# SOLUTION-GROWN CHALCOGENIDE SEMICONDUCTING MATERIALS FOR WATER PURIFICATION AND SPLITTING

Ph.D. Thesis

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# DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2021

# SOLUTION-GROWN CHALCOGENIDE SEMICONDUCTING MATERIALS FOR WATER PURIFICATION AND SPLITTING

# A THESIS

Submitted in fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

*by* MUKURALA NAGARAJU (1601281003)

Under the supervision of

Dr. Ajay Kumar Kushwaha and Dr. Amrendra Kumar Singh (Co-supervisor)



# DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2021



# INDIAN INSTITUTE OF TECHNOLOGY INDORE

# **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **SOLUTION-GROWN CHALCOGENIDE SEMICONDUCTING MATERIALS FOR WATER PURIFICATION AND SPLITTING** 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 26<sup>th</sup> December 2016 to 1<sup>st</sup> June 2021 under the supervision of Dr. Ajay Kumar Kushwaha, Department of Metallurgy Engineering and Materials Science and Dr. Amrendra Kumar Singh (Co-supervisor) Department of Chemistry.

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

Signature of the student with date (MUKURALA NAGARAJU)

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

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MUKURALA NAGARAJU has successfully given his Ph.D. Oral Examination held on 8th October 2021.

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Mukurala Nagaraju

Dedicated To

My family members

# LIST OF PUBLICATIONS

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3. <u>Nagaraju Mukurala</u>, S. Suman, A. Bhardwaj, K. Mokurala, Sung Hun Jin and Ajay K. Kushwaha<sup>\*</sup>, "Cu<sub>2</sub>FeSnS<sub>4</sub> decorated Ni-TiO<sub>2</sub> nanorods heterostructured photoanode for enhancing water splitting performance" **Applied Surface Science**, 551, 149377 (2021).

4. <u>Nagaraju Mukurala</u>, Lokanath Mohapatra, M. Krishnaiah and Ajay K Kushwaha\*, "Surface controlled synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles for enhanced hydrogen evolution reaction" **International Journal of Hydrogen Energy**, 46, (2021), 34689-34700.

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## ABSTRACT

The earth-abundant chalcogenides materials have shown a good presence in photovoltaic devices, but limited investigations are in the area of photocatalytic and water splitting toward the production of hydrogen. The Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) has lesser change to form bimetallic phases during growth and better stoichiometry can be achieved. The solution-based approach is investigated to grow the various type of materials morphologies. Due to tunability of the surface properties of solution grown CFTS, it become interesting to understand their effect on various properties of materials and subsequently over photocatalytic and photo-electrochemical water splitting properties. The water purification and photo-electrochemical water splitting both process are related to photogeneration and separation of the electron under photoexcitation. Hence, the development of efficient materials for solar (photo) driven catalytic process is the central theme of the thesis work. Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles by solvothermal process and effect of temperature, reaction time, solvents on structural, morphological, and optical properties are investigated. The variation in reaction temperature varies the crystallinity of the CFTS particles and synthesis at 200°C results in better crystallinity. The temperature variation also results in a significant difference in morphology (aggregate particles, sphere-sheet and intermixed with the aggregate-sheet) of CFTS particles. The bandgap of the CFTS particles also gets changed from 1.42 eV to 1.5 eV after varying the synthesis temperature. Similarly, the change in synthesis time leads to form porous-sphere, sheet-flakes, and intermixed flower-sheet morphologies of CFTS particles and variation in crystallinity. There is variation in the elemental composition is observed when different the synthesis is carried out at a different temperature and for different time duration. However, annealing in the Sulphur atmosphere leads better crystalline CFTS in the stannite phase.

Further, variation in solvent also shows a significant impact on morphologies of CFTS particles, flower, larger grain structure, aggregate particles, and agglomerated particles are obtained when different solvents are used. The different solvent results in the slightly different elemental composition of the CFTS particles. The bandgap of CFTS particles also varies from 1.43 eV to 1.7 eV when different solvents are used. Different sulphur precursors namely thiourea, thioacetamide, sulphur powder and sodium sulphide are also used for the synthesis of CFTS particles. The CFTS particles have noticeable variation in morphology, crystallinity, and

elemental composition when different sulphur precursors are used. The thiourea results in better crystallinity, stoichiometry and larger size grains of CFTS particles. In addition, different morphologies of CFTS particles (with surface controlled) are obtained when different surfactants i.e. thioglycolic acid (TGA), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) are used. The PVP as a surfactant result in a better crystalline phase, while impurity phases are observed in TGA, PVA. The significant change in morphology (porous particles, highly porous particles having nanosheets-nanoparticles on the surface, and uniform spherical) of CFTS particles are obtained by changing the surfactant in the synthesis process.

The application of  $Cu_2FeSnS_4$  (CFTS) particles in water purification is studied via photocatalytic and adsorption approaches. In one of the studies, the CFTS particles synthesized using different Sulphur precursors are tested for water purification. The CFTS particles synthesized using thiourea have shown the best results, and approximately 70% methylene blue dye is degraded in 60 min under white light excitation. In another study, porous CFTS particles are adopted to study the removal of organic acid fuchsin dye pollutant from wastewater by adsorption process. The porous spheres of CFTS particles have shown approximately (89.25  $\pm$ 2.21) % of acid fuchsin (AF) dye adsorption within 10 min and the value reaches (97.12  $\pm$  0.76) % in 60 min. The high adsorption capacity i.e.  $(123.12 \pm 2.09)$  mg/g is obtained for porous spherical CFTS particles. The adsorption isotherm and kinetic studies reveal that the Langmuir isotherm and pseudo-second-order kinetic model can explain the dye adsorption. The highest adsorption capacity (128.12 mg/g) and 98% acid fuchsin (AF) dye adsorption observed within 60min when porous sphere CFTS is used as an adsorbent. Further, the porous CFTS particles exhibit good stability and reusability of the adsorbent for wastewater purification. Further, the application of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles in water splitting towards hydrogen production is also investigated via electrocatalytic and photo-electrochemical methods. In the first study, different morphologies of CFTS particles are investigated to test the electrocatalytic ability for hydrogen evolution reactions (HER). CFTS particles with highly porous surface having nanosheetnanoparticles on surface (grown using PVP) exhibit excellent electrocatalytic performance. While photo-electrochemical water splitting performance of CFTS is tested with Ni-doped TiO<sub>2</sub> nanorod structure. The earth-abundant and visible light-sensitive Cu<sub>2</sub>FeSnS<sub>4</sub> layer is decorated on Ni-TiO<sub>2</sub> nanorods (CFTS/Ni-TiO<sub>2</sub> NRs) using a wet chemical approach. In which Ni-doped TiO<sub>2</sub> nanorod are hydrothermally grown. These heterostructure photoanodes demonstrated a significant increase in photocurrent from 0.730 mA/cm<sup>2</sup> to 2.09 mA/cm<sup>2</sup> (at 1.23V *vs* RHE). The lifetime of photogenerated charge carriers also improves and CFTS/Ni-TiO<sub>2</sub> NRs exhibit excellent photo-electrochemical properties with high stability; hence this heterostructure can be a potential candidate for solar energy device applications.

