In the ZnO/ITO emitters, the electrons from the conduction band or its nearest states contribute to field emission. Moreover, at an applied electric field, energy band bending generates energy well at a depleted region, where a large number of electrons accumulate and abruptly emits in larger quantity due to relatively lower Φ_{ZnO} (Figure 3.4(a)).

Stable Field electron emission (i.e., current) is one of the prerequisites for utilizing the materials to fabricate FE displays and related applications. Figure 3.4(b) shows the FE stability of ZnO/ITO emitters. The emission current (I) at an applied voltage of 10 μ A, assigned as E_{on} , was considered to confirm the stability of ZnO/ITO emitters. A negligible amount of current fluctuation (i.e., an average of \pm 5 %) was observed even after continuous emission for 180 min. These spitzer shaped 1D ZnO nanowires exhibited considerable stable and improved electron emission than that of

gold nanoparticle decorated ZnO nanopillars [27], monolayer graphene supported by well-aligned ZnO nanowire arrays grown on Si substrate [44], seed layer assisted ZnO nanorods [45], ZnO nanowires derived after annealing gold deposited Zn substrate at 400 °C [46], and ZnO multipods, submicron wires and spherical structures obtained by vapor deposition [47]. The exclusive participation of sharp tips of ZnO nanowires as emitters conceivably enhanced the emission ability.



Figure 3.4 (a) Schematic band alignment of pristine spitzer shaped ZnO nanowires and (b) Field emission current stability (I–t) plot of D ZnO nanowires

3.7 Conclusions

In conclusion, the large area array of stoichiometric and individual dispersed 1D hexagonal ZnO nanowires of spitzer shaped truncated, and very sharp pointed tips synthesized on ITO coated glass substrates; resulted in a smaller work-function of 4.9 eV, which consequently delivered significantly smaller E_{on} of 1.56 V/µm, field enhancement factor of 3924, and stable electron emission (i.e., average current fluctuations of ± 5 %). The orthodoxy test confirmed the feasibility of spitzer shaped ZnO nanowires for utilization in the vacuum based micro/nano-devices such as flat-panel displays and intense point electron source. Moreover, the ZnO nanowires hold capabilities to reduce the work-function further and improve the electron emission, as

well to expand other functionalities for various applications after controlled designing of nano-hetero-architecture with metals or high conducting materials.

3.8 References

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Chapter 4

Gas sensing of ZnO nanostructures

This chapter presents the surface morphology, structural, and elemental analysis using FESEM, XRD, RAMAN, EDS, and XPS of the hexagonal ZnO nanowires. The Ammonia, Ethanol, and Carbon monoxide gases were tested to confirm the sensing performance of ZnO nanowires at room temperatures in the detection safety limit. Finally, the experimental observations are correlated with DFT analysis.

4.1 Abstract

The well-constituted hierarchical arrangement of hexagonal ZnO nanowires of diameter < 180 nm and length of ~ 5-6 μ m with clearly visible textural boundaries provided a highly porous film thickness of ~ 1300 nm over a large area. The ZnO nanowires delivered excellent sensing performance for CO, C₂H₅OH, and NH₃, reducing gases in the detection safety limit of 50 ppm at operating temperatures of 100 °C. The maximum response of 115 % and the response and recovery time of 27 and 9 sec, respectively, was recorded for toxic 50 ppm NH₃ gas at the operating temperature of 100 °C, which is better than the previously reported performance of various pristine and doped ZnO nanostructures. The experimental observations are corroborated by first-principles density functional theory (DFT) calculations performed to unravel the reactivity of the gas molecules with hexagonal ZnO nanowires. The expedited sensing response is ascribed to the larger potential barrier offered by the well-interconnected hierarchical growth of hexagonal ZnO nanowires.

4.2 Introduction

In the recent era, smart technologies are asking for the advancement to address safety and security concerns on high priority. The enormously grown industrialization for elegance lifestyle has impaired the human and environmental health owing to the exhaust of hazardous gases and chemical compounds. Moreover, the dangerous condition of global warming is demanding the early monitoring of air quality and detecting toxic and explosive gases to govern the detrimental effect on human life and environmental health. The controlled monitoring of harmful gaseous byproducts is required urgently. The involvement of largely generated poisonous carbon monoxide in climate change and the detrimental influence of explosive ethanol (C_2H_5OH) and highly toxic ammonia (NH_3) on health has asked for immediate detection and monitoring. The nontoxic metal oxides delivering excellent electronic mobility along with thermal and chemical stability are competent candidates to assist in this purpose but suffered for selectivity and sensitivity of various gases. The gas sensing mechanism, which involves the gas-solid interaction at the surfaces, can be improved by providing the largest active surface area at nanoscale dimensions. Recent gas

sensing approaches have shown that the sensing properties of metal oxides can be significantly enhanced by controlling the nanostructure surface morphologies [1-2]. The gas sensing performance of various metal oxides such as SnO₂, In₂O₃, TiO₂, WO₃, α -Fe₂O₃, and ZnO in diverse morphological form has been investigated [1-4]. These metal oxides challenge researchers to improve sensing mechanisms due to their higher working temperature, low sensitivity, poor selectivity, short-term stability, and durability. However, widely explored ZnO, an n-type semiconductor with a large bandgap, greater electronic mobility, and ultimate chemical and thermal stability in nanosize hold good competency for further improvement in sensing ability [4-5]. Even though the crystal structure, surface morphology, chemical composition, and operating temperature governs the sensing performance of ZnO nanostructures, the doping of Ag [6], Al [7], Co [8], Cu [9], Fe [10], Mn [11], Pd [12], Pt [13], and Ta [14], etc., metals in ZnO was adopted to enhance the electronic properties for improvement in gas sensing performance. However, among all explored ZnO nanosize morphologies, one dimensional (1D) nanostructure delivers a large surface to volume ratio, and a continuous electron transfer pathway [4, 15-17] facilitates gas molecule adsorption and prompt electronic transportation in one dimension.

The working temperature monitors the reaction kinetics, conductivity, and electronic movements, which explicitly control the sensing activity of ZnO nanostructures [18-19]. Even though the surface redox reaction activates at prominent temperature and boosts the reaction kinematics for sensing activity, the ZnO nanostructures have shown prominent gas sensing performance at relatively high temperatures in the range of 300 to 500 °C [20]. These high working temperatures, however,-induce secondary grain growth, cause instability, inaccuracy, high power consumption, and lack of durability in the sensing mechanism. Therefore, reducing the operating temperature range of ZnO nanostructures is a critical challenge. Significant efforts in developing lower working temperature based ZnO gas sensors are prerequisites in light of safety concerns for the flammable and toxic gases. ZnO based sensors have detected CO, NH₃, C₂H₅OH, NO₂, C₆H₆, H₂S, etc., gases, but the prompt and high sensing responses were achieved merely at high working temperatures due to thermal excitation driven increase in the surface electrons. Albeit the significant

effect of the number of grains between interelectrode gaps on the response of ZnO nanorods and nanoparticles, the maximum response for 50 ppm NO₂ gas (i.e., 44.2) was observed at the temperature of 300 °C [21]. Moreover, the hierarchical hollow ZnO microspheres delivered a maximum response at a lower temperature of 275 °C for various C₂H₅OH concentrations (8 for 100 ppm) [22]. The randomly aligned ZnO nanowires on patterned ZnO:Ga/SiO₂/Si template delivered maximum sensor response (22.5 %) at 300 °C for 1000 ppm NH₃ gas, improved further to 36 % (@ 1000 ppm) after heavy loading of Pt nanoparticles [23]. Recently, Colak et al. [24] have observed improvement in the CO₂ sensing ability of ZnO nanorods after doping Ge, Nd, and W in a lower proportion. Still, the maximum sensing response was observed at a very high temperature of 450 °C. Moreover, hierarchical ZnO nanostructures delivered best gas response (i.e. Ra/Rg = 177.1) for 100 ppm C₂H₅OH at 450 °C than the room temperature (i.e. Ra/Rg = 24.7) [24]. Nevertheless, to the best of our knowledge, ZnO nanostructures have yet to deliver the best performance at a temperature below 150 °C for sensing CO, C₂H₅OH, and NH₃ gases for possible applications in wearable sensors.

Therefore, here we demonstrate the gas sensing performance of ZnO nanowires at lower operating temperatures. The comparative studies illustrate that ZnO nanowires synthesized by a cost-effective hydrothermal technique delivered the best sensing performance for CO, C₂H₅OH, and NH₃ gases at a relatively lower operating temperature of 100 °C. The sensor response of 29, 98, and 115 % was observed for

CO, C₂H₅OH, and NH₃ gas, respectively, at the operating temperature of $100 \,^{\circ}$ C. Furthermore, the response and recovery time of 27 and 9 sec, was recorded for toxic

 NH_3 gas at the temperature of 100 °C, indicating the faster response of ZnO nanowire to 50 ppm NH_3 gas. Furthermore, experimental observations are validated with electronic structure DFT calculations performed to systematically characterized the reactivities of CO, C₂H₅OH, and NH₃ gas towards the hexagonal ZnO nanowires.

4.3 Experimental section

4.3.1 Synthesis and characterization

The large area array of ZnO nanowires were synthesized using the hydrothermal technique. The reaction of zinc acetate dihydrate ($C_4H_6O_4Zn.2H_2O$)

and sodium peroxide (Na_2O_2) was carried out in the autoclave at an optimized temperature of 85 °C for 12 h to grow the ZnO nanowires over ITO coated glass substrates hydrothermally. The synthesis protocol of ZnO nanowires is akin to that reported in Chapters 2 and 3. The surface morphological features of ZnO nanowires were substantiated from field emission scanning electron microscopy (FESEM, JEOL, JSM 7610 F Plus). The crystal structure was analyzed using an X-ray diffractometer (D8 Advance, Bruker AXS) with Cu k α radiations (λ = 15405 Å), and micro-Raman spectrometer (Renishaw system InVia) with 532 nm incident photons from a diode-pump solid-state laser operated at a minimum power of 17 mW. The gas-sensing performance of ZnO nanowires was measured in a home-built setup [26]. The sensing measurements were performed after exposing the different amounts of reducing gases such as CO, C₂H₅OH, and NH₃ gases. Considering gas adsorption and desorption diffusion are thermally activated processes, the gas sensing performance of ZnO nanowires is related to the sensing temperature to identify optimal working/operational temperature. The sensing behavior was determined for various gas concentrations (i.e., 10, 20, 50, 100 ppm) at different operation temperatures ranging from 30 (R.T.) to 150 °C by measuring the change in the ZnO nanowires resistance in air and gas environment. The gas sensing response (S %) for the reducing gases is estimated from,

$$S(\%) = (R_{air} - R_{gas})/R_{gas} \times 100 \qquad --(4.1)$$

where, S (%) is sensor response, and R_{air} and R_{gas} are the resistance of sensor material in the air and gas environment, respectively. The response and recovery time are estimated at 90 % of the maximum and minimum resistance value observed for ZnO nanowires, respectively, during gas sensing studies [27].

4.3.2 Computational analysis

The electronic structure density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) [28], wherein the interactions between the core and valence electrons were treated using the Project Augmented Wave (PAW) method [29]. The electronic wave functions are expanded on a plane-wave basis set with a cutoff energy of 600 eV. Geometry optimizations were performed using the conjugate-gradient algorithm until the residual Hellmann–Feynman forces on all relaxed atoms reached 10^{-3} eV/Å . The electronic exchange-correlation potential was calculated using the Perdew-Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional [30]. Long-range vdW interactions were accounted for using the method of the Grimme DFT-D3 scheme [31]. The bulk ZnO was modeled in the hexagonal wurtzite phase with a $7 \times 7 \times 5$ Monkhorst-Pack k-point mesh used to sample the Brillouin zone. The screened hybrid functional HSE06 [32] was used with the exchange value of 25 % to predict the bandgap accurately. The (100) surface is generally predicted to be the most stable surface of ZnO [33,34] and expected to be the most expressed and abundant facet in the ZnO nanocrystals. The ZnO (100) surface has been used in previous studies to characterize the interaction of NO₂, NO, O, and N species. Therefore, ZnO (100) surface is preferred in the present study to describe the adsorption reactions of CO, C₂H₅OH, and NH₃ gas molecules. METADISE code [40] was utilized to ensure the creation of nondipolar stoichiometric surfaces from optimized bulk wurtzite ZnO [36]. The gas molecule adsorption calculations were carried out on a ZnO(10D)-(3x3) surface coverage, which is large enough to minimize lateral interactions between the molecules in neighboring image cells. No symmetry constraints were imposed on the structural optimization of the gas–ZnO(1010)-(3×3) systems, and in particular, the molecules are free to move away laterally and vertically from its initial binding site or reorient to find the lowest-energy adsorption configuration. A $3 \times 3 \times 1$ k-point was used for the surface calculations. Bader charge analysis [37] was used to quantify any charge transfers between the ZnO(100) surface and gas molecules.

4.4 Field Emission Scanning Electron Microscopy



Figure 4.1. (a) FESEM image and (b) EDS of large-area arrays of ZnO nanowires grown on ITO coated glass substrates. High-magnification FESEM image in the inset of (a) shows the hierarchical growth of ZnO nanowires.

Figure 4.1(a) illustrates the FESEM image of surface morphology of large-area arrays of ZnO nanowires grown on ITO coated glass substrates. High-magnification FESEM image in the inset of Figure 4.1(a) confirms that all hexagonal ZnO nanowires with clearly visible textural boundaries are confined to the diameter of < 180 nm and length of ~ 5-6 μ m. The well-constituted hierarchical arrangement of ZnO nanowires provided a highly porous ~ 1300 nm thick film over a large area. The surface morphological appearance of the hexagonal ZnO nanowires is detailed elsewhere [15]. The highly porous thin film of single-crystalline ZnO nanowires is expected to provide distinct gas sensing properties. The energy dispersive X-ray (EDX) spectra of ZnO nanowires (Figure 4.1(b)) corroborates the presence of Zn and O elements in the array of hexagonal ZnO nanowires. The presence of In and Sn is confirmed with a small peak. Moreover, the presence of a relatively very tiny peak of C confirms the presence of a negligible amount over the surface of the ZnO nanowires array. X-ray photoelectron spectroscopy (XPS) confirms the formation of stoichiometric ZnO nanowires. The XPS analysis (not provided here) is very much aking to our studies reported earlier in Chapter 3 [15]. The phase purity and crystal structure of as-synthesis ZnO nanowires analyzed from X-ray diffraction (XRD) studies confirmed the growth of hexagonal wurtzite ZnO nanowires without any defect or impurity phase. Therefore, present hexagonal ZnO nanowires with a high degree of crystallinity are expected to enable better sensing response for hazardous and toxic gases like CO, C₂H₅OH, NH₃, etc.

4.5 Raman analysis



Figure 4.2. Raman spectra of hexagonal ZnO nanowires

The Raman scattering was performed at room temperature to investigate the vibrational properties of ZnO nanowires. Figure 4.2 shows five prominent Raman active bands, which are $A_1+E_1+2E_2$ Raman active modes explained by group theory, where A_1 and E_1 are Raman and infrared active polar modes, and E_2 is Raman active nonpolar mode. The Raman bands observed at 328, 373, 431, 530, and 576 cm⁻¹ are assigned to the A_1 , A_1 , E_2 , A_1 , and E_1 modes of wurtzite ZnO, respectively [38-40].