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# Abbreviations

Ag/AgCl	Silver/silver chloride electrode
AF	Acid Fuchsin
BET	Brunauer-Emmett-Teller
CB	Conduction Band
DI	Deionized Water
DMF	N, N-Dimethyl Formamide
EDA	Ethylenediamine
EG	Ethylene Glycol

EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FTO	Fluorine-Doped Tin Oxide
FTIR	Fourier-Transform Infrared Spectroscopy
FE-SEM	Field Emission-Scanning Electron Microscopy
FWHM	Full Width Half Maximum
GCE	Glassy Carbon Electrode
HCL	Hydrochloric Acid
HER	Hydrogen Evolution Reaction
JCPDF	Joint Committee Powder Diffraction Date file
LSV	Linear Sweep Voltammetry
MG	Malachite Green
MB	Methylene Blue
M-S	Mott-Schottky
NAs	Nanowire Arrays
NRs	Nanorods
OLA	Oleyl Amine
OER	Oxygen Evolution Reaction
PVP	Polyvinyl pyrrolidone
PVA	Polyvinyl Alcohol
PECWS	Photo-Electrochemical Water Splitting
PZC	Point Of Zero Charge
RhB	Rhodamine Blue
RHE	Reversible Hydrogen Electrode
TGA	Thioglycolic Acid
UV	Ultraviolet-visible spectroscopy
VB	Valence Band
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

# CHAPTER-1 Introduction and Literature Review

## **1.1 Introduction**

Energy and drinking water both are essential for development and survival of humans. The energy become the primary tool for social and industrial development. Simultaneously, the availability of good quality drinking water is existing challenge to our society. The discharge of various toxic pollutants in water has now prompted a worldwide scarcity of fresh water. The rapid growth of industrialization has increased the severity of water pollution by releasing the toxic contaminants without filtration or purification [1]. Therefore, development of strategies to scavenge organic pollutant from wastewater to make it reusable has attracted sincere attention in recent past. The removal of diverse range of organic pollutants from wastewater are being developed by cost effective and sustainable processes [2]. The process employed to remove non-biodegradable contaminants (organic as well as inorganic wastes) and biological waste materials from the water is known as water purification. Techniques such as adsorption, photocatalysis are extensively investigated for water purification due to efficient, economical, scalable and environmentally friendly approach [2–4].

Photocatalysis have shown excellent potential when a nanostructured catalyst are used as a medium to degrade various pollutants present in the water [5]. The degradation of harmful and toxic organic pollutants has been investigated using various types of metal/semiconductor nanomaterials such as TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, etc. Most of them are wide bandgap materials and hence the use of UV radiation for their excitation creates a barrier for large scale utilization of these materials and limit the efficiency of the degradation process [6]. Recently, ptype Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) chalcogenide material was also proposed as an alternative material for dye degradation. It has high absorption coefficient (10<sup>4</sup> cm<sup>-1</sup>), minimal cost, earth-abundant and non-toxic nature [7]. The water purification has also been reported using adsorption process. Interplay between adsorbate-adsorbent synergic surface interactions give rise to adsorption phenomenon. Higher surface-to-volume ratio, layer by layer structure and adequate mechanochemical stability for faster contaminant degradation are some essential features of efficient adsorbent materials. Various nanomaterials such as metal oxides [5,8], MXenes (transition metal carbides and carbonitrides) [9,10], polymer nanocomposites [11,12], Zeolites [13] and carbon nanomaterials [14,15] have been used as adsorbents for water purification. Similarly, earth-abundant chalcogenide Cu<sub>2</sub>FeSnS<sub>4</sub> material was also incorporated as an adsorbent for removal of methylene orange from contaminated water reported by L.Ai et al. [16]. Considering the potential of copper-based chalcogenides for water purification either by photo-catalyst or adsorption based, it has motivated us to investigate the Cu<sub>2</sub>FeSnS<sub>4</sub> materials further. Solution-based approach on various properties of the materials and its role in water purification via photocatalytic and adsorption is studied in detail. Since the Cu<sub>2</sub>FeSnS<sub>4</sub> materials are showing excellent catalytic activity under solar light and specific adsorption capability due to specially designed porous structure, dual benefit can be explored for water purification.

The environment-friendly fuel is another necessity of human being for sustainable development because fossil fuels generally releases greenhouse gases which cause global warming and climate changes. Sincere efforts are required to develop clean, reliable, and sustainable energy resources. Hydrogen is one such fuel which does not emit pollutants and can be produced via an environmentally green process using solar energy. To date, 95% of hydrogen fuel is generated by fossil fuels, only 4% from electricity and 1% from biomass [17]. A sustainable way to produce hydrogen gas can be solar-driven water splitting. In 1972, Fujishima and Honda, generated H<sub>2</sub> gas from water by solar light source using TiO<sub>2</sub> based electrode as anode and Pt as cathode material. Among several nanomaterials metal oxides and metal sulfides are deployed in the past decades for the application of solar-driven water splitting [18,19]. Wide band gap materials can access only a narrow range of solar radiation for absorption and also suffers from higher recombination of charge carriers, poor stability in aqueous solution and photo corrosion. To overcome such problems and to enhance photoelectrochemical (PEC) performance, metal doping, surface modification, and heterostructure formation have been proposed, which lead to faster charge carrier transfer and separation, improving optical absorption ability [20]. Although doping is an efficient strategy to tailor opto-electronic characteristics of metal oxides yet limitations like thermal instability and impurities in semiconductors causes lower recombination of e<sup>-</sup>- h<sup>+</sup> pair result in lower performance of PEC devices. Similarly, many reports have revealed that surface modification of the photo-electrodes gradually increasing the PEC performance [21]. The development of heterostructures offers to

harvest of a wider range of solar spectrum. It can boost the photo-excited separation of charge carriers that can potentially reduce their recombination process, thus improving the PEC performance.

In recent years, the TiO<sub>2</sub>/Cu<sub>2</sub>O heterojunction based photo-electrode exhibits excellent photo-stability, with current density around 2.3 mA/cm<sup>2</sup> during light illumination [22]. Approximately 23 times higher photocurrent has reported when uniform CZTS layer constructed covering the entire surface area of TiO<sub>2</sub> nanowire arrays (NWs) electrode [23]. Hence, the surface coating of visible light active materials on wide band gap materials has shown promising solar-driven electrochemical water splitting. The one-dimensional nanostructured platform-based electrodes further enhance the performance i.e TiO<sub>2</sub> nanorods coated with earth-abundant chalcogenides semiconductor. Henceforth, our studies are also dedicated to developing the doped TiO<sub>2</sub> nanorod then coating with Cu<sub>2</sub>FeSnS<sub>4</sub> to prepare the heterostructured electrode for photoelectrochemical water splitting. In this thesis, Cu<sub>2</sub>FeSnS<sub>4</sub> has been consider as primary materials. The solution-based approach is investigated to grow the various type of materials morphologies. Due to the tunability of the surface properties of solution grown Cu<sub>2</sub>FeSnS<sub>4</sub>, it become interesting to understand their effect on various properties of materials and subsequently over photocatalytic and photo-electrochemical water splitting properties. Further, we investigated Ni-doped TiO<sub>2</sub> nanorods by hydrothermal method as base platform, then the CFTS decorated Ni-TiO<sub>2</sub>NRs based heterostructure for photo-electrochemical water splitting performance are studied.

# **1.2 Water purification**

Water purification is a process in which diverse range of non-biodegradable contaminants (organic as well as inorganic wastes) and biological waste materials are scavenged from the wastewater [24] to provide drinkable fresh water. Regular excretion of various toxic pollutants in the fresh water has prompted a worldwide catastrophe of wastewater pollution. The escalated industrialization and tremendous population explosion since last century gave rise to a hike in the release of toxic organic pollutant into the nature [25,26]. As a outcome, only 3% of water is considered pure out of 75% ground water, where only 1% of water is drinkable. Several toxic compounds are releasing from the industry, municipal waste, and domestic wastes, which leads to contaminate the water and soil resources. The wastewater not only decreases the freshwater

resources but also affects the environment and waterborne disorders [27]. The various pollutants produce from the different industries, for example, dye is considered to be harmful because numerous dyes exhibit cytotoxicity to many organisms either in a direct or passive manner through their absorption. Dyes are majorly generated as the excretion products of various industries viz., paper, food, textile, cosmetic, plastic, and leather [1,28]. The detrimental effects of these dyes are not only limited to a long lasting cytotoxicity in the organisms but also affect the quality of drinking water resources. Higher concentration intake of such chemicals results in vomiting, heart disorders, and tissue necrosis in humans [29]. Dyes can be broadly categorized as Cationic/ basic dyes and Anionic/ acidic dyes. A commonly available cationic dye is Malachite green (MG) which is extensively used for its disinfecting properties and is also a well reputed coloring agent for varieties of industrial clothing materials. MB dye causes carcinogenic, mutagenic, and affects mammal cell. These dyes affect the kidneys, liver, bowels and gonads of organisms [30]. Methylene Blue (MB), another commonly available dye, is employed to color cotton and silk materials and its over exposure to the skin causes mechanical irritation which results in soreness and itching.



Figure 1.1: Various methods for water purification [31].

Quantitative scavenging of such contaminating dyes from water resources has gathered a globally indispensable research interest because the presence of even tiny portion of them is

considered detrimental to human/ animal health and also easily realized with naked eyes. In this context, several techniques, such as adsorption, photo-catalysis, membrane separation, photo-electrocatalysis, reverse osmosis along with biological precipitation, electrochemical approaches, ion exchange, and desalination, are being utilized for water purification [2–4]. Among these, adsorption and photo-catalysis has been proved to be very facile, efficient, economically scalable, environmentally friendly processes [31].

# **1.3 Water purification using photocatalyst**

## **1.3.1** Principle of photocatalysis

Photo-catalysis is a promising technique for water purification that uses catalyst (semiconductor) as a medium to degrade various pollutants present in the water using a solar light source [32]. Photo-catalysis technique utilizes various radiation wavelengths of solar spectrum (ultraviolet, visible, and infrared radiation) to accelerate the chemical reaction rate. Typically, after absorbing a certain range of radiation, a photo-catalytic material gets involved in the chemical transformation of the pristine reactant species [33]. Generally, semiconducting materials are considered for catalytic medium in photocatalytic degradation, which generates charge carriers due to absorbing light energy higher than its bandgap energy [34]. The photogenerated  $e^{-}h^{+}$  pair produces highly reactive radicals, such as super oxides (O<sub>2</sub><sup>-</sup>), hydroxyl ions (OH<sup>-</sup>) in water. These radicals, thereafter, lead to secondary reaction pathways to break down the otherwise non-degradable organic/inorganic molecules remaining in the wastewater. The contaminant degradation may also take place by directly transferring the photo-generated  $e^{-}h^{+}$ from surface of catalyst to contaminant molecules. Figure 1.2 depicted the process of photocatalysis that occurs over a nano-dimensionally fabricated semiconducting catalyst surface. Photocatalysis can be recognized as a surface phenomenon which can be explained as a sequential combination of five fundamental steps [35].

(i) reactant diffusion to the catalyst surface, (ii) reactant adsorption on the catalyst surface, (iii) occurrence of chemical reaction at catalyst surface sites, (iv) Desorption of the newly transformed species from catalyst surface, followed by (v) product diffusion drifting away from the catalytic surface. The possible course of degradation of organic pollutants (example: MB, RhB) in water through photocatalysis is shown in the following equations [33].

Semiconductor + 
$$h\vartheta \rightarrow h^+$$
 (VB) + e<sup>-</sup> (CB) (1.1)  
 $H_2O + h^+(VB) \rightarrow OH^* + H^+(aq)$  (1.2)  
 $O_2 + e^-(CB) \rightarrow O_2^-$  (1.3)

$$2H^{+} + 0_{2}^{-} \rightarrow H_{2}0_{2}^{*}$$
(1.4)

$$H_2 O_2^* + 20 H^*$$
 (1.5)

(Protonation of superoxide anion)

$$OH^* + Organic dye \rightarrow CO_2 + H_2O (dye intermediate)$$
 (1.6)

Organic dye + 
$$h^+$$
 (VB)  $\rightarrow$  Oxidation products (1.7)

Organic dye + 
$$e^{-}$$
 (CB)  $\rightarrow$  Reduction products (1.8)



Figure 1.2: Schematic representation of a photocatalytic process [33,36].

## **1.3.2 Photocatalytic materials**

The decomposition of organic contaminants has been demonstrated using wider range of metal oxide nanomaterial (i.e. ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.) through the photocatalytic process [37]. These materials are having low cost, chemical stability, nontoxicity. Although, these materials absorbed UV light that confines its usefulness due to fast recombination of charge carriers resulting in lower performance [6,38]. To overcome this problem, various modifications of photo-catalyst including metal doping, decoration with quantum dots and formation of heterostructures [39]. Doping with an appropriate quantity of dopant cations can

support the electron entrapment and hinder charge carrier (electron-hole) recombination, therefore enhancing the photo-catalytic performance of the catalyst. L.Pan et al. have been reported that degradation of methyl orange using metal ions ( $Cu^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$ ) modified TiO<sub>2</sub> shown better photocatalytic performance than the pristine TiO<sub>2</sub> [40]. This is because of the fact that metal cation doping might result into defect site formation in the TiO<sub>2</sub> lattice or even can prompt an alteration in crystallinity thereof, inhibiting the charge carrier recombination [41]. Metal doping creates defects and thermal stability resulting in weaker performance of organic pollutants [39,42]. Further, various researchers investigated non-metal doping, causing band gap reduction by changing the valance band (VB) and the formation of an oxygen-deficient site. Non-metallic impurity level created above the valence band of the TiO<sub>2</sub>, enhances the absorption of radiation as well as (e<sup>-</sup> - h<sup>+</sup>) segregation of the TiO<sub>2</sub> [43,44].