The peak around 373 cm⁻¹ ascribed to the transverse optical A₁ mode resulted from the polarized A₁ and E₁ modes of vibrations. A highly intense Raman band at 431 cm⁻¹ is assigned to the well crystallinity of hexagonal ZnO nanowires array [41]. The Raman band at 576 cm⁻¹ corresponds to the E₁ mode for the presence of oxygen vacancies and interstitial, and complexes of Zn [42]. However, relatively lower intensity indicates that ZnO nanowires exhibit a smaller amount of oxygen vacancies. Moreover, the red shifting of the Raman bands in ZnO nanowires (Table 4.1) than the other reported nanostructure morphologies and bulk wurtzite structure of ZnO indicate the phonon-confinement. This reconfirms that the hexagonal wurtzite ZnO nanowires grown on ITO coated glass substrates are well crystalline with the very minimum amount of oxygen deficiency.

Table 4.1: The comparative parameters obtained from the Raman scattering spectra of hexagonal ZnO nanowires and ZnO nanowires (@Si) [38], micro-tubes [39], quantum dots [41], and bulk wurtzite structure [40] reported in the literature.

Raman mode	A ₁	A ₁	E ₂	A ₁	E_1	Reference
Morphology						
ZnO nanowires	328	373	431	530	576	Present work
ZnO Nanowires/Si	332	-	436.5	-	583	[38]
∆f(nanowires-nanowires/Si)	-4		-5.6		-7	
ZnO micro-tubes	331	377	437	-	-	[39]
$\Delta f(nanowires-micro-tubes)$	-3	-4	-6			
ZnO quantum dots	348	-	440	-	576	[41]
$\Delta f(nanowires-quantum dots)$	-10		-9		0	
Bulk Wurtzite ZnO	333	378	438	536	590	[40]
Δf(nanowires- bulk)	-5	-5	-7	-6	-14	

4.6 X-ray Diffraction

The phase purity and crystal structure of as-synthesis ZnO nanowires were analyzed from X-ray diffraction (XRD) studies. Figure 4.3 shows diffraction peaks located at 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, 69.0°, 72.5°, and **B**are well indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201),

(004), and (202) crystalline plane, respectively, of hexagonal wurtzite phase of ZnO (JCPDS Card No. 76-0704) allotted to the space group of P63mc (lattice constants, a = b = 3.25 Å and c = 5.21 Å). The dominant peaks centered at 31.72° and 36.20° confirm the preferred growth orientations of the randomly aligned ZnO nanowires along the (100) and (101) directions. The greater thickness of ZnO nanowires has resulted in the untraceable diffraction peaks of the ITO thin film. This confirms the growth of hexagonal wurtzite ZnO nanowires without any defect or impurity phase. Therefore, present hexagonal ZnO nanowires with a high degree of crystallinity are expected to enable better sensing response for hazardous and toxic gases like CO, C₂H₅OH, NH₃, etc.



Figure 4.3. XRD spectra of large-area arrays of ZnO nanowires.

4.7 Gas sensing measurements

The temperature-dependent sensing performance of ZnO nanowires arrays was performed for various concentrations of CO, C_2H_5OH , and NH_3 , reducing gases. The optimized gas sensing performance is confirmed in resistive mode. Figure 4.4 shows the temperature-dependent real-time dynamic resistance response transients of ZnO nanowires for 10 to 100 ppm of CO. A sequential exposure of 10, 20, 50, and 100 ppm CO to ZnO nanowires maintained at room temperature (i.e., 30 °C) confirmed cyclic variation in the resistance. A similar trend is observed in the resistance variation when ZnO nanowires were maintained at a temperature of 50, 100, & 150 °C. The resistance of ZnO nanowires has reduced with increasing CO concentration, which further altered

with temperature variation. Figure 4.4 (b) illustrates the influence of temperature and CO concentration on the sensing response of ZnO nanowires, respectively. The sensing response of ZnO nanowires has improved with an increased concentration of CO from 10 to 100 ppm for all studied temperatures. Even though the best response was observed for 100 ppm, the compelling response was estimated for the 20 ppm CO. The best response of 17.4, 23.6, 31.6, and 28.3 % observed for 100 ppm CO, and the relatively compelling response of 11.5, 13.7, 30.3, and 20.2 % were observed for 20 ppm CO, when ZnO nanowires were maintained at a temperature of 30, 50, 100 and 150 °C, respectively. However, temperature influenced sensing response effectively for all the concentrations of CO. The response has improved with the increase in the temperature and reduced for higher temperatures beyond 150 °C after attending maximum response at 100 °C (Figure 4.4(b)). A fitted logarithmic plot between response (S %) and gas concentration (Figure. 4.4(c)) illustrates the gas detection limit of ZnO nanowires. The estimated detection limit for CO shows a progressive decrease of 3.57, 1.07, 1, and 1.02 ppm with increasing operating temperature from 30 °C to 150 °C, respectively [43]. The highest response of 26.2, 30.3, 31.9, and 31.6 % were observed for 10, 20, 50, and 100 ppm CO (Figure 4.4(d)), respectively, at a temperature of 100 °C. The saturation of adsorption and desorption reaction processes might have resulted in a steady response above 50 ppm. The response and recovery time estimated at 100 °C is 25.0 and 17.5 Sec., 15.1 and 12.5 Sec. for 50 and 100 ppm CO, respectively, which is relatively better (Table 4.2). Furthermore, ZnO nanowires showed better sensing response at 100 °C for the 50 ppm CO by delivering a maximum response of 31.9 %. Hexagonal ZnO nanowires exhibit excellent and faster response in the detection safety limit for CO (i.e., ~ 50 ppm) for relatively very significantly lower temperature compared to pristine and metal-doped ZnO nanostructures listed in Table 4.2



Figure 4.4. (a) Time-dependent response-recovery behavior of ZnO nanowires with different concentration of CO gas at various operating temperatures (i.e., 30, 50, 100, and 150 $^{\circ}$ C) (b) Temperature-dependent response behavior of ZnO nanowires for different concentrations of CO gas, (c) CO concentration-dependent response behavior of ZnO nanowires for different operating temperatures. (d) The optimum sensing response of the ZnO nanowires sensor as a function of CO concentrations at the operating temperature of 100 $^{\circ}$ C.

Table 4.2: The comparative summary of the response and recovery time of the ZnO nanostructure for CO gas.

Morphology	Response and recovery time (Sec.)	Gas concentration	Temp. (°C)	Ref.
ZnO nanowires	15.1 and 12.5	50 ppm	100	Present
ZnO tetrapods	~ 55 and >100	50	300	[40]

ZnO nanowires	20 and 60	500	320	[45]
ZnO nanoflowers	25 and 150	200	300	[46]
Au adsorbed ZnO nanowires	40 an 80	50	350	[47]
ZnO honeycomb structure	~180 and ~210	500 ppm	300	[49]

Table 4.3: The comparative summary of the sensing performance of ZnOnanostructure-based CO gas sensors.

Morphology	Response	Temperature (°C)	Reference
ZnO nanowires	31.9 % @50 ppm	100	Present work
ZnO nanorods	2 % @ 50 ppm	350	[8]
flower-like ZnO microstructures	3.8 % @200 ppm	400	[50]
ZnO tetrapods and nanoparticles	< 20 % @ 50 ppm	250	[44]
ZnO nanowires by VLS method	1.5 % @50 ppm	250	[51]
Co-doped ZnO nanorods	16 % @ 50 ppm	350	[8]
Pd-ZnO thin film	7 % @1000 ppm	200	[54]
Pt-ZnO nanosheets	3.57 % @ 50 ppm	180	[13]
Al-ZnO nanoparticles	1.6 @50 ppm	300	[7]

Likewise, Figure 4.5 shows temperature-dependent real-time dynamic resistance response transients of ZnO nanowires for 10 to 100 ppm of C₂H₅OH. A sequential assortment of 10, 20, 50, and 100 ppm C₂H₅OH at room temperature (i.e., 30 °C) confirmed cyclic variation in the resistance akin to that observed for CO gas. Similar behavior is observed at 50, 100, and 150 °C. The resistance of ZnO nanowires has reduced with increased concentration of C₂H₅OH, which is further altered after varying the temperature. Figure 4.5 (b) illustrates the influence of temperature and C₂H₅OH concentration on the sensing response of ZnO nanowires, respectively. The sensing response is influenced remarkably by the temperature for all concentrations of C₂H₅OH studied. The response has improved with an increase in temperature but decreased for higher temperatures (i.e., 150 °C) after attending maximum response at 100 °C for all the C₂H₅OH concentrations.



Figure 4.5. (a) Time-dependent response-recovery behavior of ZnO nanowires with different concentration of C_2H_5OH gas at various operating temperatures (i.e., 30, 50, 100, and 150 °C) (b) Temperature-dependent response behavior of ZnO nanowires for different concentrations of C_2H_5OH gas, (c) C_2H_5OH concentration-dependent response behavior of ZnO nanowires for different operating temperatures. (d) The optimum sensing response of the ZnO nanowires sensor as a function of C_2H_5OH concentrations at the operating temperature of 100 °C.

The best sensing response for all the concentrations of C₂H₅OH is observed at the temperature of 100 °C. The response value of 55.7, 63.2, 101.9, and 82.8 % was observed for 10, 20, 50, and 100 ppm C₂H₅OH, respectively, at the temperature of 100 °C. The sensing response of ZnO nanowires has improved with an increased concentration of C₂H₅OH from 10 to 100 ppm, but reduced further for 150 °C C₂H₅OH independent of temperatures. The highest sensing response of 58.4, 73.7, 101.9, and 86.9 % is observed at the temperature of 30, 50, 100, and 150 °C, respectively, after exposing ZnO nanowires to 50 ppm C_2H_5OH . The reason for the reduction in the response at 150 °C C₂H₅OH is not well understood, but the saturation of adsorption and faster desorption reaction processes might be the origin. The detection limit of ZnO nanowire sensors for C₂H₅OH gas is estimated from the linear fitting of the log-log plot of response and gas concentration shown in Figure. 4.5(c). The detection limit of 4.98, 1.34, 1.01, and 1.02 ppm was observed decreasing for the operating temperature from 30 to 150 °C, respectively. Moreover, the response and recovery time estimated for 50 ppm C₂H₅OH at 100 °C is 40.3 and 19.4 s., respectively, which is relatively more significant than ZnO nanorods (53 and 48 s for 50 ppm at 340 °C) [55]. Overall, ZnO nanowires showed better selectivity at 100 °C for the 50 ppm C_2H_5OH by delivering a maximum response of 101.9 % (Figure 4.5(d)). This sensing response of ZnO nanowires is very high at a relatively lower temperature compared to pristine, doped, and decorated ZnO nanostructures listed in Table 4.4. Moreover, ZnO nanowires delivered better responses than the values reported by Guo et al. [56] for ZnO nanowires (i.e., 3.7 % at 380 °C), which attended a value of 33.6 % (@ 380 °C) after functionalizing with Au nanoparticles. Wang et al. reported that the hydrothermally synthesized ZnO nanorods provided a maximum response of ~ 22 % for 50 ppm at 320 °C but not responded below 200 °C [55]. Even though, Al-doped ZnO nanostructure embedded in multi-microstructures has delivered a sensing response of ~ 40 % at 160 °C, the exceptionally high exposure of 3000 ppm C_2H_5OH is playing a significant role and strongly influencing this gain [57].

Table 4.4: The comparative summary of the sensing performance of ZnO nanostructure-based C_2H_5OH gas sensors.

Morphology	Response	Temp. (°C)	Reference
ZnO nanowires	101.9 % @50 ppm	100	Present work
ZnO nanoplates	23.3 % for 400 ppm	350	[58]
hierarchical ZnO nanoflowers	30.4 % for 400 ppm	350	[58]
sputtered ZnO film	6.2 % for 100 ppm	400	[14]
ZnO nanorods	1.6 % for 50 ppm	350	[8]
flower-like ZnO microstructures	3.5 % @ 50 ppm	400	[50]
vertically aligned ZnO nanorods	1.33 % for 500 ppm	260	[12]
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Ta doped ZnO thin film	9.8 % for 100 ppm	400	[14]
Co-doped ZnO nanorods	1.85 % for 50 ppm	350	[8]
TiO ₂ modified ZnO tetrapods	~ 20 % for 50 ppm	300	[44]
Pd-nanoparticle decorated ZnO	5.12 % for 500 ppm	260	[12]
nanorods			
high density Pd-ZnO nanowires	44.5 % for 500 ppm	170	[59]



Figure 4.6. (a) Time-dependent response-recovery behavior of ZnO nanowires with different concentration of NH₃ gas at various operating temperatures (i.e., 30, 50, 100, and 150 °C) (b) Temperature-dependent response behavior of ZnO nanowires for different concentrations of NH₃ gas, (c) NH₃ concentration-dependent response behavior of ZnO nanowires for different operating temperatures. (d) The optimum sensing response of the ZnO nanowires sensor as a function of NH₃ concentrations at the operating temperature of 100 °C.

Subsequently, ZnO nanowires arrays were subjected to NH₃ gas sensing. Figure 4.6 shows the real-time dynamic resistance response transients of ZnO nanowires for a controlled NH₃ atmosphere (i.e., 10 to 100 ppm) at various temperatures. Sequential exposure of 10, 20, 50, and 100 ppm NH₃ gas atmosphere at room temperature (i.e., 30 °C) confirmed distinct variation in the resistance (Figure 4.6(a)) akin to that observed for C_2H_5OH and CO gases. The resistance of ZnO nanowires has reduced with an increase in the NH₃ gas concentration. A similar trend is observed for 50, 100, and 150 °C, besides the significant decrease in the resistance with a temperature change. Figure 4.6(b) illustrates the effect of temperature and concentration of NH₃ gas on the sensing performance of ZnO nanowires, respectively. The sensing response is influenced by temperature irrespective of variation in the concentrations of NH₃. The response has enhanced with temperature but decreased after attending maximum response at 100 °C for all the concentrations. The best response of 105.5, 109.7, 115.9, and 128.9 % was observed for 10, 20, 50, and 100 ppm NH₃, respectively, at a constant temperature of 100 °C. Moreover, the sensing response has increased with an increase in the NH₃ concentration, irrespective of temperature. The higher sensing response of 71.0, 85.7, 128.9, and 103.5 % is observed after exposing ZnO nanowires to 100 ppm NH₃ at the temperature of 30, 50, 100, and 150 °C, respectively. However, ZnO nanowires have shown excellent response at 100 °C irrespective of the concentration of NH₃. The maximum response of 115.9 and 128.9 % is observed at 100 °C for 50 and 100 ppm NH₃, respectively (Figure 4.6(d)). The detection limit of 5.93, 1.02, 1.01, and 1.02 ppm was estimated for NH₃ gas at the operating temperature of 30, 50, 100, and 150 °C, respectively. (Figure. 4.6(c)). The estimated response and recovery times at 100 °C are 18.3 and

10.8 s, 20.7 and 13.5 s, for 50 and 100 ppm NH₃, respectively, which is relatively better than various ZnO nanostructures reported in the literature. (Table 4.5) This confirms that ZnO nanowires deliver a relatively faster response to NH₃ than the C_2H_5OH and CO gases. Moreover, hexagonal ZnO nanowires have delivered excellent response for NH₃ gas at a relatively lower temperature (i.e., 100 °C) than the various pristine and metal-doped ZnO nanostructures mentioned in Table 6. Recently, Tharsika et al. [60] revealed the sensing response of 285 % toward 400 ppm NH₃ at

400 °C for ZnO nanorods deposited over SnO_2 thin film, but the reduction in the concentration of NH₃ has enormously reduced the response. Li. et al. [61] reported the sensor response of 57.5 % for 600 ppm NH₃ at 150 °C using ZnO nanoparticles, but it was reduced to 18 % for 50 ppm.

Table 4.5: The comparison	parative summary	of the response and	recovery time of	f the ZnO
nanostructure for NH	H ₃ gas.			