Recently, Metal-organic frameworks (MOFs) have been explored for purification of wastewater. It has porous nature, high surface to volume ratio, which absorbs toxic pollutants by removing contaminated particles and heavy metals via light illumination [45,46]. It is promising to select suitable materials to construct MOFs with a better photocatalytic property because the exciting materials are the main active sites of the photocatalytic reaction [47]. To construct the stable MOFs nanoparticles using quantum dots, graphene, metal oxides and carbon related materials (carbon nanotubes). It shows the better performance of photocatalytic activity over MOFs [48]. The core-shell heterostructure photo-catalyst ZnO@MOF-46 demonstrated higher photocatalytic performance than pure ZnO [49]. Also, metal chalcogenide materials viz., MoS<sub>2</sub>, SnS<sub>2</sub>, TiS<sub>2</sub>, WS<sub>2</sub> are emerging materials for photocatalysis application due to their attractive electronic properties. For example, 2D nanosheet structural units of MoS<sub>2</sub> are being produced in order to ensure a direct bandgap of approximately 1.96 eV owing to the proper band positions. The absorption affinity for visible range light leads to higher photo-catalyst performance.

Further, earth-abundant Copper derivative chalcogenide compounds, viz.,  $Cu_2ZnSnS_4(CZTS)$  and  $Cu_2ZnSnSe_4(CZTSe)$  catalytic material have been used for purifying the water from the wastewater treatment [50,51]. It has a suitable bandgap, large absorption coefficient, earth-abundant constituent elements it more suitable for dye degradation (water purification) [52]. CZTS based materials have been used to degrade organic pollutants, showing excellent photocatalytic performances [53]. Also, heterostructure-based Pt-CZTS and Au-CZTS

were used for the degradation of RhB dye which demonstrated better performance [54]. Similarly, various research authors have been investigated dye degradation (water purification) from wastewater using CZTS materials displayed higher photodegradation [53,55–57]. Recently p-type  $Cu_2FeSnS_4(CFTS)$  material has been considered as another alternative material for dye degradation, it has similar properties of CZTS i.e. high absorption coefficient  $(10^4 \text{ cm}^{-1})$  and earth-abundant, low cost, and non-toxic material. The optical band gap of CZTS materials decreases when the replacement of Zn with Fe enhances the photocatalytic performance [58]. Furthermore, Y.Gao et al. reported that when they partially replaced Zn with Fe, the dye degradation was improved from 62% to 92%, suggesting that the importance of Fe in the CZTS structure. CFTS have a higher surface area, low bandgap, earth-abundant and suitable for photocatalytic application. The development of high-quality earth abundant photo catalyst in large scale is challenging task that can improve the photocatalytic performance. The chalcogenide materials offer higher absorption coefficient, constituent elements are abundance, lower recombination rate of electron-hole pair, higher surface area. Thus, further investigation on earth abundant chalcogenide materials as photo-catalyst material for organic dye decomposition in the contaminated water is required.

# **1.4 Water purification via adsorption process**

## **1.4.1 Principle of adsorption process**

Interplay between adsorbate-adsorbent synergic surface interactions give rise to adsorption phenomenon [31]. This physicochemical phenomenon is determined by distinct factors including pH of the medium, concentration, temperature, adsorbent-adsorbate interactions acting at the interfacial sites [32]. Higher surface-to-volume ratio, layer by layer structure and adequate mechano-chemical stability to propagate faster contaminant decomposition in aqueous medium are some essential features of efficient adsorbent materials. Adsorption mechanism can be understood using various kinds of isotherms. Interaction between adsorbate and adsorbent often determine the course of adsorption to be chemisorption or physisorption. A chemical reaction between adsorbent and adsorbate propagates the chemisorption in an irreversible manner. Further, physisorption can be achieved by the presence of a range of weak interacting forces, including Hydrogen bonding, Van der Waals interaction, dipole-dipole attraction, etc. The reversibility of this adsorption process provides it with a more promising applicative outlook in terms of higher plausibility catalyst recovery and reusability.



Figure 1.3:Water purification through adsorption process [59].

#### **1.4.2 Adsorbent materials for water purification**

Materials such as metal oxides ( $TiO_2$ ,  $Fe_3O_4$ , CuO etc.)[5,8], MXenes (transition metal carbides and carbonitrides) [9,10], magnetic nanomaterials [60], gels (aerogels, xerogels) [61,62], polymer nanocomposites [11,12], Zeolites [13] have been studied for water purification. Natural materials such as agricultural and industrial residues, and bio-sorbents have been described as a cost effective adsorbent for the dye removal from aquous medium [27]. Similarly, carbon nanomaterials [(carbon nanotubes (CNTs), graphene, fullerenes, carbon nanofibers, nanoporous carbon (NPCs), and graphitic-carbon nitride  $(g-C_3N_4)$  [14,15,63,64] is also very effective and efficient materials in this context. Carbon material has exhibited an excellent adsorption ability to remove organic dyes but use of extravagant initial precursors, slow process kinetics, complex synthetic methods, low efficiency and difficulty of recycling has limited their large-scale application [65,66]. Abhijit dan et al. have reported that chitosan-graphene oxide hydrogels with embedded magnetic iron oxide nanoparticles have demonstrated excellent adsorption property for removal of dye from waste water [66]. Recently, L.T.Ha et al. have reported that magnetic (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles modified biochar from the pomelo peel have exhibited a promising material for removal of organic dye from wastewater [67]. A large-scale synthesis of mesoporous hematite (Fe<sub>2</sub>O<sub>3</sub>) nanorods demonstrated rapid, superior, and selective adsorption efficiency toward Congo red (organic dye) dye present in the wastewater [68]. Manganese and samarium doped and co-doped zinc sulfide phosphors have shown better dye

adsorption properties investigated by Yuranan.H [69]. Aminotetrazole functionalized MgO-SiO<sub>2</sub> (MSNT) nanocomposites exhibits rapid and selective adsorption of acid fuchsin dye reported by D.K. Rai et al. [70].

Metal chalcogenides (MoS<sub>2</sub>, ZnS, ZnSe et al.) [71–73] have also been extensively explored as adsorbents to remove organic pollutants. Chalcogenide  $Cu_2FeSnS_4(CFTS)$  are promising adsorbent for removal of organic pollutant (i.e methyl orange) from wastewater due to their size and shape-dependent properties, earth-abundant, environmentally friendly nature [16]. Adsorbents can be easily regenerated for their use in the subsequent process and ease of operation, make the adsorption process very versatile for wastewater treatment. Till date various kinds of semiconductor materials such as metal oxides, metal sulfides, carbon related material, natural material (agricultural wastes, and bio-sorbents) were reported as adsorbents for the removal of organic pollutant from wastewater. These materials have a higher surface area, porosity, layer structure, and reusability for removal of organic pollutant but limited for largescale application due to the expensive initial precursors and complex synthesis methods. Therefore, the development of more efficient and sustainable adsorbents for the removal of organic pollutant from wastewater is great importance in environmental engineering. Herein, a part of thesis work focus on earth abundant chalcogenide materials as adsorbent for water purification because of constituent materials have earth abundant, high surface area, porous type morphology, low-cost synthesis process.

## **1.5 Water splitting**

The alternative to fossil fuels is hydrogen gas, clean, renewable, and high energy density fuel [74]. It is easily storable and transportable; it has been used for various applications such as combustion engines, fuel cells, chemical industries to produce different chemicals. Still, to date, 95% of hydrogen fuel is generated by fossil fuels, only 4% from electricity and 1% from biomass [17]. Generally, hydrogen is produced via coal gasification, steam reforming process, and water splitting methods [75]. Hydrogen production from the non-renewable energy sources is achived using steam reforming and coal gasification, however such processing requires higher temperature and pressure [76]. The steam reforming and coal gasification use the conventional fossil fuels for hydrogen gas evolution, hence, releasing toxic gases (CO and CO<sub>2</sub>) to the atmosphere that severely affects the environment and human being [75]. On the other hand,

hydrogen gas generation from water splitting technique is a extremely promoted and clean due to these following advantages: i) low energy requirement for water splitting, ii) primarily segregated production of hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) gases, eliminating the extra step of gas separation and iii) both the parent as well as the resultant species (H<sub>2</sub>O and H<sub>2</sub>, O<sub>2</sub>, respectively) are benign for environment [77]. Basically, water splitting involves two half-cell electrochemical reactions wherein cathodic reaction leads to hydrogen production via hydrogen evolution reaction (HER) [78] while anodic chamber generates oxygen via anodic chemical reactions and is known as oxygen evolution reaction (OER) [79].

Water splitting is a source of hydrogen generation that can be mostly obtained via electro-catalytic and photocatalytic/photo-electrochemical process [80]. In this method, H<sub>2</sub> and  $O_2$  are generated at higher potential in the presence of Pt-/Ir-metal derived catalysts [19]. In electrochemical water splitting, high power consumption and expensive catalysts hamper large-scale hydrogen production [81]. In contrast, electrochemical water splitting shows excellent adaptability, producing hydrogen and oxygen from the intermittent energy source [81–84]. Majority of the reports recently surfaced in this research area are driven towards solar light to hydrogen evolution due to the unlimited access of sunlight [81,85].

#### **1.5.1** Photo-electrochemical (PEC) water splitting

In the photo-electrochemical (PEC) method, the essential solar-to-hydrogen (STH) conversion process is a photo-electrochemical system to generate hydrogen gas by water splitting [86,87]. A classical PEC cell is comprised of- i) an electrolyte, which can propagate facile mass transport to each electrode surface, ii) a working electrode consisting of a semiconducting material that can be either of the n-type or p-type semiconducting material ( to generate the electron and holes pairs) and iii) to balance the primary catalytic process (reduction reaction to generate the H<sub>2</sub> gas), a counter electrode is introduced [87]. Figure 1.4 depicts schematic representation of photo-electrochemical water splitting processes. Initially, upon light exposer on semiconductor material, electrons and hole pairs are generated.

 $h\vartheta$  + semiconductor  $\rightarrow 2e^- + 2h^+$  (1.9)

The valence band (VB) electrons in the material are then elevated to the conduction band (CB) through photo excitation. Further, these electron-hole pairs are separated to electrons and holes, move towards cathodic and anodic surfaces, respectively. When the working electrode act as a

photoanode, oxidation half-reaction occurs at the electrode surface, and electrons move towards the counter electrode surface in order to accomplish the reduction half-cell reaction (Figure 1.4 and Figure 1.5b) [10].

Anode ... ... 
$$h^+ + H_2 0 \rightarrow 0_2 + H^+$$
 (1.10)

Cathode ... ... 
$$H^+ + e^- \rightarrow H_2$$
 gas (1.11)



Figure 1.4: Schematic representation of photo-electrochemical water Splitting [87].

If the working electrode is a photocathode, a reduction reaction occurs at the surface of the electrode (excited electrons accumulate on the surface), and an outer circuit is employed to transfer the holes so that they can reach the counter electrode surface in order to undergo oxidation half-reaction (Figure 1.5a).

Anode: 
$$4H_2O + e^- \rightarrow 2H_2 + 4OH^+$$
  $E_{H_2O/H_2} = -0.828 V$  (1.12)

While holes oxide water to form oxygen gas at the semiconductor surface

Cathode:  $40H^+ + 4h^+ \rightarrow 4H_20 + 0_2$   $E_{O_2/OH^-} = 0.401 V$  (1.13)

Overall reaction for the photo-electrochemical water-splitting is.

$$H_20 + h\vartheta \to H_2 + 1/20_2$$
 (1.14)

 $\Delta G = 237 \text{ kJ/mole}$ 

Under standard conditions, minimum potential required for water electrolysis is 1.23V at room temperature. According to the Gibbs free energy relation  $\Delta G = nF.\Delta E^{\circ}$ . Where  $\Delta G$  is the
standard Gibbs free energy change ( $\Delta G = 237$ kJ/mol) i.e., this much of energy supplied from an external power source to electrolyze water, F is the faraday constant and  $\Delta E^{\circ}$  is the standard electric potential of the reaction [80].



Figure 1.5: Schematic diagram of the (a) photocathode and (b) photoanode in a typical PEC water splitting technique where electrode materials are comprised of semiconductors. Reproduced with permission from Ref. [88] copyright 2014 Royal Society of Chemistry.

## 1.5.2 Nanomaterials and nanostructures for PEC water splitting

In 1972, Fukushima and Honda first introduced PEC WS to generate hydrogen and oxygen gas from water using  $TiO_2$  semiconducting material as photoanode [89,90]. To procure high photo-conversion efficiency, photo-anodes have to be proficient in solar spectrum harvesting and also should accelerate charge transfer along with good durability against aging or instability arising due to multiple uses [87,91]. Nanomaterials have a high surface area, strong absorption coefficients and smaller size resulting in higher conversion efficiency of solar to hydrogen fuel [91]. The band gap of nanomaterials can be tune by varying the size, shape, and synthesis process, nano materials (particles) are the building block for the photo-catalyst due to the mass and charge transportation is more and enhanced light absorption and diminish light scattering [92]. The nanoparticles can be deposited on the conductive substrate or dissipate in reaction medium (water) for photocatalytic application to improve efficiency. The increment in PEC efficiency was majorly seen at the places where restricted movement of metal nanoparticles was secured, i.e., at the semiconductor/electrolyte interface, due to minority charge transport to

the electrolyte from the electrode. Nanomaterials can be categorized on the dimensionality such as O-D, 1-D, 2-D, and 3-D dimensional nanostructures. Zero dimensional nanostructures (i.e nanoparticles that as spherical particles and quantum dots) are generally used in the generation of hydrogen by photo-electrochemical water splitting, to improve the light absorption and scattering of light, leading to higher efficiency [93]. In addition, 1D nanostructures such as nanorods (TiO<sub>2</sub>, ZnO), nanowire (Fe<sub>2</sub>O<sub>3</sub>, CdS), nanotubes (TiO<sub>2</sub>) and nanoplates (Figure 1.6) are attractive photoelectrodes for water splitting application due to its higher aspect ratio, higher surface area and better photoactive nature [94].



Figure 1.6: Various morphology of nanomaterials (a) Nanorods, (b) Nanowires, (c) Nanotubes, (d) Nanoplates [94].