Morphology	Response and	Gas	Reference
	recovery time (Sec.)	concentration	
ZnO nanowires	18.3 and 10.8	50 ppm	Present
			WOLK
defect controlled ZnO nanorods	64 and 28	25 ppm	[62]
tapered ZnO nanostructures	49 an 19	25 ppm	[62]
Cu-doped ZnO	32 and 56	100 ppm	[9]
ZnO nanorods	351 and 125	1000 ppm	[63]
ZnO nanoparticles	660 and 160	600 ppm	[61]
Cd/Mg/Y doped ZnO	183/49 and 162/58	50 ppm	[64]

Table 4.6: The comparative summary of the sensing performance of ZnOnanostructure-based NH_3 gas sensors.

Morphology	Response	Temperature (°C)	Reference
ZnO nanowires	115.9 @ 50 ppm	100	Present
	128.9 @ 100 ppm		work
Vertical ZnO nanorods	~ 5 % @ 100 ppm	150	[62]
Tapered ZnO nanostructures	~ 85 %for 100 ppm	150	[62]
ZnO nanorods	10.1 % @ 100 ppm	300	[63]
ZnO nanoflowers	49.5 % for 50 ppm	250	[65]
Fe doped ZnO thick film	75 % for 50 ppm	30	[10]
Al monodoped n-ZnO	< 10 % for 600 ppm	100	[66]
AlN codoped p-ZnO	< 20 % for 600 ppm	100	[66]
AlAs codoped p-ZnO	< 65 % for 600 ppm	100	[66]
Al-doped ZnO nanoflowers	33 % for 75 ppm	190	[67]

Cu-doped ZnO nanoellipsoids	12.9 % for 100 ppm	100	[9]
Mn-doped ZnO microspheres	8.9 % for 100 ppm	100	[11]
Ag-doped ZnO nanoellipsoids	29.5 % for 100 ppm	150	[6]



Figure 4.7. (a) histogram of the maximum sensor response and (b) variation in selectivity parameter (β) of ZnO nanowires sensor for 50 ppm CO, C₂H₅OH, and NH₃ gases at an operating temperature of 100 °C

Figure 4.7 represents the histogram of the most effective sensing performance (Figure. 4,7(a)) and selectivity performance (Figure. 4.7(b)) of ZnO nanowires at the optimal working temperature of 100 °C for the CO, C_2H_5OH , and NH_3 gases. The selectivity describes the ability of a sensor to differentiate a specific target gas from

other interfering gases. The selectivity parameter (β) is generally defined as [48] β =S_{interfering}/S_{target}, where S_{target} and S_{interfering} is the response of the target gas (NH₃) and other gases (CO and C₂H₅OH), respectively. The estimated selectivity parameter is shown in Figure 6 (b). The value of β lies within the 0.24-0.88 range, where maximum values of 0.88 and 0.27 were obtained for 50 ppm concentration of C₂H₅OH and CO gases, respectively, at the optimum temperature of 100°C. The Hexagonal ZnO nanowires delivered the best response for detection safety limit (i.e., ~ 50 ppm) of all the studied gases at 100 °C, \ assigned to the deactivation of desorption and diffusion reaction processing, and inefficient adsorption and faster desorption below and above 100 °C, respectively [51]. Moreover, the adsorption and desorption of oxygen species transform the resistance of ZnO nanowires with a rise in the temperature and dramatically control the response. Pristine ZnO nanostructures seldomly offered a perfect NH₃ sensing performance, but at the higher temperature. Even though few studies have reported the sensing response of ZnO to NH₃, the sensible response was obtained either at higher temperatures or after doping metals (Table 4.6). The ZnO nanowires in the present work have delivered the highest response for NH_3 at 100 °C, which can be attributed to the well defined hexagonal morphology, clearly visible textural boundaries, single-crystalline nature, and well interconnections of the nanowires owing to the hierarchical arrangement.

To gain further atomic-level insights into the gas sensing response of ZnO nanowires, we have performed first-principles DFT simulations of the adsorption reactions between CO, C₂H₅OH, and NH₃ molecules and ZnO (100) surface. Before investigating the adsorption reactions, the bulk ZnO was modeled in the hexagonal wurtzite phase with space group *P63mc* (no. 186), as shown in Figure 4.8(a). The fully optimized lattice parameters predicted of a = b = 3.275 Å and c = 5.284 Å were in excellent agreement with experimentally observed lattice parameters. The partial density of states (Figure 4.8(b)) reveals the valence and conduction band edges are dominated by O(2p) states with a small contribution from Zn(3d) states. The bandgap of 3.24 eV predicted from the screened hybrid HSE06 functional [68] is consistent with experimentally reported values for ZnO [4]. Considering the key role of surface



Figure 4.8. Ball and stick model of (a) optimized hexagonal wurtzite bulk ZnO, (b) the corresponding partial density of states (PDOS); (c) surface structure of oxygen covered (pink atoms) $O_2/(100)$ -(3x3); (d-f) lowest-energy adsorption structures of CO, C_2H_5OH , and NH₃, respectively. Colour code: light grey = Zn; red = O; black = C; blue = N; white = H, pink = O_{mol} .

oxygen species in the gas response process over ZnO surfaces, the adsorption of oxygen molecule on ZnO(100) surface was first explored and found to preferentially adsorb dissociatively, as shown in Figure 4.8(c). Bader population shows that the dissociated O atoms gained 0.87 e⁻ each from the interacting surface Zn sites resulting in the formation of 2O⁻ species. The adsorption energy (E_{ads}) of the gas molecules, which gives a measure of the strength of the gas–ZnO interactions, is calculated as E_{ads} = $E_{surf.+gas} - (E_{surf.} + E_{gas})$, where $E_{surf.+gas}$ is the total energy of the surface and gas system in the equilibrium state, $E_{surf.}$ is the total energy of the isolated oxygen covered O₂/ZnO(100) surface and E_{gas} is the total energy of the isolated gas molecules. Accordingly, a negative value of E_{ads} indicates exothermic and stable adsorption, whereas a positive value suggests unstable adsorption. The lowest-energy adsorption configuration of CO, C₂H₅OH, and NH₃ gas molecules is shown in Figure 4.8(d-f). The CO molecule released the least adsorption energy of -1.35 eV, compared to C₂H₅OH and NH₃, which released adsorption energies of -1.87 and -2.11 eV, respectively, indicating that the order of binding strength as CO < C₂H₅OH < NH₃. The stronger binding of NH₃ is consistent with the observed higher maximum response from ZnO nanowires. From Bader charge analyses, the adsorption of CO, C₂H₅OH, and NH₃, on the O₂/ZnO(100) surface demonstrate that the CO molecule acts as a charge acceptor, withdrawing 0.58 e⁻ from the surface after adsorption, whereas C₂H₅OH and NH₃ molecules act as charge donors, transferring approximately 0.02 and 0.08 e⁻ per gas molecule to the surface.

4.8 Gas sensing mechanism

4.8.1 Generalized gas sensing mechanism

The gas sensing mechanism is surface dependent property but determined by the change in electrical properties of sensor materials after exposure to test gases environments. The resistance showed inverse behavior with temperature for n-type metal oxides; nevertheless, for ZnO, the adsorbed oxygen molecule is transferred in to oxygen ions such as O_2^- (below 100 °C) O⁻ (100 to 300 °C) and O²⁻ (above 300 °C) by extracting free electrons at a certain temperature, which leads to an increase in the resistance [6, 11-12]. The adsorption of oxygen molecules arrests the conduction bond electron and reduces the density of conduction, forming a depletion layer on the surface of ZnO nanowires. After that, the depletion layer obstructs the charge, carries transportation, and leads to the change in the resistance of ZnO nanowires. The following equations explain this process of oxygen ion formation-

$$O_2(ads) + e^- \rightarrow O^-(ads) \quad 2 \quad --(4.2)$$

$$O_2(ads) + 2e^- \rightarrow 2O^-(ads) --(4.3)$$

$$0^{-}(ads) + e^{-} \rightarrow 0^{2^{-}}(ads) --(4.4)$$

When the reductive gases like CO, C_2H_5OH , and NH_3 are introduced into the chamber, the amount of gas adsorption and reaction rate increase with increasing temperature. However, the gas adsorption rate becomes close to the gasdesorption rate at 100 °C and delivered maximum sensor response. Above 100 °C, reduced sensor response indicates the decrease in the quantitative adsorption of gases. Hence, the possible gas reaction with altering the resistance of hexagonal ZnO nanowires are as follows [52,53].

$$CO + O_{ads}^{-} \rightarrow CO_2(gas) + e^{-}$$
 --(4.5)

$$C_2H_5OH + 60^- \to 2CO_2 + 3H_2O + 6e^- \qquad --(4.6)$$

$$2NH_3 + 30^- \to 3H_2O + N_2 + 3e^- \qquad --(4.7)$$

Thus, NH₃ reacts with adsorbed oxygen ions along the surface of ZnO nanowires after exposure, releasing the captured electrons and reducing the potential barrier and thickness of the space-charge layer. This consecutively decreases the resistance, and hence gas sensing performance increased. Furthermore, reducing NH₃ gas influence the width of the space charge region by discharging extra electrons during the interaction and decreasing the resistance [6].



Figure 4.9. Schematic diagram representing the sensing mechanism of vertically growth ZnO nanorods (left panel) and hierarchically grown ZnO nanowires (right panel).

This phenomenon largely depends on the total surface area accessible for the interaction of gas molecules and expedited by textural (or grain) boundaries contributing as a resistive barrier. The high resistance in the present hexagonal ZnO nanowires array is assigned to a larger number of grain boundaries and contacts established between ZnO nanowires. The corresponding schematic diagram is shown in Figure 4.9. Vertically grown individual nanowires (Left panel, Figure 4.9) restricted total surface area and potential barriers (i.e., grain boundaries and point contacts). Therefore, most of the electrons from ZnO nanowires directly flow with ease to the electrode. However, hierarchically arranged ZnO nanowires (right panel, Figure 4.9) furnished a relatively much larger surface area and more potential barriers (i.e., grain boundaries and point contacts). Most of the electrons need to flow across the grain boundaries and transfer through the point contacts established in the hierarchical arrangement. Hence, the electron suffers a larger barrier before reaching the electrode, expedite the gas sensing mechanism. As a result, present ZnO nanowires have provided a higher response at a relatively lower temperature than the various ZnO nanostructures reported in the literature.

4.8.2 Sensing mechanism for NH₃ gas

The sensing response of ZnO nanowires has increased up to 100 °C and then decreased with an increase in temperature. The temperature-dependent response of the ZnO nanowires can be ascribed to the operating temperature. Moreover, the literature illustrates that O₂ (oxygen molecules) generally physisorbed on the metal oxide surface at low temperature (> 100 °C) and form O₂⁻ (ads) ions but at moderate (100-300 °C) and high (< 300 °C) temperature the chemisorption results in to O⁻ and O²⁻ ions respectively [6, 26, 69]. Therefore, after exposing ZnO with reducing gas like NH₃ at moderate temperature, the oxygen species interact with NH₃ molecules to release the electrons to the conduction band, which can be given by the reaction

$$4NH_3 + 30^- \rightarrow 6H_20 + 2N_2 + 3e^- --(4.8)$$

These free electrons are given back to the conduction band of ZnO and result in an increase in carrier concentration. This leads to a decrease in the electrical resistance of the ZnO nanowires in the ammonia environment. However, the possible reaction at high temperature (> 100 $^{\circ}$ C) is

$$2NH_3 + 30^- \to 3H_20 + N_2 + 3e^- \qquad --(4.9)$$

The above redox processes confirm that four NH₃ molecules react with three $O_{\overline{2}}$ to release 3 electrons (i.e., eq. 4.8), while at temperature > 100 °C, two NH₃

molecules are sufficient to react with O^- . However, the mechanism of interactions becomes more complicated at temperatures > 100 °C in the ammonia environment due to the presence of many types of adsorbed species on the surface in atomic and molecular forms [70]. There is a possibility of formation of NO_x in the presence of oxygen species as represented below,

$$4NH_3 + 50^- \rightarrow 6H_20 + 4N0 + 5e^-$$
 --(4.10) Or

$$2NH_3 + 4O_0 \rightarrow 3H_2O + N_2O + 8e^{-} - -(4.11)$$

$$2NH_3 + 3O_0 \rightarrow 3H_2O + 2NO + 10e^{-} --(4.12)$$

In such formation of oxidizing NO_x , the thickness of the depletion layer increases, and hence the electrical resistance of metal oxides increases [66]. However, the decrease in the electrical resistance (Table 4.7) in the ammonia environment rules out the formation of NO_x and gas sensing mechanisms related to it. Thus, our experimental conditions propose the formation of N_2 only and not NO_x by the reaction on NH₃.

We had also observed variation in sensor resistance values in the air when the ZnO sample was subjected to different temperatures from 30 °C to 150 °C. The change in the resistance values of ZnO is provided in Table 4.7. These values are in kilo-ohm (i.e., $k\Omega$), but actual resistance values are in mega-ohm (i.e., $M\Omega$). Therefore, this change in the resistance is not visible in the figures.

Table 4.7. The change in the resistance of ZnO in different gas environments to air resistance. The observed resistance values were in kilo-ohm (i.e., k Ω), and during gas sensing measurement, the resistance values observed were in mega-ohm (i.e., M Ω). Therefore, this change in the resistance is not visible in the figures.

Operating Temperature	50 °C	100 °C	150 °C
Gas	Resistance (kΩ)		
NH ₃	33.16	44.44	29.61
C2H5OH	128.41	1324.82	49.82
CO	46.94	181.76	6.68

4.9 Conclusions

In conclusion, hierarchical ZnO nanowires demonstrate excellent sensing performance for toxic gases. ZnO nanowires delivered excellent sensing performance in the detection safety limits of 50 ppm for CO, C₂H₅OH, and NH₃ gases at relatively lower operating temperatures of 100 °C. The ZnO nanowires provided a maximum sensing response of 115 % for toxic NH₃ gas and also delivered a faster response and recovery time of 27 and 9 sec, respectively, for 50 ppm NH₃ at the temperature of 100 °C, which is better than the variety of pristine, defect controlled, and doped ZnO nanostructures. The complementary DFT analysis predicted the CO < C₂H₅OH < NH₃ order of gas molecules binding strength. The excellent sensing response of hierarchical hexagonal ZnO nanowires is ascribed to the well defined hexagonal morphology, clearly visible textural boundaries, single-crystalline nature, and well interconnections of the nanowires. This sensing performance can be further improved after forming tunable hetero-architectures with metal nanoparticles.

4.10 References

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Chapter 5 Field emission of Au @ZnO nanoheteroarchitectures

This chapter elaborates on the synthesis of Au nanoparticles and their controlled decoration over the hierarchical ZnO nanowires to form Au@ZnO nano-heteroarchitectures. The influence of Au nanoparticle decoration on the surface morphology, chemical composition, and work function of host ZnO nanostructures were studied by the FESEM, XPS, and UPS spectroscopy. The field electron emission studies performed on Au@ZnO nano-heteroarchitectures are discussed in depth.

5.1 Abstract

The spitzer shaped pointed ZnO nanowires of diameter 120 nm and length ~ 5-6 µm synthesized via hydrothermal techniques were decorated with Au nanoparticles of diameter < 20 nm along their textural boundaries. The turn-on field (E_{on}) of 1.56 V/µm required to draw current density of 10 µA/cm² from ZnO nanowires was reduced further to 0.96 V/µm after the controlled decoration of Au nanoparticle, which is significantly lower than pristine/doped ZnO nanostructures, Ag@ZnO, Au@ZnO, Au@CuO, and MoS₂@TiO₂ heterostructure based field emission (FE) devices. The orthodoxy test confirmed the feasibility of the field-enhancement factor (β_{FE}) of 4477 for Au/ZnO/ITO emitters. The enhanced FE behavior is attributed to pointed nanotips, individual dispersion of Au nanoparticles along the textural boundaries of ZnO nanowires, and enhanced energy well formation at their interface. Moreover, the density of the state increases enormously due to the hetero-structured interface of Au@ZnO, and a significant amount of electrons from both Au and ZnO contribute to enhanced emission current density (2.1 mA/cm² @ 1.92 V/µm) and greatly stable electron emission. Our experiments suggest that the tunable heteroarchitectures of Au nanoparticles@ZnO nanowires hold promise for applications in display screens and intense electron sources.

5.2 Introduction

Precisely controlled dimensions of nanostructures and their decoration are found to exhibit unexpected physical properties, such as tailoring of work function, energy band alignment, energy barrier formation, etc. Therefore, interface engineering is imperative in determining the performance of the field electron emission devices. Inducing higher electric fields, modifying emitter geometry, and impinging impurities without altering interfacial electronic structure are the emerging practices [1-6]. Nevertheless, considering the moderate electric conductivity of most metal oxides, developing the one-dimensional (1D) morphologies of the metal oxides and further decorating them with highly conducting metal/semiconducting nanoparticles is more feasible for fabricating field emission (FE) displays with improved emission ability. The high aspect ratio, sharp tip features, better conductivity, and oxidation resistance projected as additional prerequisites to enhance the field electron emission and improve current stability are feasible in the 1D metal oxide nanostructures. Moreover, various 1D morphologies are observed to control the FE properties. Therefore, the researchers are increasingly engrossed in exploring the 1D metal oxide nanostructures to develop efficient display devices and sources for electron microscopes, including energy storage and conversion devices [7-11]. Although ZnO was one of them, it was moderately explored for FE displays due to its large work function of 5.3 to 5.6 eV, limited hexagonal morphologies, random dispersion, and electron field screening effect [12-16]. The larger work function of ZnO nanostructures was further tailored after doping with Ga [2], Mg [17], In [3], Al [18], Co [19], Cu [20], and C [5], etc., or decorating with Ag [4], and annealing in different environments [21] to improve the electron emission. The doping and annealing in different environment modify the electronic structure and significantly induce conductivity, are the motives for improved electron emission. The metal oxide nanostructures combined or modified with conducting particles/layers to form layered nano-hetero-architectures have shown substantial enhancement in their properties and operation in FE, in particular [22]. Moreover, hetero-architectures of Ag and ZnO have shown improvement in optoelectronic properties. Chang et al. [23] have attained the turn-on field (E_{on}) of 2.39 V/µm after controlling the density of ZnO nanopillars employing self-assembled Ag nanoislands and nanolayers. Ag-ZnO nanocomposites prepared on alloy substrates by employing hydrothermal and electrophoretic techniques have conceived E_{on} in the range of 1-3.19 V/µm. In fact, the composites of Ag/ZnO and Ag/Graphene oxide/ZnO have shown the potentials of FE [6]. Although Chang et al. [13] reported FE properties of Au nanoparticle decorated ZnO nanopillars with E_{on} of 2.65 V/µm, their findings on E_{on} and field enhancement factors were not justified with the theoretical approach provided by Forbes et al. [24] Employment of Au catalyst for the growth of ZnO nanopillars known to appear at the tip of 1D morphology might have significantly assisted for lower E_{on} of 3.15 V/µm (for ZnO nanopillars), that is the reason why E_{on} was further reduced only by 0.5 V/µm even after the sputtered decoration of Au nanoparticles on ZnO nanopillars. However, despite the enhancement obtained by all these approaches, the effect of decorating Au over the ZnO is not convincing.

Oxidation effect and uncontrolled growth of metal particles (including Au) are addressed reasons for impediment in the progression of FE. Therefore, reducing the tip size and decorating the emitters with the metal shall be the perfect combination for further enhancement in FE properties. Considering the potentials of hetero-architectures and metal nanoparticles, controlled decoration of ZnO nanostructures with Au nanoparticles will further advance FE displays.

Owing to the excellent electron affinity, high electronic/chemical stability, and biocompatibility, Au nanoparticles are increasingly engrossed in the modification of optoelectronic properties of metal oxides for applications in UV detectors [25], photocatalysis [26], sensors [27], and displays, etc. Despite the larger work function of 5.35 to 5.76 eV, Au nanoparticles were found to perform better because of enhanced electron transfer and surface interactions [26]. Recently, Li et al. [28] reported electron FE from Au nanoparticle decorated CuO nanoplates, but the minimum E_{on} was restricted to 6.7 V/µm due to the random distribution of irregular size and shape of nanoplates. Singh et al. [29] have decorated ZnO nanotapers with Au islands to improve electron emission. Lin et al. [30] performed FE studies on ZnO nanowires modified with Au nanoparticles. The unoptimized coating of Au nanoparticles along the wire body has resulted in the E_{on} of 2 V/µm, defined at a very low current density of 1μ A/cm². Ghosh et al. [31] have reported enhanced FE performance even after the larger work function values (i.e., 5.04-4.7 eV) for randomly oriented and highly oxygen defective ZnO nanostructures capped at its tip with Au nanoparticles. Consequently, for further enhancement in FE behaviors, modification of the electronic properties of ZnO nanostructures with tip morphology by the controlled decoration of Au nanoparticles along the textural boundaries is of scientific and technological importance.

In this work, we present Au nanoparticle decorated ZnO nanowires as excellent field emitters. The Au nanoparticles of various concentrations were decorated along the ZnO nanowire body at optimized conditions. The influence of the concentration of Au nanoparticles on the structural, chemical, and field electron emission properties of ZnO nanowires was studied methodically. The surface morphology, chemical composition, and electronic structure of Au decorated ZnO nanowires were explored utilizing field-emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). The FE behaviors of Au decorated ZnO nanowires were compared after performing measurements at optimized anode-cathode separation. The Au@ZnO nano-hetero-architectures obtained after decorating Au nanoparticles over ZnO nanowires for 24 hrs exhibited excellent FE properties.

5.3 Experimental Section

The 0D Au nanoparticles were synthesized by the citrate reduction method. The 0.1 gm of Trisodium citrate ($Na_3C_6H_5O_7$) solution prepared in 15 ml deionized was continuously added to Chloroauric acid (HAuCl₄; 12 mM/L) dissolved in 25 mL deionized water for 30 min under a controlled temperature of 98 °C. The reaction was continued for 15 min to obtain Au nanoparticle of uniform dimensions. The Zinc Acetate dehydrates (C₄H₆O₄Zn.2H₂O, 98 %, Sigma Aldrich) and Sodium peroxide (Na₂O₂, 97 %, Sigma Aldrich) were hydrothermally reacted at 85 °C for 12 hr to grow large-area arrays of ZnO nanowires over the ITO coated glass substrate. A detailed protocol for synthesizing a large area array of the spitzer shaped ZnO nanowires is reported in chapters 2 and 3. Thus independently synthesized ZnO nanowires and Au nanoparticles were subjected to the formation of their nano-hetero-architectures. Assynthesized ZnO nanowires arrays were transferred to the mobilized solution of Au nanoparticles, and Hexadecanethiol (HDT, 20 pmol/L) was added to the solution to conform the functionalization of Au nanoparticles along the ZnO nanowires. Assynthesized ZnO nanowires arrays were immersed in the mobilized solution of Au nanoparticles for 4, 8, 12, 24, and 48 hr to ensure the controlled decoration of Au nanoparticles. After that, the surface morphology of Au decorated ZnO nanowires was confirmed using a field emission scanning electron microscopy (FESEM, Carl Zeiss, Merlin 6073). The chemical states of Au decorated ZnO nanowires were analyzed utilizing an X-ray photoelectron spectrometer (XPS, Thermo Scientific Inc. Ka) with a microfocus monochromated Al Ka X-ray. The valence band spectra (VBS) was measured using the Omicron energy analyzer (EA-125, Germany) at angle incidence photoemission spectroscopy (AIPES) beamline on Indus-1 synchrotron source at RRCAT, Indore, India. The vacuum in the analyzer chamber was of the order of 10^{-10}

¹⁰ Torr. The FE studies of pristine and Au coated ZnO nanowires were carried out in a vacuum chamber maintained at a base pressure of ~ 7.5×10^{-9} Torr. The anode, a semi-transparent phosphor screen, was maintained at distances of 2000 µm from Au decorated ZnO nanowires. (\equiv Au/ZnO/ITO emitters), which was optimized for the specimen of pristine ZnO nanowires (\equiv ZnO/ITO emitter). The field emission measurements procedure adopted for spitzer shaped ZnO nanowires is elaborated elsewhere [1]. To avoid the influence of contamination and loosely bound Au nanoparticles in FE, samples were preconditioned by applying a voltage of ~ 3 kV for 30 min at a base pressure of ~ 7.5×10^{-9} Torr. Field emission current (I) was measured with an electrometer (Keithley 6514) at direct current (dc) voltage (V) applied using a high-voltage dc power supply (0-40 kV, Spellman). The long-term stability of the field emission current was recorded for Au/ZnO/ITO emitters.

5.4 Field Emission Scanning Electron Microscopy

The FESEM images in Figure 1 show the surface morphology of a large area array of Au decorated ZnO nanowires synthesized over conducting glass substrate. The hexagonal ZnO nanowires distributed over a large area array were confined to a limited range, and all were smaller than the diameter of ~ 200 nm. The nanowires of the average diameter of ~ 120 nm and ~ 5-6 μ m long were well separated with their clearly visible textural boundaries. The self-assembled hexagonal ZnO nanowires were conical in shape at their tip. After the confirmation of the formation of ZnO nanowires, these randomly aligned ZnO nanowires were subjected to the controlled decoration of Au nanoparticles over the surface of the wire body. The ZnO nanowires were decorated with Au nanoparticles by monitoring the reaction time for 4, 8, 12, 24, and 48 hr in the solution of Au nanoparticles at optimized concentration and temperature. The change in the decoration time has resulted in the variation of the concentration of Au nanoparticles over the surface of ZnO nanowires. The representative FESEM images in Figure 5.1(a and c) shows the surface morphology of Au nanoparticle decorated ZnO nanowires at a reaction time of 8 and 24 hr, respectively. A close examination from the top view of the portion of the array (Figure 5.1(a)) shows no agglomeration of the Au nanoparticles over the array of ZnO.



Figure 5.1. FESEM images show the surface morphological features of ZnO nanowires decorated with Au nanoparticles after a reaction time of (a) 8 h and (c) 24 h. (b) The single nanowire extracted from the array of Au@ZnO nanowires decorated for 8 h showing the uniform distribution of Au nanoparticles along the textural boundaries. (d) Both arrays are composed of the ZnO nanowires with spitzer shaped truncated tip mostly (left panel) and very sharp pointed tips partially (right panel).

However, the Au nanoparticles were uniformly decorated along the textural boundaries of hexagonal ZnO nanowires. High magnification FESEM image in Figure 5.1(b) shows single ZnO nanowires extracted from the array decorated for 8 hr in the solution of Au nanoparticles. ZnO nanowire was uniformly decorated with the Au nanoparticles. The Au nanoparticles, all are smaller than the diameter of ~ 20 nm, were decorated along the hexagonal facets of ZnO nanowires and not along the edges. Further increase in the decoration time has resulted in the increased concentration of Au nanoparticles, evidenced by the top view FESEM image in Figure 5.1(c). Even though agglomeration of Au nanoparticles was observed along the hexagonal facets of ZnO nanowires, slightly additional agglomeration was observed outside the ZnO nanowires array in the high magnification FESEM images in the inset of Figure 5.1(c). The agglomeration has increased further for a reaction time of 48 hr and gave an appearance of nanocomposite formation of Au nanoparticles and 1D ZnO nanowires. The close observation of the ZnO nanowires grown over a large area array confirmed that the facets of the wires were curtailed at the end and provided either spitzer shaped truncated tips or very sharp pointed tips as shown in the left and right panel of Figure 5.1(d), respectively. Most of the ZnO nanowires have spitzer shaped truncated tip of a diameter less than ~ 30 nm (left panel Figure 5.1(d)), but the diameter of the very sharp pointed tip was less than ~ 10 nm (right panel, Figure 5.1(d)). This spitzer shaped truncated tip and very sharp pointed tip appearance of ZnO nanowires along with Au nanoparticles are expected to play a vital role in enhancing FE properties.

5.5 X-ray Photoelectron Spectroscopy

The XPS investigations were performed to confirm the electronic structure and chemical properties of Au decorated ZnO nanowires. Figure 5.2 illustrates the high-resolution XPS spectra of the Zn(2p) and Au(4f) recorded after the decoration of Au nanoparticles at the reaction time of 8 and 24 hr on the ZnO nanowires. Figure 5.2(a) illustrates the Zn(2p) XPS spectra of Au@ZnO nanowires. The clearly visible two peaks feature of Zn(2p_{3/2}) and Zn(2p_{1/2}) located at a binding energy of 1020.9 (\pm 0.1) and 1043.9 (\pm 0.1) eV, represents the core level of Zn²⁺ cations, respectively [32,33]. The energy separation of 23.1 eV assigned to ZnO and not too metallic Zn [34] was

maintained irrespective of Au decoration along the textural boundaries of ZnO nanowires. This indicated that the Au had not altered the stoichiometry or chemical properties of ZnO nanowires. The decoration of Au nanoparticle of < 20 nm in diameter at a reaction time of 8 and 24 hr along the textural boundaries of ZnO nanowires resulted in the reduction of the intensity of Zn(2p) peaks, on account of the permitted fine-depth profiling only within 10 nm in XPS. The reduction in the intensity of Zn(2p) confirms the increased amount of Au nanoparticles decoration over ZnO nanowires after 8 and 24 hr. On the other hand, the distinct XPS peaks for Au(4f) along with Zn(3p) were observed for the decorated ZnO nanowires and are shown in Figure 5.2(b). Two peak features for Zn(3p) and no peaks of Au(4f) were observed for pristine ZnO nanowires. However, the double peak feature of the Au(4f) peak was observed for the reaction time of 8 hr. The intensity of the Au(4f) peak has further increased with an increase in reaction time to 24 hr, which indicates an additional increase in the amount of Au nanoparticles decorated over ZnO nanowires.

The intensity of the Au($4f_{7/2}$) and Zn($2p_{3/2}$) peaks was considered to understand the effect of reaction time on the amount of Au nanoparticle decorated over ZnO nanowires. Figure 5.3 shows a comparison of the intensity of the Au($4f_{7/2}$) and Zn($2p_{3/2}$) peaks with respect to the reaction time for the decoration of Au nanoparticles. The inversely proportional variation in the intensity of Au($4f_{7/2}$) and Zn($2p_{3/2}$) peaks was observed. The observed intensity of both the peaks was well fitted using the exponential growth equation,

$$I = A - Be^{-\iota/\tau} \qquad \qquad --(5.1)$$

Where I is the intensity of peak, t is the reaction time, A and B are initial constants, and τ is the curve fitted constant. However, the exponential fitting for Au(4f_{7/2}) peaks is considered to identify the decoration rate of Au nanoparticles over ZnO nanowires.

The decoration rate of Au nanoparticles is,

$$\frac{dl}{dt} = (\frac{B}{t})e^{-t/t} \cong 793 \cdot e^{-t/94}$$
 --(5.2)



Figure 5.2. High-resolution XPS spectra of the (a) Zn(2p) and (b) Au(4f) and Zn(3p) core levels of pristine and Au nanoparticles decorated ZnO nanowires for 8 and 24 h.