2-D nanostructures such as thin-film are interesting photo-electrode materials for water oxidation in PEC. It has high surface area and smaller thickness, which provide a wider portion of light-harvesting that supports easy transport of charge carrier onto the surfaces and enhances generation of hydrogen [95]. For example, 2-D WO<sub>3</sub> (5-10nm thickness) photoanodes were fabricated by hydrothermal method; it has observed that thickness of the film influences the process of photo-excited e<sup>-</sup> transport [96,97]. Further, 3-D nanostructures (i.e. dendritic a-Fe<sub>2</sub>O<sub>3</sub>) are also involved for designing better performance electrode to provides adequate light absorption [98]. Under simulated solar light, dendritic Fe<sub>2</sub>O<sub>3</sub> nanostructure photoanode have been demonstrated around 2.2 mA/cm<sup>2</sup> at 1.23 V *vs* RHE [99]. Among these 1-D nanostructure materials have interesting photoelectrical performance compared to the other dimensionality materials. 1-D nanostructure inherit quick diffusion in a single direction with higher surface area and more efficient transport of charge carrier result in a lower recombination of electron-hole pairs [94]. TiO<sub>2</sub> nanorods as photoanode materials for PEC application have higher charge transport, which leads to higher solar to fuel conversion efficiency.

### **1.5.3 Earth abundant nanomaterials for water splitting**

#### **1.5.3.1 Metal oxide-based materials**

Metal oxides have attractive materials because of its outstanding chemical stability, favorable band edge position, earth-abundant, tunable band gaps and low cost [100]. Figure 1.7. depicts wide distribution of bandgap and band edge positions of metal oxide. Generally, the valance band (VB) and conduction band (CB) of metal oxides have O 2p and transition metal (s, d or p) characteristics, respectively. Various earth-abundant metal oxide semiconductor materials, including TiO<sub>2</sub>, ZnO, BiVO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> [101,102], SnO<sub>2</sub>, Cu<sub>2</sub>O [103,104], WO<sub>3</sub>, BiVO<sub>4</sub> [105] and SrTiO<sub>3</sub> have been explored thoroughly for PEC WS application. Because of higher chemical stability, easy fabrication, and low cost [87]. However, it has wide band gaps and absorbs a limited portion of the solar spectrum, higher recombination of charge carrier, poor stability in aqueous solution, and poor conversion efficiencies [87]. Further, ternary oxides-based abundant materials, including CuFeO<sub>2</sub>, CuCrO<sub>2</sub> have been investigated for PEC application. It has a smaller bandgap, higher absorption coefficient, good charge carrier mobility [106]. However, further studies are needed to explore the viability of this type of material. In addition, a spinnel structure-based metal oxide material i.e CaFe<sub>2</sub>O<sub>4</sub> and CuBi<sub>2</sub>O<sub>4</sub> have also been investigated for PEC application. These materials have earth-abundant p-type semiconducting nature and reported for water reduction, because of low cost, and suitable band gap i.e. 1.9 eV (CaFe<sub>2</sub>O<sub>4</sub>) photocathode [107]. Doping strategy enhances the photo-electrochemical properties of spinel structure materials. Limitation of this material is requirement of high temperature synthesis, higher charge recombination and poor charge transport resulting in lower performance of PEC [107].

Many metal oxide materials hold great potential for photo-electrodes or catalysts. Several challenges remain to be addressed such as poor electrical conductivity and inadequate absorption of most metal oxides, when utilized as photo-electrodes for PEC WS. Increase doping efficiency, control the dopant concentration will help to fulfil the above metal oxide limitation. The electrical conductivity of metal oxides is insufficient to improve the conductivity, and novel synthetic techniques are essential to synthesize the metal oxide nanostructures. Post-growth treatment via chemical modification with doping may also be crucial to enhance their PEC performance.



Figure 1.7: Band edge positions of various semiconductors. HER and OER redox potentials are also presented or comparison. Reproduced with permission from Ref. [108] copyright 2016 Royal Society of Chemistry.

### 1.5.3.2 Metal sulfide-based nanomaterial for PEC water splitting

Several metal sulfide materials have been investigated for water splitting application [109]. Metal sulfide allow better response to the broad solar spectrum compared to metal oxide [19]. Various binary metal sulfide materials (SnS, ZnS, CdS, MoS<sub>2</sub>, WS<sub>3</sub>, CoS<sub>2</sub>, NiS<sub>2</sub>, Bi<sub>2</sub>S3, PbS, Ag<sub>2</sub>S), ternary metal sulfide material have been investigated for PEC water splitting application [19]. Which is having higher absorption coefficient, and earth-abundant and better electronic properties, and a suitable bandgap. Which leads to higher performance of PEC device. The limitation of this material is photo corrosion and reducing the drawback of this material, which required sacrificial agents to reduce the photo corrosion [19]. To improve the PEC performance, doping of metal ions (such as Cu, Cd, Ni, Mn) on metal sulfide thin films has enhanced PEC performance under visible light. Another alternative route is the decoration of noble metal (Pt, Au, Pd, Ru) on metal sulfide materials [110] to improve the photo corrosion and oxidation resistance.

Furthermore, the formation of heterojunctions with metal sulfide and other materials, especially metal oxide (TiO<sub>2</sub>) has enhanced photoconductivity, reduced the recombination of charge carriers to enhance the PEC performance. For example, TiO<sub>2</sub>/Cu<sub>2</sub>S heterostructure could increase the photocurrent due to reducing the recombination of charge carriers in the TiO<sub>2</sub>/Cu<sub>2</sub>S heterostructure [111]. However, the limitation of the metal sulfide is chemical stability due to this easily oxidizing and its leads to reduce performance device over as result of corrosion.

Chemical stability of metal sulfides and its wide range of pH is a technical barrier that needs to be addressed. In addition, the PEC performance was enhanced by transition metal doping, surface modification of metal oxide leads to improvement in PEC efficiency [19]. Moreover, smaller particle size materials decorate on metal oxide to form a heterojunction device, leads to enhanced photocurrent density of the overall device.

### 1.5.3.3 Chalcogenide semiconductor materials

Efficient and economically viable way to generate hydrogen through PEC water splitting is a challenging task. The working electrode semiconductor materials should be earth-abundant constituents and suitable band gap. Most well-known earth-abundant material i.e. cuprous oxide (Cu<sub>2</sub>O), is one of the favorable abundant p-type semiconductor photo-electrode for PEC WS. Copper is abundant and easily available in the earth. The limitation of this material is photo corrosion. Therefore, to overcome this problem, surface protection was used to reduce the photo corrosion leads to improve the performance and stability of the Cu<sub>2</sub>O photocathode in the PEC device. Similarly, numerous typical binary light-absorptive materials that fit these conditions have been proposed, such as iron disulfide (FeS<sub>2</sub>) [112], copper(I) sulfide (Cu<sub>2</sub>S) [111], tin sulfide (SnS) [113], tin selenide (SnSe) [114] and bismuth sulfide (Bi<sub>2</sub>S<sub>3</sub>) [115]. Another alternative earth-abundant chalcogenide semiconductor well known materials for photovoltaics, with power conversion efficiency of 22.6%. Firstly, CIGS-based photocathode materials have been investigated for PEC application, and the solar to hydrogen efficiency is achieved 10%. Due to high cost of indium and gallium elements in CIGS devices is limited to further study. Further, replacing indium and gallium with low cost, di and trivalent cations (i.e Zn<sup>2+</sup> and Sn<sup>4+</sup>) forms a Cu<sub>2</sub>ZnSnS<sub>4</sub> semiconductor as shown promising materials for PEC application. Because of environmentally friendly, high absorption coefficient, earth-abundant and non-toxic nature [116]. One of the main advantages of this material is tuning the bandgap from 1eV (CZTSe) to 1.5eV (CZTS) while changing the S and Se ratio. CZTS material was introduced as a photocathode electrode for PEC application demostracted, photocurrent density around 0.1mA/cm<sup>2</sup> [117]. To improve the photocurrent density , various surface modifications with TiO<sub>2</sub>, ZnS, SnS, and CdS have been investigated to promote charge separation and transportation in the PEC device [118]. After optimization surface modification, CZTS photocathode with CZTS/CdS/TiO<sub>2</sub>/Pt structure fabricated by solution approach and revealed current density value

around 9mA/cm<sup>-2</sup> [119]. To development of an efficient photocathode material for solution process CZTS thin film remain an area to be explored.