Figure 5.3. The intensity variation of the Au $(4f_{7/2})$ and Zn $(2p_{3/2})$ core levels of Au@ZnO nano-hetero-architectures observed by decorating Au nanoparticles over ZnO nanowires for various optimized reaction times.



Figure 5.4. High-resolution XPS spectra for Au(4f) and Zn(3p) core levels of a large area array of 1D ZnO nanowires (upper panel) and Au nanoparticles decorated ZnO nanowires for the reaction time of 8 h (middle panel) and 24 h (lower panel).

To make a distinction between Au(4f) and Zn(3p), and also for precise determination of their double-peak feature, the XPS spectra in Figure 5.2(b) was

deconvoluted via Voigt curve fitting function within the Shirley background. The deconvoluted XPS spectra for pristine ZnO (upper panel) and Au@ZnO (middle and lower panel) nanowires is shown in Figure 5.4. The perfect fit for four distinct peaks has shown the double peak features of Au($4f_{7/2}$) and Au($4f_{5/2}$) for Au(4f), and Zn($3p_{3/2}$) and $Zn(3p_{1/2})$ for Zn(3p), respectively. Two peaks located at binding energy of 88.2 (± 0.03) and 90.7 (\pm 0.05) eV evidenced Zn(3p_{3/2}) and Zn(3p_{1/2}) core levels of Zn²⁺ cations only, respectively. The energy separation of 2.5 eV observed in ZnO nanowires (upper panel, Figure 5.4) was maintained even after the decoration of Au nanoparticle along their textural boundaries. The two peaks located at the binding energy of 82.9 (± 0.05) and 86.7 (± 0.05) eV evidenced Au $(4f_{7/2})$ and Au $(4f_{5/2})$ core level of pure metallic Au only, respectively. The energy separation of 3.8 (±0.02) eV between Au $(4f_{7/2})$ and Au $(4f_{5/2})$ core level was observed even after varying the amount of Au decoration over ZnO nanowires (middle and lower panel, Figure 5.4). The blue shift of 1.6 eV in binding energy observed than that of the gold doped compounds [35] can be attributed to the pure metallic form of Au and not to the chemically reacted Au over the ZnO surface. Moreover, the blue shift in the binding energy is assigned to the strong electron exchange between the metal oxide and Au nanoparticles [36,37].





Figure 5.5. Field emission J–E curves of Au@ZnO nano-hetero-architectures derived after decorating Au nanoparticle along the surface of ZnO nanowires for various optimized reaction times (i.e., 4, 8, 12, 24, and 48 h)

The FE measurements of Au decorated ZnO nanowires (\equiv Au/ZnO/ITO) were performed in the planer diode configuration on the emission area of ~ 0.30 cm² at the optimized anode-cathode separation of 2000 µm. The change in the electron emission current density (J) with variation in the applied electric field (E) (i.e., J-E plot) of Au/ZnO/ITO emitters is shown in Figure 5.5. Owing to the random alignment of Au@ZnO nanowires over the ITO coated substrates, the applied electric field $(E=V/d_{sep})$ is treated as the average field and not a uniform field between the electrodes separated by the distance d_{sep} . In the beginning, the pristine ZnO nanowires (= ZnO/ITO) were subjected to electron FE at the separation of 1500, 2000, and 2500 μ m. More details on these field emission measurements are available elsewhere [38]. The higher current density was observed for pristine ZnO nanowires at the separation of 2000 μ m; therefore, the FE studies of Au@ZnO nanowires (= Au/ZnO/ITO) were performed at the anode-cathode separation of 2000 µm. The amount of Au decorated along the textural boundaries of ZnO nanowires has distinctly altered electron emission current (Figure 5.5). The Au/ZnO/ITO emitters have delivered larger emission current density at a relatively lower applied field than that of pristine ZnO nanowires. Especially, decoration of Au nanoparticles for 24 hr along the textural boundaries of ZnO nanowires yields a larger emission current density of 2.1 mA/cm² at a lower applied field of 1.92 V/µm. Moreover, emission current density (i.e., 2.1 mA/cm²) achieved from Au@ZnO nanowires (\equiv Au/ZnO/ITO) at lower applied field (i.e., 1.92 V/ μ m) is relatively higher than the values reported for Ag/GO/ZnO composites [6], CNT-ZnO composites [39], ZnO nanowire/CNT heterojunction [40], pristine ZnO nanopillars [23], metal particle decorated ZnO nanorods [41], Au decorated ZnO nanowires/nanopillars [13,30], and CuO nanoplates [28], and pristine and MoS₂ decorated β -TiO₂ nanorods [22,42]. The E_{on} of ZnO/ITO (i.e., $E_{on} = 1.56$ $V/\mu m$) required to acquire a current density of $10\mu A/cm^2$ is reduced considerably after the controlled decoration of various amounts of Au nanoparticles. The Eon of 1.36, 1.38, 1.32, 0.96, and 1.46 was observed after the controlled decoration of Au nanoparticles over ZnO nanowires for 4, 8, 12, 24, and 48 hrs, respectively. Likewise, the E_{thr} of ZnO/ITO (i.e., 1.9 V/µm) corresponding to the current density of 100 μ A/cm² is reduced to 1.7, 1.9, 1.86, 1.2, and 1.81 V/ μ m for the respective decoration

of Au nanoparticles. The decoration of Au nanoparticles over ZnO nanowires for 24 hrs have provided the lowest E_{on} value (i.e., 0.96 V/ μ m @ 10 μ A/cm²) than that of pristine ZnO emitters of various morphological forms such as a rod, wires, cones, pillars, and needles, etc. mentioned above [12-16,23,43]. The Eon observed for Au@ZnO nanowires hetero-architectures after the decoration of Au nanoparticles for 24 hr is reasonably lower than that reported for Ag and Graphene oxide decorated ZnO nanowire array (i.e., 1.4 V/µm) [6], ZnO nanowire/CNT heterojunction (i.e., 1.5 V/µm at the current density of 1μ A/cm²) [40], nitrogen implanted ZnO nanowires (i.e., 2.4 V/ μ m at the current density of 0.1 μ A/cm²) [44], Ag and Pt decorated ZnO nanorods (i.e., 1.9 and 2.6 V/µm, respectively) [41], and Au decorated CuO nanoplates (i.e., 6.7 V/μ m) [28]. The non-uniform and limited distribution of Au nanoparticles over the ZnO nanowires restricted the E_{on} to 2 V/µm (defined at 1µA/cm²) [30]. Even though CNT are known for their very high conductivity, the composite of ZnO with CNT could not provide better Eon than present Au@ZnO nano-hetero-architectures might be because of their non-optimized compositions [39,45]. Au@ZnO nanorods have shown compatibly good performance than the Ag nanoparticle coated ZnO nanorods array. However, one should consider that the alloy substrate (details not mentioned in the manuscript) might have backed up for better electron emission and lower E_{on} in Ag@ZnO nanorods [4]. The larger diameter of ZnO nanopillars (i.e., > 200 nm) limited the E_{on} to 2.65 V/µm even after decoration with Au nanoparticles [13]. Moreover, the use of Au nanoparticles as a catalyst to grow ZnO nanopillars, known to appear at the tip of nanopillar morphology, might have aid significantly for the E_{on} of 3.15 V/ μ m (for ZnO nanopillars), which was further reduced only through 0.5 V/ μ m after decorating Au nanoparticles on ZnO nanopillars. In fact, controlled decorations of Au along the textural boundaries of ZnO have conceived relatively better field electron emission and lower Eon then the composites of Ag/ZnO and Ag/Graphene oxide/ZnO (i.e., 1.4 V/ μ m defined at 1 μ A/cm²) [6] Even though, Singh et al. [29] have reported relatively lower E_{on} of 0.97 V/µm for Au island decorated ZnO nanotapers, one cannot neglect the one-to-one interaction of the ZnO nanorods with AFM tip employed for this lower value measurement. The reduction in the E_{on} of Au@ZnO nanorods might be observed because of both the sharp and spitzer shaped

pointed tip, as well as reduction in the resistance of ZnO after the uniform decoration of highly conducting Au nanoparticles along their textural boundaries. The uniform distribution of Au nanoparticles was observed along the textural boundaries of ZnO up to 24 h. Although agglomeration of Au was observed after decoration for 24 h, it was limited to the bottom of the nanowires array, and tips of the nanowires were exclusively available for emission. The enormous agglomeration was observed all over the array after decorating Au nanoparticles for 48 hr, which might have resulted in a further increase in the E_{on} . The agglomeration has resulted in both the non-uniform distribution of Au along the textural boundaries and inaccessibility of ZnO nanowires tips for emission. Moreover, the agglomeration of Au had made highly conducting centers over the ZnO nanowires array. It resulted in the non-uniform distribution in conductivity, as reported by She et al. [46] for the correlation between resistance and FE performance of ZnO nanostructures. Consequently, the emission ability of Au@ZnO nanowires further decreased, and the value of E_{on} increased.



Figure 5.6. UPS valence bands spectra of Au@ZnO nanowires decorated for a reaction time of 24 h. The inset shows magnified valence bands spectra at higher binding energy.

The alterations in the work function endorse the FE properties. Therefore, Ultraviolet Photoelectron Spectroscopy (UPS), employed to determine the work function Au/ZnO/ITO emitters, is utilized as a fingerprint to reveal the reason for
lower E_{on} and improved emission current density. The UPS spectra recorded at an energy of 23 eV for Au decorated ZnO nanowires shown in Figure 5.6 is utilized to calculate the work functions. There are noticeable changes in the shape of valence band spectra for Au@ ZnO emitters compared to ZnO emitters [38]. Two distinct peaks are observed in the VBS of Au@ZnO nanowires, where lower and higher binding energy peaks are assigned to the nonbonding O(2p) orbitals and hybridization of the O(2p) and Zn(4s) orbitals, respectively [47]. Significant attenuation in the width of the band of ZnO is observed after the decoration of Au nanoparticles. Moreover, the work function was estimated from the equation [48]

Where h ω is the energy of the source used ($\equiv 23 \text{ eV}$), E_{sec} is the onset of the secondary emission, and E_{FE} is the Fermi edge. The sharply pointed tip appearance of ZnO nanowires resulted in the work-function of 4.3 eV (i.e., $\Phi_{Au@ZnO}$) after decorating Au nanoparticles for 24 hr, which is remarkably lower than reported for Al-doped ZnO nanowires [18], Ag decorated ZnO nanorods [4], and Au faceted oxygen-deficient ZnO nanostructures [31]. The Au nanoparticles might have interacted with the ZnO through the surface oxygen atoms and lead to their hybridization. This resulted in the stimulation of charge transfer from Au nanoparticles to oxygen, thereby reducing the work function of the Au decorated ZnO nanostructures [31]. This reduced value of work-function might be one of the drives for enhancement in the FE performance of Au decorated ZnO nanowires.

A modified Fowler–Nordheim (F–N) equation mentioned below is utilized to elucidate the applied field dependent modification in the emission current density of Au/ZnO/ITO emitters,

$$J = \alpha \, a \Phi^{-1} E^2 \beta^2 \exp\left(-\frac{b\Phi}{E} - \frac{3/2}{\beta_{FE} E^F} \nu\right) - \dots (5.4)$$

Where, *J* is the average FE current density of the device, α_f is a macroscopic preexponential correction factor, *a* and *b* are constants ($a = 1.54 \times 10^{-6} \text{ AeV/V}^2$, $b = 6.83089 \times 10^3 \text{ eV}^{-3/2} \text{ V/}\mu\text{m}$), Φ is the work function of the emitter (i.e., $\Phi_{ZnO}= 4.9 \text{ eV}$ and $\Phi_{Au@ZnO}= 4.3 \text{ eV}$), *E* is the applied average electric field, β_{FE} is the local electric field enhancement factor, and v_F is a specific value of the principal Schottky-Nordheim barrier function *v* (i.e., correction factor). The emission surface is treated to be rough for Au/ZnO/ITO emitters because of the decoration of ZnO nanowires. Therefore, the ratio of both applied and local electric fields, which differ from each other at emission sites (i.e., ZnO and Au), is identified as the β_{FE} . A plot of $\ln\{J/E^2\}$ versus (1/E), recognized as the F-N plot, is described by equation (5.4). Therefore, the field enhancement factor (β_{FE}) is estimated from equation

$$\beta_{FE} = \frac{-sb\phi^{3/2}}{s} ---(5.5)$$

Where s (= 0.95) is the slope correction factor for the Schottky-Nordheim barrier. In the present case, it is treated as s = 1 for simplicity.

The F-N plots for Au controlled Au/ZnO/ITO emitters are shown in Figure 5.7. The distinct F-N plots substantiate the well-defined band alignment of Au nanoparticles and ZnO nanowires after their controlled decoration one over the other. The amount of Au decoration over Au/ZnO/ITO emitters has tailored the values of β_{FE} . The β_{FE} values evaluated for various Au/ZnO/ITO emitters fabricated after decorating Au nanoparticles over ZnO nanowires at a reaction time of 4, 8, 12, 24, and 48 hr are 3744, 4270, 4477, 5784, and 3124, respectively. These evaluated β_{FE} values for Au/ZnO/ITO emitters are higher than those reported for various ZnO nanostructures morphologies [15,16,49]. Moreover, it is also larger than doped and decorated ZnO nanostructures, such as the Au nanoparticle decorated ZnO nanopillars [13] and CuO nanoplates [28] Al, C, and In-doped ZnO nanowires grown on flexible substrates [3,5,18] Mg-doped ZnO nanostructures [17], and Carbon nanotube-ZnO composites [45]. Although, Premkumar et al. [12] and Wang et al. [6] have reported very high values of β_{FE} for pristine and Ag nanoparticle decorated ZnO nanostructures, respectively, the orthodoxy test was not performed to support their claim. The unoptimized coating of Au nanoparticles along the body has conceived the β_{FE} of 29000 [30], but one cannot neglect that orthodoxy test or theoretical calculations have not been performed to confirm the viability of this high value. That is why the feasibility of the FE measurements and β_{FE} of Au/ZnO/ITO emitters was verified after performing the orthodoxy test using the spreadsheet made available by Forbes in the reference [24]. The scaled-barrier-field (f) values estimated for Au/ZnO/ITO emitters decorated with Au nanoparticles after controlling reaction time from 4 to 48 hr are given in Table. 5.1



Figure 5.7 F-N plots obtained from J–E curves measured for nano-hetero-architecture of controlled Au nanoparticle decorated ZnO nanowires (≡Au/ZnO/ITO) for various optimized reaction times.

The emission situation is orthodox during all controlled Au decorated Au/ZnO/ITO emitters for both the lower (f_{low}) and higher (f_{high}) Scaled-Barrier-Field (f) values. The decoration of Au along the textural boundaries of ZnO nanowires demonstrated an apparently reasonable emission condition for f_{high} values, which are reduced significantly after decorating ZnO nanowires with Au nanoparticles for 24 hr. The optimized and controlled loading of highly conducting Au nanoparticles along the textural boundaries of ZnO nanowires and their well-defined band alignment (i.e., the metal-semiconductor junction of Au and ZnO) has emerged as improved values of β_{FE} and lower Eon than that of ZnO/ITO emitters. After decorating Au along the ZnO nanowires for 24 h, maximum Au nanoparticles were accommodated along the textural boundaries, and partial aggregation of Au nanoparticles limited to the bottom of the nanowires array conceived the enhancement in the conductivity of exclusively available tips of the nanowires. Therefore, most of the injected electrons from both Au centers and ZnO nanowires are transported efficiently towards the emission sites. This cut down the voltage drop along the Au@ZnO nanowires and improves the effective field at the sharp tips of ZnO nanowires and surface of Au nanoparticles, which give rise to the observed enhancement of FE.

Table 5.1: Scaled-Barrier-Field (*f*) values evaluated from F-N plots for Au decorated ZnO nanowires (i.e., Au/ZnO/ITO) emitters using the spreadsheet provided in Reference [24]

Materials	Reaction time (h)	flow	fhigh	Orthodoxy test result
Au nanoparticles @ZnO nanowires	4	0.27	0.56*	Apparently reasonable
	8	0.28	0.66*	Apparently reasonable
	12	0.27	0.71*	Apparently reasonable
	24	0.24	0.49	Pass
	48	0.22	0.44	Pass

(* Single asterisk on f_{high} values indicates the apparently reasonable values (i.e., $f_{high} < 0.75$)



Figure 5.8. Schematic band alignment of nano-hetero-architecture of Au nanoparticles @ ZnO nanowires (i.e., ≡Au/ZnO/ITO emitters)

This can be more elaborated by the band alignment of Au and ZnO showed in Figure 5.8. Therefore, the enhanced FE behavior with higher values of β_{FE} and lower E_{on} is expected after the decoration of Au nanoparticles over ZnO nanowires, owing to its lower work function (i.e., 5.3 eV). The metallic Au, an excellent source of the electron, provides a relatively immense number of electrons, which were commended by the electrons accumulated in the energy well of ZnO. Besides, the energy well of ZnO enhanced further due to the alteration of energy band bending at the interface after decorating Au nanoparticles along the textural boundaries of ZnO nanowires. Consequently, the density of the state increases enormously, and a significant amount of electrons from both Au and ZnO contribute to enhanced emission current density

(Figure 5.8). The smaller values of Φ provide a reduced barrier for the emission of an electron. Therefore, a reduction in the work function of Au decorated ZnO nanowires (i.e. $\Phi_{Au@ZnO} = 4.3 \text{ eV}$) has resulted in the enhanced electron emission at the relatively lower applied electric field, which turned out as lower E_{on} .



Figure 5.9. Field emission current stability (I–t) plot of nano-hetero-architectures of Au@ZnO observed by the optimized decoration of Au nanoparticle over ZnO nanowires at different reaction times

Steady Field electron emission (i.e., current) is essential for the fabrication of FE displays and other related appliances. Figure 5.9 shows the FE stability of Au controlled Au/ZnO/ITO emitters. The recorded emission current (I) preset at the value of 10 μ A, which was considered for E_{on} , not showed obvious depreciation for uninterrupted emission until 180 min. The lower current fluctuation (i.e., \pm 10 %) in Au/ZnO/ITO emitters confirm the improvement in the stability of Au/ZnO/ITO emitters. The Au/ZnO/ITO emitters where Au nanoparticles were decorated for 24 hr are observed comparatively more stable with negligible current fluctuations of \pm 4 %.

The exclusive availability of sharp tips of ZnO nanowires and uniform distribution of maximum Au nanoparticles along their textural boundaries after decoration time of 24 hr contribute enormously as emitters perhaps are the cause of enhancement in the emission ability.

5.7 Conclusions

In conclusion, the large area array of ZnO nanowires synthesized on ITO coated glass substrates was decorated with Au nanoparticles. The XPS analysis confirmed the decoration of pure metallic Au nanoparticles over the stoichiometric ZnO nanowires. The controlled decoration of Au nanoparticles along the textural boundaries of sharply pointed ZnO nanowires resulted in a lower work-function of 4.3 eV. The E_{on} was significantly reduced to 0.96 V/µm by the controlled decoration of Au nanoparticles over ZnO nanowires. The Au/ZnO/ITO emitters showed highly stable emission (with current fluctuations of ± 4 %) of the electron, besides a larger emission current density of 2.1 mA/cm² at a lower applied field of 1.92 V/ μ m. The decoration of Au along the surface of ZnO nanowires dramatically increased the density of state and reduced work function (i.e., 4.3 eV) for a reaction time of 24 h, which induced almost all emitted electrons to transfer easily towards the emission sites, is responsible for the enhancement in FE behavior and reduction in E_{on} . The tunable nano-hetero-architecture of Au decorated ZnO nanowires of sharp-tip morphology can be a promising candidate for field electron emission based vacuum micro/nano-devices, including flat-panel displays and intense point electron source. Moreover, this approach implemented to enhance FE behavior after controlling nanohetero-architectures can be extended further to manufacture portable FE devices and improve other functionalities for various applications.

5.8 References

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Chapter 6 Photoelectrochemical activities of Au@ZnO nano-heteroarchitecture

This chapter elaborates on the photoelectrochemical performance of controlled nano-hetero-architectures of 0D Au nanoparticles and 1D ZnO nanowires. The characterization techniques such as FESEM, TEM, HRTEM, XRD, and XPS performed are complimenting the observed PEC results.

6.1 Abstract

Heteroarchitectures have delivered phenomenal photoelectrochemical performance owing to their excellent physicochemical properties. We report on the utilization of controlled Au@ZnO nano-hetero-architectures for efficient water splitting. The ZnO nanowires of average length and diameter of ~ 5-6 µm and 120 nm, respectively, synthesized by the hydrothermal method, were subjected to the controlled decoration of Au nanoparticles of diameter ~ 20 nm. The cubic crystalline Au nanoparticles were decorated on the hexagonal wurtzite ZnO nanowires under controlled reaction time. The 12 h reaction time has resulted in the uniform decoration of Au nanoparticles along the surface of ZnO nanowires. A further increase in the reaction time ensued their agglomeration in the array of ZnO nanowires. The XPS analysis revealed the existence of a pure metallic Au on ZnO nanowires without altering the stoichiometry. The Au@ZnO nano-hetero-architecture with 12 h reaction time delivered maximum photocurrent density of 1.04 A/cm², is a 52-fold increase than that of pristine ZnO nanowires. The ABPE value of 0.59 %, which is approximately five-fold higher than the pristine ZnO nanowires. This reveals that the controlled decoration of Au nanoparticles along the surface of ZnO nanowires has significantly altered the Fermi energy position and expedited the electron injection from Au into the conduction band of ZnO, effectively.

6.2 Introduction

The energy consumption rate is expected to increase enormously with the industrial demands for the luxury of society. The environmental pollution and deterioration of non-renewable energy sources are projecting the scientific and industrial community to focus on clean, renewable, and sustainable energy sources to raise the daily energy needs. The abundant solar energy and the water sources are of particular attraction to put efforts in the development of highly efficient, eco-friendly, and clean energy technologies. Solar-driven artificial photosynthesis, i.e., water splitting for hydrogen generation, holds the potentials to come up with the present technological demands. Therefore, researchers across the world are focusing on the photoelectrochemical (PEC) water splitting. Among various kinds of nanostructured

morphology, the utilization of isolated zero-dimensional (0D) nanostructure providing a high surface area is limited due to charge recombination loss and charge trapping at grain boundaries. On the other hand, one dimensional (1D) nanostructures with a larger aspect ratio offer significant irradiation pathway, small diffusion length, and moderate recombination loss [1-4]. The relatively smaller surface area of 1D nanostructures than that of 0D morphologies limits the charge capturing capability in water-splitting reaction [5]. Hydrogen from the photocatalytic water splitting process. The local surface plasmon of 0D metallic nanoparticles by strong electron-electron scattering can improve the water splitting, but the tunable resonance and stability constrained the utilization to Ag and Au, only [6,7] Moreover, oxides of Cu, W Ti, Ni, and Fe, etc. [8-13] have been studied widely as a photoanode for PEC applications, owing to their excellent photoelectric performance for efficient solar energy conversion. The ZnO nanostructures have gained special attraction because of better intrinsic stability, faster charge mobility, efficient electron transformation, ecofriendly character, high photo corrosion resistance, etc. [14,15].

Limited efforts are made to draft the nano-hetero-architectures of Au and metal oxide semiconductors to improve photoanode performance. Chen et al. [5] reported the effect of plasmon excitation on Au nanostructures@ZnO nanorods array in the photochemical reaction. Wu et al. [16] employed a hydrothermal and photoreduction approach to growing the matchlike heterostructure of Au nanoparticles over the tip of ZnO nanorods. The photocurrent density reached 9.11 mA/cm², but the observed photoconversion efficiency of 0.48 % asked for additional optimization of Aucontent for further improvement. The polycrystalline branched ZnO nanowires transferred from ZnS after pretreatment were coated with Au nanoparticles through facile ionic layer adsorption. The limited loading of Au nanoparticles in the crowded 3D ZnO nanowires network restricted the photocurrent density to 1.45 mA/cm², and hence, the photoconversion efficiency to 0.52 % [17]. It was improved further to 3.02 mA/cm² for 3D honeycomb ZnO/GaN heterostructures anchored by multiwalled carbon nanotubes. The inevitable surface defects of GaN induced surface band bending and severely restricted PEC conversion efficiency [18]. Even though ZnO nanowires were coated with TiO₂ shells to improve electron-hole separation efficiency, but the

protective ability of TiO₂ produced a very low photocurrent of 0.40 mA/cm² [19]. Likewise, the Au nanoparticles were employed along with TiO₂ [20-23] and WO₃ [24] nanostructures to explore the possibility of improvement in the photo activities. The layer of Au nanoparticles drop-coated over the thin films of WO₃ nanoparticles produced the photocurrent density of 0.44 mA/cm² (at 1V) found suitable as photoelectrode for water splitting. Therefore, the comprehensive exploration of tunable nano-hetero-architectures of metallic 0D Au nanoparticles and 1D ZnO nanostructures for the utilization as photoelectrode/photoanode is of vital importance in the quest of enhanced photoelectric performance.

I report the synthesis of optimized nano-hetero-architectures of 0D Au @1D ZnO as a photoanode for water splitting in this work. 0D Au nanoparticles of various concentrations were decorated along the 1D ZnO nanowires body at optimized conditions to form controlled nano-hetero-architectures for efficient photoanode in photoelectrochemical (PEC) solar-driven water splitting. The decoration of Au along the surface of the ZnO rod body controlled with governing the reaction time and identified as pristine ZnO, Au@ZnO (8 h), Au@ZnO (12 h), Au@ZnO (24 h), and Au@ZnO (48 h). The influence of the pure metallic Au nanoparticles on the chemical, structural, and photoelectrochemical properties of ZnO nanowires was explored meticulously. The surface morphology and hetero-architecture formation are confirmed from field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and Ultraviolet Photoelectron Spectroscopy (UPS) studies were employed to reveal the crystal structural, purity of phase, chemical composition, and electronic structure of the pristine ZnO and hetero-architecture of Au@ZnO. The photoelectrochemical performance of the hetero-architectures of Au nanoparticle decorated ZnO nanowires analyzed at optimized conditions. The decoration of Au nanoparticles for 12 h over the surface of ZnO nanowires (i.e., Au@ZnO-12 h) revealed excellent PEC water splitting properties.

6.3 Experimental Section

The ZnO nanowires and Au nanoparticles were prepared independently by the hydrothermal reaction and citrate reduction methods. The Zinc Acetate dehydrates (C₄H₆O₄Zn.2H₂O, 98 %, Sigma Aldrich) and Sodium peroxide (Na₂O₂, 97 %, Sigma Aldrich) hydrothermally reacted at 85 °C for 12 h to grow large-area arrays of ZnO nanowires over the ITO coated glass substrate. A detailed protocol for the synthesis of ZnO nanowires is reported elsewhere [25]. Likewise, the Trisodium citrate (Na₃C₆H₅O₇; 0.1 gm @ 15 ml deionized H₂O) and Chloroauric acid (HAuCl₄; 12 mM/L @ 25 mL deionized H₂O) solutions were prepared at a controlled temperature of 98 °C and reacted together for 15 min to obtain Au nanoparticle of uniform dimensions. Thus, independently synthesized ZnO nanowires and Au nanoparticles were subjected to the formation of nano-hetero-architectures. Hexadecanethiol (HDT, 20 pmol/L) was added to the mobilized solution of Au nanoparticles to conform functionalization of Au nanoparticles along the ZnO nanowires. As-synthesized ZnO nanowires arrays were immersed in the mobilized solution of Au nanoparticles for 8, 12, 24, and 48 h. to ensure the controlled decoration of Au nanoparticles. Subsequently, the surface morphology of Au decorated ZnO nanowires was confirmed using a field emission scanning electron microscopy (FESEM, Carl Zeiss, Merlin 6073). Transmission electron microscope (TEM, TECNAI G2 instrument) with HRTEM was utilized to confirm the formation of single-crystalline ZnO nanowires and Au nanoparticles. The structural analysis was carried out using an X-ray diffractometer of Cu ka ($\lambda = 1.54056$ Å) (XRD, D8 advance, Bruker AXS). The chemical states and electronic structure of Au@ZnO nano-hetero-architecture were analyzed using an X-ray photoelectron spectrometer (XPS, Thermo Scientific Inc. Ka) with a microfocus monochromated Al Ka X-ray. The photoelectrochemical behaviors of working electrodes were tested using PEC three-electrode cell in 0.5 M Na₂SO₄ electrolyte (pH of 6.8) at ambient conditions. The Au@ZnO nano-hetero-architecture was used as a photoanode, a Pt as a counter electrode, and Ag/AgCl as a reference electrode. Photocurrent data was obtained at a scan rate of 10 mV/s with a potentiostat (PERSTAT 3000, Princeton Applied Research, USA, and Metrohm Autolab, M 204) under illumination using a solar simulator (300 W xenon lamp) set with 1.5 AM.

Moreover, the photocurrent transient responses were recorded by illuminating the sample with 365 by applying a small bias 0.3 V to prevail the ohmic losses in the electrolyte and metal contacts. The Ultraviolet Photoelectron Spectra (UPS) was obtained from the Omicron energy analyzer (EA-125, Germany) at angle incidence photoemission spectroscopy (AIPES) beamline on Indus-1 synchrotron source at RRCAT, Indore, India.

6.4 Field Emission Scanning Electron Microscopy

The randomly aligned hexagonal nanowires, smaller than the diameter of ~ 200 nm, were hydrothermally synthesized over ITO coated glass substrates. The surface morphological analysis of these hexagonal ZnO nanowires with clearly visible textural boundaries reported elsewhere [25] confirmed the average length and diameter of ~ 5-6 µm and 120 nm, respectively. The diameter of the nanowires has decreased further along the wire growth direction and resulted in the tip like appearance with the tip diameter up to 30 nm. (Figure 6.1(a)). The hexagonal ZnO nanowires grown over ITO coated glass substrates were subjected further to decorate Au nanoparticles along the surface. The reaction time up to 48 h leads to the controlled growth of Au nanoparticles over the surface of ZnO nanowires. FESEM images in Figure 6.1 (a & b) depict the decoration of Au nanoparticles over the surface of ZnO nanowires after the reaction time of 12 and 48 h, respectively. The FESEM images confirmed the random alignment of ZnO nanowires forming the dense forest of the tree-like morphologies. Their respective high-magnification FESEM images in the insets show the decoration of Au nanoparticles long the surface of ZnO nanowires. The reaction time of 12 h resulted in the well-distributed uniform decoration of Au nanoparticles along the surfaces of all hexagonal ZnO nanowires (inset of Figure 6.1(a)). Although traces of insignificant agglomeration of Au nanoparticles have been observed seldomly along the surface of nanowires, no agglomeration has been found between the nanowires. The increase in the reaction time for 48 h has further increased the actual accumulation/decoration of Au nanoparticles in the ZnO nanowire array. The increase in the concentration of Au nanoparticles reflected in their agglomeration, not along the textural boundaries of ZnO nanowires, but at the bottom end and in between the ZnO

nanowires (inset of Figure 6.1(b)), giving an impression of forming the composites of Au nanoparticles and ZnO nanowires.