Another alternative chalcogenide semiconductor material i.e Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) material, has similar properties of CZTS, i.e suitable bandgap (1.28-1.50eV) and higher optical absorption coefficient (>  $10^4$ cm<sup>-1</sup>), low cost, earth-abundant and non-toxic materials [120]. Substitution of Zn by Fe in CZTS material reduces the optical bandgap, because Fe is more stable in the lattice thus improving solar conversion efficiency. Most recently, the CFTS materials used for counter electrodes in dye-sensitized solar cells (DSSCs) [121] absorber layer for thin-film solar cells and dye degradation application [122]. CFTS nanostructures were synthesized by solvothermal, hydrothermal, hot injection and microwave-assisted [7]. On the other hand, CFTS thin films were fabricated by chemical technique, including chemical bath deposition, spin coating, spray pyrolysis and successive ionic layer adsorption and, and physical techniques such as sputtering, pulsed layer deposition (PLD) etc. [7]. The CFTS material has a suitable bandgap, earthabundant, low cost and non-toxic, it is suitable for the photo-catalyst application. Recently, the degradation of methylene blue dye degraded using CFTS nanoparticles synthesized by hot injection method [123]. Degradation of organic pollutants from wastewater using CFTS particles were also reported [122,123]. Similarly, we believe that CFTS material is suitable for PEC application because of the suitable bandgap and higher absorption coefficient. The major challenge toward realistic application of photo-electrochemical water splitting is the lower efficiency. In addition development of stable working electrode for longer duration, abundant and non-toxic materials, and heterostructure photoelectrode to harvest the wider solar spectrum are the existing research challenges.

# **1.5.4 Strategies to enhance the PEC water splitting performance of nanomaterials**

Approaches such as doping, surface modification, and heterojunction formation were developed to improve the PEC performance of the nanostructure photoelectrodes. This facilitates the better charge carrier transfer and separation, improves the optical absorption ability, and leads to enhancement in performance.

### 1.5.4.1 Doping

Electronic and optical properties of semiconductors can be modified by doping with suitable materials. Various metal or non-metal have been doped into photoanode materials to induce redshift of bandgap absorption, such as metal (Mn, Fe, Co) [124], Nb [125], Bi [126], Sn [127], nitrogen [128], Sulphur [129], fluorine [130] doped TiO<sub>2</sub>. J. Bene et al have reported that Fe-doped TiO<sub>2</sub> nanorods demonstrated higher light absorption and charge carrier density leads to photocurrent conversion efficiency compared to un-doped TiO<sub>2</sub> [131]. In addition, Cobalt (Co) is a suitable dopant for semiconductor oxides due to its incorporation into crystal lattice of oxides, to influence the nanostructure morphologies, crystalline size and surface area. Which significantly increases the photo-generated charge carriers leads to higher PEC performance [132]. Transition metal (Fe, Mn, Co) doped TiO<sub>2</sub> nanorods array were synthesized by wet chemical process, significantly improving the photo response in the visible light region. Thus, increase carrier density of TiO<sub>2</sub>, resulting in effective charge carrier separation and transportation [124]. However, doping of metal causes degradation in thermal instability and creates impurities, resulting in lower performance of PEC device [39,86].

### 1.5.4.2 Surface modifications and heterostructure formation

Surface modification of the photo-electrodes also significantly increases the PEC performance. These, modifications adjust the band-edge potential, flat-band potential and chemical stabilities of the electrodes. As a result quantum efficiency, onset potential, and stability are improved. Modification of surface layer is generally less than 0.1 $\mu$ m thick and noticeably higher than the causal photon absorber. Consequently, modified electrodes do not influence the photoexcitation procedure, but preferably promote development of an internal electric field, passivation of surface states [10,11][133], and the degradation of the surface photoelectrode [12]. Thus, explorations of surface modification play dynamic role in the improvement of efficient stable photo-electrodes. Generally, TiO<sub>2</sub> is the most used surface modifiers. For example, photo corrosion take place on the epidermis of the photo-electrode, metal oxides has been used actively for better stability of electrode materials. Seger et al. reported silicon photoelectrode covered with a 100 nm TiO<sub>2</sub> layer displayed substantial enhancement in stability (>72 hours) [134]. TiO<sub>2</sub> shielded with silicon photo-electrode exhibited stable PEC water oxidation for more than 100 h [135]. Similarly, Mo-doped BiVO<sub>4</sub> photo-electrode exhibited excellent

stability (1000 h) at 0.4 V vs reversible hydrogen electrode (RHE) reported by Domen and his group in 2016 [136].

On applying several layers as surface modifiers, loss of illuminated light and interface recombination will occur due to the presence of photo absorbers. Development of multi-functional layers will be crucial for obtaining efficient energy conversion in the future. To improve efficiency of PEC device, formation of heterostructure (i.e. combination of one or more semiconductor or metal) is considered a favorable route to harvest the visible light. This heterostructure absorbed full range of spectral light sources and can boost photo-excited charge carrier separation, reducing  $e^-h^+$  recombination thus improving the PEC performance.

The heterostructure of metal oxide material with typical band gaps can absorb the wider range of light absorption spectra. There are three main types of heterojunction based on each position of each semiconductor's valence and conduction band as shown in Figure 1.8. Type-1 generally does not contribute to increases in activity of the system due to both electrons and holes moving to one semiconductor, resulting in an accumulation [137]. Type-2 allows better charge separation efficiency, longer lifetime of electron-hole pair, and decreased recombination rates. This is achieved through semiconductor-2 having a lower conduction band (C.B) and valence band (V.B) than semiconductors having both the C.B and V.B lower than the other. Here, an electron mediator is required to connect the two semiconductors [137]. Among these three, type-II based heterostructure (Figure 1.8) can facilitate efficient separation of photogenerated charge carrier under light irradiation [138]. The semiconductor-2 act as a photo absorber that assist internal electric field across the interface. Internal potential bias remarkably supports charge carrier separation and transportation across the interface of the dual electrode material decreases recombination of electron-hole pair.