Figure 6.1. FESEM images showing the decoration of Au nanoparticles over the ZnO nanowires at the reaction time of (a) 12 h. and (b) 48 h. The inset shows the (a) uniform decoration of Au nanoparticles along the facets of ZnO nanowires and (b) agglomeration of Au nanoparticles at the bottom of the ZnO nanowires array.

6.5 Transmission Electron Microscopy

The single ZnO nanowire decorated with Au nanoparticles for 12 h was extracted from the large area array to confirm the morphological feature of Au@ZnO nanowires. Figure 6.2 shows the surface morphology and crystalline nature of Au@ZnO nanowires obtained after the Au decoration of 12 h. The high magnification FESEM image (Figure 6.2(a)) shows the uniform decoration of Au nanoparticles along the hexagonal facets of ZnO nanowires without any agglomeration and/or altering the surface morphology of ZnO nanowires. Each Au nanoparticle decorated on the ZnO nanowires is nearly spherical with clearly visible textural boundaries. The diameter of

all the Au nanoparticles is ≤ 20 nm, with a limited variation of ~ 10 %. A statistical histogram of the distribution of the Au nanoparticle is shown in figure 6.2(b). The statistical histogram of Au nanoparticle distribution confirms that most nanoparticles are distributed in the range of 12-30 nm. However, the maximum number of Au nanoparticles are of diameter ~ 18-21 nm. The size distribution of Au nanoparticles fitted by log-normal size distribution function as follows [26]

$$f_N(x) = \frac{A}{x\sigma\sqrt{2\pi}} exp\left[-\frac{\ln[x/x]^2}{2\sigma^2} - -(6.1)\right]$$

Where x is the size of Au nanoparticles; $\overline{x} (= 19.03 \pm 0.49 \text{ nm})$ is the mean size of the Au nanoparticles; A (= 227.37 ± 39.66) is the initial constant; $\sigma (= 0.14 \pm 0.04)$ is the standard deviation in the size of Au nanoparticles. The log-normal distribution of Au particle diameter is asymmetric. The smaller standard deviation of the diameter distribution ($\sigma \le 0.25$) confirms that the Au nanoparticles are well confined to the limited diameter range.

Further, the Au@ZnO nanowires extracted from the large area array were examined to confirm the crystal structure and interface of Au nanoparticle and ZnO nanowire. Figure 6.2(c) reveals the crystal structure of both Au nanoparticles and ZnO nanowires for Au@ZnO nano-hetero-architectures obtained at the decoration time of 12 h. The TEM image showed the decoration of the ZnO nanowire of the diameter of ~ 100 nm with the Au nanoparticle of size ≤ 20 nm without any agglomeration. The high-resolution TEM image of the Au nanoparticle and the outer surface of ZnO nanowires in the upper left inset and lower right inset (Figure 6.2(c)) shows well defined independent lattice fringes for the highlighted portion of the Au@ZnO nanohetero-architecture. The lattice fringes spacing of 0.23 nm obtained for the Au nanoparticles (upper left panel of Figure 6.2(c)) is assigned to the (111) planes of the cubic crystalline phase. The interplanar spacing of 0.28 nm obtained on the outer surface nanowire body is akin to the (002) plane of the hexagonal wurtzite crystalline phase of pristine ZnO nanorods and not too metallic Zn [15]. Neither a thin layer of Au along the surface of the ZnO nanowire body nor the alterations in the crystal structure of the ZnO nanowires observed after the decoration of Au nanoparticles. This confirms that the Au nanoparticles are attached to the surfaces and not incorporated deep inside the ZnO nanowire.



Figure 6.2. (a) High magnification FESEM image, (b) statistical histogram for diameter distribution of Au nanoparticles, and (c) TEM image of the portion of hexagonal ZnO nanowire with the uniform decoration of distinct Au nanoparticles extracted from large area array of Au@ZnO (12 h). The inset in the (c) shows the HRTEM image of Au nanoparticles (upper left inset) and ZnO nanowires (bottom right inset) of the area marked by circle and rectangle, respectively.

6.6 X-ray diffraction analysis



Figure 6.3. X-ray diffraction pattern of (a) pristine and (b) Au nanoparticle decorated ZnO nanowires.

Furthermore, the X-ray diffraction studies were performed on both pristine ZnO nanowires and Au@ZnO nano-hetero-architectures to confirmed the formation of pure and crystalline nanostructures. Figure 6.3 shows X-ray diffraction of pristine and Au decorated ZnO nanowires deposited over ITO coated glass substrate. The XRD in the upper panel of Figure 6.3 shows the sharp characteristics peaks at $2\theta = 31.7^{\circ}$, 34.4° , 36.2° , 47.6° , 56.6, 62.8° , 66.9° , 67.9° and 69.0° of the crystalline planes of (Ω (002), (101), (102), (110), (103), (200), (112) and (201), for the hexagonal wurtzite crystal (JCPDS No.76-0704) assigned to the space group of P6₃mc with the lattice constant of a = 3.253Å, b = 3.253Å and c = 5.213Å. Moreover, additional peaks identified by asterisks (*) at $2\theta = 30.3^{\circ}$, 35.2° , 50.6° , and 60.2° are assigned to **t**e

crystalline planes of (222), (400), (441) and (622), respectively, for the ITO (JCPDS No: 39-1058, Space group: I2₁3). This confirms the formation of randomly oriented pristine ZnO nanowires without any impurity or defects. The XRD pattern of Au@ZnO in the lower panel (of Figure 6.3) obtained for 12 h Au decoration is akin to that of the pure ZnO nanowires provided in the upper panel, except the appearance of the prominent peak at $2\theta = 38.1^{\circ}$, which was absent in pristine ZnO. This peak is assigned to the (111) plane of cubic crystalline Au nanoparticles. Overall, XRD spectra showed a resemblance with the above-discussed TEM analysis, which reconfirms that the decoration of Au long the surface of hexagonal ZnO nanowires has not incorporated inside the nanowire body or altered the crystalline form of the ZnO nanowires.

6.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) employed for the qualitative investigation of electronic structures, chemical composition, and oxidation states of Au@ZnO. Figure 6.4 shows the high-resolution XPS spectrum of the core levels of the Zn(2p), O(1s), and Au(4f) recorded for the ZnO nanowires after the decoration of Au nanoparticle for 12 h. reaction time. All the spectra of the core-levels were decomposed via the Voigt curve fitting function within the Shirley background. Figure 6.4(a) illustrate Zn(2p) XPS spectra of Au@ZnO illustrate perfect fit for two distinct peaks of $Zn(2p_{3/2})$ and $Zn(2p_{1/2})$ located at the binding energy of 1020.9 (±0.1) and 1043.9 (± 0.1) eV, respectively, pertain to Zn⁺² cations [4,15]. Moreover, the observed spin-orbital splitting in Zn (2p) energy level, Zn(2p) split into of binding energy separation of 23.0 eV between the $Zn(2p_{3/2})$ and $Zn(2p_{1/2})$ core levels reflect the presence of oxidized Zn (i.e., ZnO) and not metallic Zn (i.e., Zn⁰) [25]. Figure 6.4(b) illustrates the deconvolution of O(1s) XPS spectra, with two separate peaks at the binding energy of 529.76 (\pm 0.1) and 531.30 (\pm 0.1) eV. The peak at 529.76 eV pertains to O²⁻ anion presence and the existence of surface contamination, i.e., hydroxyl type oxygen anion adsorbed on the surface of Au @ ZnO nanowires reflected from the peak at 531.30 [27]. The Au(4f) XPS spectra of Au @ ZnO were recorded to confirm the effect of Au decoration on the stoichiometry of the ZnO nanowires.



Figure 6.4. High-resolution XPS spectra of (a) Zn(3p) (b) O(1s) and (c) Au(4f) core levels Au@ZnO nano-hetero-architecture obtained at the reaction time of 12 h. The XPS spectra were deconvoluted via the Voigt curve fitting function within the Shirley background.

Figure 6.4(c) shows the high-resolution XPS spectra of core levels Au(4f)accompanied by the core levels Zn(3p). The deconvolution confirmed the presence of four distinct peaks assigned to the double peak features of $Zn(3p_{3/2})$ and $Zn(3p_{1/2})$ for Zn(3p) and Au(4 $f_{7/2}$) and Au(4 $f_{5/2}$) for Au(4f). The two peaks located at 88.3 (± 0.1) and 90.7 (\pm 0.1) eV with energy separation of 2.4 eV confirm the exitance of Zn(3p_{3/2}) and $Zn(3p_{1/2})$ core levels of Zn^{2+} cations [28]. However, the other two peaks at a binding energy of 82.9 (\pm 0.1), and 86.6 (\pm 0.1) eV separated with an energy of 3.7 eV reflects the Au($4f_{7/2}$) and Au($4f_{5/2}$) core levels of pure metallic Au exclusively. The blue shift of 1.6 eV in the position of Au $(4f_{7/2})$ and Au $(4f_{5/2})$ core levels observed after the decoration of Au on the surface of ZnO nanowires than that of the Au doped compounds [29] revealed the existence of pure metallic Au nanoparticles over the surface of ZnO nanowires and not of chemically reacted Au. It also indicates the strong exchange of electrons between the ZnO nanowires and Au nanoparticles [30]. Detail explanation of the reaction-time dependent variation in the amount of decoration of Au nanoparticles along the surface and within the array of ZnO nanowires is provided elsewhere [28].

6.8 Photoelectrochemical analysis

The photoelectrochemical (PEC) measurements were performed to confirm the effect of decoration of Au nanoparticles along the surface on ZnO nanowires in the PEC water splitting from the nano-hetero-architecture of Au@ZnO. Figure 6.5 shows PEC measurements performed in the 0.5 M Na₂SO₄ electrolyte under simulated solar light illumination. Figure 6.5(a) shows the linear sweeps measurements for pristine and Au decorated ZnO nanowires at a scan rate of 10 mV/s in the 0.5 M Na₂SO₄ electrolyte. The photocurrent density was negligible in dark conditions. However, after illumination, it has increased significantly, which extensively improved further for Au nanoparticles decorated ZnO nanowires. Especially, Au@ZnO nano-hetero-architectures obtained after the decoration of Au nanoparticles for 12 h gained maximum photocurrent density than those obtained for 8, 24, and 48 h. The photocurrent at zero bias is relatively similar for pristine and controlled Au decoration over ZnO nanowire, except Au@ZnO nano-hetero-architecture of 12 and 24 h reaction

time, which delivering photocurrent of 0.41 and 0.29 mA/cm², respectively. Moreover, the photocurrent density has linearly enhanced further with the increase in the applied potential. The photocurrent density of 0.424 mA/cm² observed at an applied bias of 1.5 V (vs. Ag-AgCl) in the dark has improved to 1.204 mA/cm² for pristine ZnO nanowires, which increased further to 1.693 mA/cm² after the decoration of Au nanoparticles for 8 h and gained maximum photocurrent density of 3.313 mA/cm² for 12 h (i.e., Au@ZnO 12 h). Further increase in the amount of Au decoration after a reaction time of 24 and 48 h has resulted in reduced photocurrent density to 2.375 mA/cm² and 0.271 mA/cm², respectively. The Au@ZnO nano-hetero-architectures consisting of homogeneously decorated Au nanoparticles delivered an 8-fold increase in the photocurrent density. These values of photocurrent density of Au@ZnO nanohetero-architectures are comparatively better than the Au nanoparticle decorated branched ZnO nanowires array [17], TiO₂ nanowires decorated with Au nanoparticles [20], Au nanoparticles decorated over WO₃ thin films [22], the core-shell structure of ZnO nanowires decorated with TiO_2 nanoparticles [19], TiO_2 nanotubes coupled with Au nanocrystal [21]. Moreover, the photocurrent density has not reached its saturation values for pristine, and Au decoration ZnO nanowires at an applied bias of 1.5 V. The enhanced absorption of visible light and efficient transfer of the electron at the interface of Au and ZnO might be the reasons to attribute for to the increase in the photocurrent density of Au@ZnO nano-hetero-architectures. Likewise, the enhanced photocurrent density for 12 h reaction shall be assigned additionally to the effective local surface plasmon and collective photon harvesting [5]. Further, the 24 and 48 h decoration of Au provided relatively more Au nanoparticles in the array. The maximum number of Au nanoparticles were agglomerated not along the textural boundaries of ZnO nanowires but at the bottom end and in between the ZnO nanowires. Which might have hindered the absorption of light, blocked the plasmonic effect of most of the Au nanoparticles, and easy access of the electron at the Au-ZnO interface.



Figure 6.5. PEC performance of pristine and Au decorated ZnO nanowires. (a) Photocurrent densities vs. potential (J-V) curves acquired for under dark, and light illumination condition, (b) the applied bias to potential conversion efficiency (ABPE %), (c) electrochemical impendence spectra, and (d) time-dependent photocurrent density measurements of pristine and Au decorated ZnO nano-hetero-architectures.

The effect of the Au decoration in the PEC efficiency of Au@ZnO nanohetero-architectures illustrated from the applied bias photon-to-current efficiency (ABPE) of pristine and Au decorated ZnO nanowires estimated by

ABPE (%) =
$$\frac{cm^2}{p} \frac{(\frac{mW}{m}) \times (123 - [V_{app}])(V)}{(\frac{mW}{m})} \times 100$$
 --(6.2)

Where J is the observed photocurrent density, $|V_{app}|$ is applied a potential to gain the photocurrent (i.e., J), P_{light} is the power density of the light source, and 1.23 V is the standard reversible potential for water. Figure 6.5(b) shows the potential dependent ABPE values estimated for pristine ZnO nanowires and Au@ZnO nano-hetero-architectures. The ABPE value of 0.16 % observed under illumination for ZnO

nanowires has improved further after Au decoration. The Au@ZnO nano-heteroarchitecture with 12 h reaction time delivered a maximum ABPE value of 0.59 %, which is approximately five-fold higher than then pristine ZnO nanowires. The reaction time of 8, 24 and 48 h of Au@ZnO nano-hetero-architectures delivered ABPE of 0.27 %, 0.40 % and 0.15 %, respectively. Moreover, the improved current density and ABPE of Au@ZnO (12 h) nano-hetero-architecture are significantly similar to Au NP's coupled BiVO₄/SnO₂ (\equiv 0.39 %) [31], TiO₂@rGO@Au (\equiv 0.38 %) [32], Au sensitized ZnO nanorods@ nanoplates (J = 0.06 mA/cm² & 0.69 %) [33], and Ag decorated ZnO nanorods (J = 0.32 mA/cm² & 0.53 %)[34], but are relatively larger than BiVO₄ (J = 0.5 mA/cm² & 0.3 %) modified with Ag metal (J = 1.7 mA/cm² & 0.5 %) [35], BiVO₄ nano-warm morphology (\equiv 0.002 %) [36], Au decorated TiO₂ nanorods [20], Sandwich structure ZnO/ZnS/Au (J = 0.58 mA/cm² & 0.21 %) [37], and Au functionalize ZnO nanowires (J = 0.75 mA/cm² & 0.13 %) [38].

The electrical properties, textural boundaries, and core of the nanostructures, play a dominating role in the photoelectrochemical activities, along with the amount of materials utilized as a catalyst. Therefore, the electrochemical impedance spectroscopy was used to understand their effect on the charge transfer of photoelectrodes. Typical Nyquist plots of pristine and Au decorated ZnO nanowires in the 0.5 M Na₂SO₄ electrolyte solution at a potential of 0.1 V (vs. Ag-AgCl) is shown in Figure 6.5(c). All the EIS spectra for ZnO nanowires and Au@ZnO nano-heteroarchitectures showed semicircular arc with various diameters confirming the variation in the charge transfer resistance at the semiconductor-electrolyte interface. The larger semicircular spectra of ZnO nanowires reduced further with an increase in the amount of Au decoration over it, which indicates the larger resistance at electrolyte interface offered by ZnO nanowires than that of Au@ZnO nano-hetero-architecture. The amount of metallic Au decorated along the surface of ZnO nanowires acted as a better electron source assisting ZnO nanowires and reflected in reduced diameter of the semicircle with more Au decoration. The reduction in the resistance evidence a faster charge transfer rate from the photoelectrode to the electrolyte after the decoration of Au nanoparticles over the ZnO nanowires. The lowest semicircular arc for 48 h decoration time of Au@ZnO nano-hetero-architectures indicates lower resistance due

to the high density and accumulation/agglomeration of Au nanoparticles, which contribute to increased concentration of photogenerated electron at the interface of photoelectrode. However, the lowest photocurrent density observed for Au@ZnO nano-hetero-architecture with Au decoration of 48 h is an interesting contradiction with the EIS measurements. Although the higher concentration of Au furnishes higher photoelectron generation, the corresponding self-blocking of photoelectrons by metallic Au nanoparticles contributes to faster recombination [5], and hence, the lower photocurrents even after their lowest resistance.

The photocurrent measurements of Au@ZnO hetero-architectures were carried out under visible light illumination with continuous ON/OFF cycles of 30 sec. Figure 6.5(d) depicts photocurrent densities measured at 3 V (vs Ag/AgCl) for continuous cycles of 360 sec. The photocurrent density of 0.02 A/cm² is observed for pristine ZnO nanowires, which is further enhanced after the controlled declaration of Au nanoparticles. The maximum photocurrent density of 1.04 A/cm² observed for the decoration of Au nanoparticles for 12 h over the ZnO nanowires is a 52-fold increase than that of pristine ZnO nanowires. The optimal repeatability/stability with negligible reduction of the photocurrent for various ON-OFF cycles is in consonance with the CoNi@ZnO core-shell structures [39], sol-gel driven core-shell structure of 0D TiO₂ nanoparticle over 1D ZnO nanowires [19], Au nanoparticle decorated WO₃ thin films [22], and Au loaded branched ZnO nanowires [17]. The well-controlled declaration of Au nanoparticles along the textural boundaries of ZnO nanowires has delivered a larger photocurrent density than the Au decorated branched ZnO nanowires synthesized by chemical route [17]. The photocurrent density has reduced with a further increase in the Au decoration time to 24 and 48 h. The variation in the photocurrent density is attributed to the generation and recombination of photo electron-hole pairs. The even distribution and agglomeration of Au nanoparticles in the array of ZnO nanowires might have self-blocked photo-generated electron-hole pairs and further reduced the photocurrent generation.

6.9 Ultraviolet Photoelectron Spectra



Figure 6.6. UPS valance bands spectra utilized to evaluate the Fermi energy level of Au@ZnO nano-hetero-architecture.

The Fermi energy levels of hetero-architectures consisting of metallic Au nanoparticles and semiconducting ZnO nanowires attain equilibrium and assists in the easy electron transfer after illumination. Therefore, the Fermi level of Au decorated ZnO hetero-architectures is estimated from Ultraviolet Photoelectron Spectra (UPS) recorded at an energy of 23 eV. The apparent changes in the shape of the valance band spectra of pristine and Au nanoparticle decorated ZnO nanowires showing two distinct peaks of nonbonding O(2p) orbital and hybridization of the O(2p) and Zn(4s) orbital is reported elsewhere [25,28]. The decoration of Au nanoparticles along the ZnO nanowires has resulted in a reduction in the work function from 4.9 to 4.3 eV [25,28], where the Fermi energy of Au@ZnO hetero-architecture is ~ 2.74 eV (± 0.1 eV) (Figure 6.6). Therefore, easy electron transfer is expected from Auto ZnO at the interface of the Au@ZnO nano-hetero-architecture. The Schottky barrier height at the Au/ZnO interface can be tailored by altering the dimensions of the Au nanoparticles [40, 41]. However, in the present case, the decorated Au nanoparticles are confined to the uniform diameter of 20 nm to understand the effect of Au concentration along the ZnO nanowires (i.e., Au@ZnO) in the enhancement of photoelectrochemical activities.

$Glass 2H + 2e H_2$ $Glass 2H' + 2e + V_2O_2 H_2O$ $Glass 2H' + 2e + V_2O_2 H_2O$

6.10 PEC charge-separation mechanism

Figure 6.7. Schematic representation of (a) the PEC device, (b) the charge-separation mechanism of typical Au decorated ZnO nano-hetero-architecture. A single ZnO nanowire decorated with Au nanoparticles is shown on the right side of (a).

Figure 6.7(a) shows the schematic representation photo-electrochemical cell consisting of large-area arrays of Au@ZnO nanowires grown over the ITO coated glass as an active photoelectrode and Pt electrode as a reference electrode. Under the light illumination, the incident photon energy absorption at the pristine ZnO nanowire excites the electrons of the valence band to the conduction band by leaving a hole behind and contribute to the reduction process at the Pt electrode, whereas the leftover holes during the process participate in the oxidation reaction. The decoration of Au nanoparticles assists this process of ZnO nanowires. The electron transfer mechanism of the Au@ZnO photoanode assisting the PEC water splitting under light illumination is schematically represented in Figure 6.7(b). The large bandgap of the ZnO relatively hamper the electron-hole pair formation and further restrict the photocurrent density and photo-electrochemical performance [42]. However, Au being the larger electron source, facilitates efficient charge separation by capturing the photo-generated holes,

leaving electrons in ZnO. The holes will be quenched subsequently by a sacrificial hole trap. Because the majority of electrons are generated close to the surface without recombination, and they will reduce hydrogen ions in the aqueous solution by forming hydrogen gas. The uniform decoration of Au nanoparticles along the ZnO surface for 12 h reaction time might have significantly captured the photo-generated holes of ZnO. But further agglomeration of Au nanoparticles could not improve this process of hole capturing.

6.11 Conclusions

In conclusion, we have demonstrated the utilization of a large area array of Au@ZnO nano-hetero-architectures for efficient photoelectrochemical performance. Hexagonal ZnO nanowires synthesized by the hydrothermal method were subjected to the formation of Au@ZnO nano-hetero-architectures under controlled Au decoration time. The 12 h reaction time has resulted in the uniform decoration of Au nanoparticles along the surface of ZnO nanowires, a further increase in the reaction time ensued their agglomeration in the array of ZnO nanowires. The TEM and XRD analysis confirmed that the cubic crystalline Au nanoparticles were decorated on the hexagonal wurtzite ZnO nanowires under controlled reaction time. The well spherical and uniformly distributed Au nanoparticles effectively improve the light-harvesting capability resulting in an enhancement in solar-driven photoelectrochemical (PEC) water splitting performance. The 0D Au @ 1D ZnO obtained after 12 h decoration has conceived a maximum photocurrent density of 1.04 mA/cm² and ABPE value of 0.59 %, which is 52-fold and 5-fold higher than pristine ZnO nanowires, respectively. In the case of Au@ZnO-12 h nano-hetero-architectures, the controlled homogeneous dispersion of Au nanoparticles along the surface of ZnO nanowires has altered the Fermi energy position, and expedited injection of hot electrons from the SP state of Au into the conduction band of ZnO might be the reason to deliver the enhanced photocurrent density.

6.12 References

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Chapter 7 Summary and Conclusions

This chapter includes the summary and conclusion of the thesis. I have briefly discussed the outcomes of my research work explained in chapters 3 to 6. At the end of this chapter, I have discussed the future scope to continue this work.

7.1 Summary and Conclusions

ZnO nanostructure morphologies are explored to control electronic properties for their potential exploration in multifunctional applications. The larger work function (i.e., 5.3 to 5.6 eV), limited vertically aligned morphological forms, and field screening effect from uncontrolled dispersion of ZnO left with the alternative of modification in the geometry, induction of impurities, and decoration of metal nanostructures for applications in field emission. Likewise, high working temperature (i.e., 300-500 °C) induces secondary grain growth caused instability, inaccuracy, high power consumption, and lack of durability in the sensing mechanism of ZnO. Therefore, reducing the operating temperature range of ZnO nanostructures for sensing the flammable and toxic gases in the detection safety limit of 50 ppm was a critical challenge. Moreover, besides better intrinsic stability, faster charge mobility, efficient electron transformation, eco-friendly character, and high photo corrosion resistance, the ZnO nanostructures asked for doping or decorating noble metal particles to improve light absorption and photocurrent density for enhanced PEC performance. Therefore, my efforts were directed towards the synthesis of welldefined hierarchical growth of the sharp tip featured morphologies of ZnO, and the formation of its controlled nano-hetero-architectures with the Au nanoparticles, for applications in field emission, gas sensors, and PEC water splitting.

The hierarchical morphologies of ZnO nanowires were synthesized over a large area on ITO coated glass substrates at an optimized reaction time of 12 h. and temperature of 85 °C utilizing a hydrothermal approach. The 0D Au nanoparticles of uniform dimensions were synthesized under a controlled temperature of 98 °C using the citrate reduction method. The independently synthesized ZnO nanowires and Au nanoparticles were subjected to the formation of their nano-hetero-architectures. Assynthesized ZnO nanowires arrays were reacted with Au nanoparticles for 2, 4, 8, 12, 24, and 48 h to ensure the controlled decoration of Au nanoparticles. The spitzer shaped 1D hexagonal ZnO nanowires synthesized in the hierarchical form on ITO coated glass substrates. The ZnO nanowires of average diameter ~ 120 nm and length of ~ 5-6 μ m, which were further decorated with the 0D Au nanoparticles of the average diameter of ~ 20 nm to form heteroarchitectures. These 1D ZnO nanowires and 0D

Au@1D ZnO nano-heteroarchitectures were characterized methodically to understand their morphological, structural, chemical, and electronic properties. The observations on the field emission and gas sensing behavior of ZnO and field emission and PEC water splitting of 0D Au@ 1D ZnO nano-heteroarchitectures are thoroughly discussed in Chapter 3, Chapter 4, Chapter 5, and Chapter 6, respectively. Following is a summary of my observations.



Figure 7.1. FESEM image of spitzer shaped ZnO nanowires (left panel) and their schematic band diagram (right panel)

Spitzer shaped ZnO nanowires arranged like the forest of well separated and periodically organized Christmas trees (Figure 7.1 left panel). The spitzer shaped 1D hexagonal ZnO nanowires of truncated and very sharp pointed tips resulted in a smaller work-function of 4.9 eV. The reduced work function of ZnO nanowires provided a significantly smaller barrier for direct emission of an electron toward the emission site (Figure 7.1 right panel) and contributed to the lowest turn-on field of

 $1.56 \text{ V/}\mu\text{m}$ and stable electron emission (i.e., average current fluctuations of $\pm 5 \%$). These ZnO nanowires hold capabilities to reduce the work-function further and improve the electron emission, as well to expand other functionalities for various applications after controlled designing of nano-hetero-architecture with metals or high conducting materials.



Figure 7.2. Sensing mechanism of hierarchically arranged ZnO nanowires (upper panel) and their DFT analysis (lower panel).

The larger surface area and increased point contacts of hierarchically arranged ZnO nanowires in the form of well-constituted Christmas trees (Figure 7.2 upper panel) delivered excellent sensing performance in the detection safety limits of 50 ppm for CO, C₂H₅OH, and NH₃ gases at relatively lower operating temperatures of 100 °C. The ZnO nanowires provided 29 and 98 % response for CO and C₂H₅OH, respectively, but the maximum sensing response of 115 % was recorded for toxic NH₃ gas. Furthermore, ZnO nanowire delivered a faster response and recovery time of 27 and 9 sec, respectively, for 50 ppm NH₃ at the temperature of 100 °C, which is better than the variety of pristine, defect controlled, and doped ZnO nanostructures. The experimental observations agree with complementary DFT calculations, which predict the order of gas molecules binding strength to be CO < C₂H₅OH < NH₃ (Figure 7.2 lower panel). The excellent sensing response of hierarchical hexagonal ZnO nanowires is ascribed to the well defined hexagonal morphology, clearly visible textural boundaries, single-crystalline nature, and well interconnections of the nanowires

owing to hierarchical morphology. The 1D ZnO nanowires hold great potentials for further improvement in the sensing performance after forming tunable heteroarchitectures with metal nanoparticles.



Figure 7.3. FESEM images of Au nanoparticles decorated (left panel) spitzer shaped and tipped ZnO nanowires (right upper panel), and their schematic band diagram (right lower panel)

The controlled nano-hetero-architectures of Au nanoparticles decorated (Figure 7.3, left panel) spitzer shaped and tipped ZnO nanowires (Figure 7.3, right upper panel) resulted in a lower work-function of 4.3 eV (right lower panel). Au/ZnO/ITO emitters have significantly reduced E_{on} to 0.96 V/µm and showed highly stable electron emission (with current fluctuations of ± 4 %) of the electron, besides larger emission current density of 2.1 mA/cm² at a lower applied field of 1.92 V/µm. The decoration of Au along the surface of ZnO nanowires dramatically increased the density of state and reduced work function for a reaction time of 24 h, which induced almost all emitted electrons to transfer quickly towards the emission sites, is responsible for the enhancement in FE behavior and reduction in E_{on} (Figure 7.3, right lower panel) The tunable nano-hetero-architecture of Au decorated ZnO nanowires of sharp-tip morphology have the potential to be a promising candidate for applications

in field electron emission based vacuum micro/nano-devices including flat-panel displays and intense point electron source.



Figure 7.4. TEM images of Au nanoparticles decorated ZnO nanowires (left and right upper panel) and their schematic band alignment (lower left panel)

The well spherical Au nanoparticles uniformly distributed on the hexagonal wurtzite ZnO nanowires under controlled reaction time have effectively improved the light-harvesting capability and resulted in an enhancement in solar-driven PEC water splitting performance. Au@ZnO nano-hetero-architecture of uniformly decorated Au nanoparticles along the surface of ZnO nanowires (Figure 7.4, right upper panel) evidence the surface attachment and not chemical reaction of Au with ZnO at the interface nanowires (Figure 7.4, left panel). The 0D Au @ 1D ZnO obtained after 12 h decoration has conceived a maximum photocurrent density of 1.04 mA/cm² and ABPE value of 0.59 %, which is 52-fold and 5-fold higher than pristine ZnO nanowires, respectively. In the case of Au@ZnO-12 h nano-hetero-architectures, the controlled homogeneous dispersion of Au nanoparticles along the surface of ZnO nanowires has altered the Fermi energy position, and expedited injection of hot electrons from the SP state of Au into the conduction band of ZnO might be the reason to deliver the enhanced photocurrent density (Figure 7.4, right lower panel).

7.2 Future Scope

The present studies involve the synthesis, characterization of 1D hexagonal

ZnO nanowires, and 0D Au@ 1D ZnO nano-heteroarchitecture for applications field electron emission, gas sensor, and PEC water-splitting. Nevertheless, this methodical and thorough investigation leaves the scope for exploring the doping and decoration of various metal nanostructures with the ZnO or other related metal oxides, such as,

- a) Study the effect of various dimensions and morphologies of Au nanoparticles on the performance of ZnO nanowires.
- b) Study the effect of decoration of different metal nanoparticles (Ag, Pt, and Pd) over the ZnO nanostructure in the field electron emission, gas sensing, and PEC water splitting behaviors.
- c) Study the effect of doping of metals in the ZnO nanostructures. The effect of doping would be interesting in field emission and gas sensing performance.
- d) A comparative study on the effect of doping or decorating Au nanoparticles on the sensing and emission performance of various metal oxides.