For example, formation of P-N junction by modifying the TiO<sub>2</sub> nanostructures with Cu<sub>2</sub>O particles as shown in Figure 1.9, facilitate separation of the excited electrons and holes [139]. It has widely useful for improving the PEC performance of TiO<sub>2</sub> through, modification with visible-light materials such as CdS, Bi<sub>2</sub>WO<sub>6</sub>, CuS, Fe<sub>2</sub>O<sub>3</sub> etc. [22,140–142]. Recently, the TiO<sub>2</sub>/Cu<sub>2</sub>O core-shell (Figure 1.9) heterojunction photo-electrode demonstrated remarkable photostability and attains a stable photocurrent around 2.3 mA/cm<sup>2</sup> during light illumination [22]. The enhanced photocurrent due to the efficient transfer and separation of photo-generated



Figure 1.8: Various types of heterojunction [137].

electrons and holes at heterojunction [22]. Further, the of n-type  $Bi_2S_3/TiO_2$  heterostructure fabricated by thermal process revealed a better photocatalytic activity and long-term stability [143]. Quantum sized particles of CdS, ZnS and PbS on TiO<sub>2</sub> heterostructure showing higher photocurrent density and stability [109]. In 2015, earth abundant chalcogenide material based hetero-structure have been reported for PEC application. CZTS nanocrystal decorated on TiO<sub>2</sub> nanorods arrays have demonstrated higher current density around 2.92 mA/cm<sup>2</sup> at 1.23 V vs RHE than TiO<sub>2</sub> nanorods [144].

Furthermore, surface passivation with ZnS on CZTS/TNR arrays resulted in improvement in PEC performance with photocurrent density about 6.91mA/cm<sup>2</sup> was observed [144]. In addition, CZTS was enclosed uniformly entire the surface of TiO<sub>2</sub> nanowire arrays (NWs) via wet chemical process have been demonstrated 23 times greater than TiO<sub>2</sub> NWs based electrode [23]. Similarly, highest photocurrent density around 15.05 mA cm<sup>-2</sup> at 1.23 V vs normal hydrogen electrode(NHE) is observed when Ternary photo-electrode (CZTS /Zn(O,S) /TNR) is used. Their suitable band gap energy, low-cost, earth-abundancy [145].



Figure 1.9:Transport mechanism of photo-generated charge carriers in TiO<sub>2</sub>/Cu<sub>2</sub>O heterojunction nanostructure. Reused with permission from Ref.[22] Copyright 2018 Elsevier.

Further, design and development of earth-abundant, visible-light absorbing CZTS NPs decorated on Sulphur doped TiO<sub>2</sub> nanostrutures shows higher efficiency for solar water splitting. Earth-abundant semiconductors materials have also been investigated for PEC water splitting. In which, recombination of electron-hole pair, light absorption properties and stability are least investigated [107,146]. Heterostructure photoelectrodes have exhibited higher photo-conversion efficiency due to higher charge separation and transfer, lower recombination of photo-generated charge carriers [75,109]. 1-D nanostructure based flatform and earth-abundant chalcogenides semiconductor CFTS as visible light absorption material might have potential properties to study.

## **1.6 Scope and objectives of the thesis work**

The water purification and photo-electrochemical water splitting both the process are related to photo-generation and separation of the electron under photoexcitation. In this study, the development of efficient materials for solar (photo) driven catalytic process is the central theme. The earth-abundant chalcogenides materials have shown a good presence in photovoltaic devices. However, a limited investigation is reported in the area of photocatalytic and electrochemical water splitting toward the production of hydrogen. Considering the excellent properties and suitability of Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) for photocatalytic and photo-electrochemical

water splitting, it is indeed become the first choice to investigate. However, CZTS suffer from multi or bimetallic phase formation during fabrication and also stability is limited under solar excitation in the presence of an electrolyte. The Cu<sub>2</sub>FeSnS<sub>4</sub> is relatively stable and also has lesser change to form bimetallic phases during growth. Hence in this study, Cu<sub>2</sub>FeSnS<sub>4</sub> has been consider as primary materials. The solution-based approach is investigated to grow the various type of materials morphologies. Due to tunability of the surface properties of solution grown Cu<sub>2</sub>FeSnS<sub>4</sub>, it become interesting to understand their effect on various properties of materials and subsequently over photocatalytic and photo-electrochemical water splitting properties.

The specific objectives of the thesis project are as follows:

- Optimized the growth process for the development of Cu<sub>2</sub>FeSnS<sub>4</sub> particles by solution approach.
- Study the effect of solvents on structural and morphological optical properties of CFTS particles.
- Investigate the effect of various sulphur precursors on structural and morphological, optical properties of CFTS particles and removal of organic dye from water via photocatalytic process.
- Development of porous Cu<sub>2</sub>FeSnS<sub>4</sub> particles and removal of organic pollutant from wastewater using via adsorption process and electro-catalytic water splitting.
- Development of CFTS decorated Ni-TiO<sub>2</sub> NRs based heterostructure for photoelectrochemical water splitting performance.

## **1.7 Thesis outline**

Overall, the thesis is organized into seven chapters. *Chapter-1* provides an overview of recent development in water purification and splitting, the basic principle of photoelectrochemical water splitting and objective of the research work. *Chapter-2* presents that synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub>(CFTS) particles and investigation on the effect of temperature, time and solvents on structural, morphological, and optical properties. In this study, different temperatures (160 °C, 180 °C, 200 °C, 220 °C), reaction time (6 h, 12 h, 18 h, 24 h) and different solvents such as N, N-dimethyl formamide (DMF), oleylamine (OLA), deionized water (DI) and ethylenediamine (EDA) are used for synthesis of CFTS particles and its effect on physical properties of CFTS particles are studied. *Chapter-3* reports on Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles using various sulphur precursors and study their structural, optical, and photocatalytic properties. Various sulphur precursors namely sulphur powder, thiourea, sodium sulphide and thioacetamide is used for the synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles and study its effects on crystallinity, morphology, band gap and elemental composition. Chapter -4 reports that synthesis of porous Cu<sub>2</sub>FeSnS<sub>4</sub> particles and elimination of organic acid fuchsin dye pollutant from wastewater by adsorption process. In this study, distinct reaction time in synthesis leads to have a porous sphere, sheet-flakes, and intermixed flower-sheet morphologies of CFTS particle synthesized at 200 °C different time. *Chapter-5* represent surface controlled Cu<sub>2</sub>FeSnS<sub>4</sub> particles synthesized using different surfactants i.e. thioglycolic acid (TGA), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA). Then effect of surfactants on crystal structure, morphology, elemental composition and electro-catalytic properties of CFTS particles are investigated. The significant change in morphology (porous-sheet, porous and uniform spherical) of CFTS particles when the changing the surfactant in the synthesis process. Highly porous CFTS particles render better electrocatalysis water splitting properties. Chapter-6 describe the fabrication of Cu<sub>2</sub>FeSnS<sub>4</sub> decorated Ni-TiO<sub>2</sub> nanorods based photoanode for enhancing water splitting performance. We fabricated the CFTS decorated Ni-TiO<sub>2</sub> NRs heterostructure photoanode to harvest the wider solar spectrum. Initially, TiO<sub>2</sub>, Ni-TiO<sub>2</sub> NRs and CFTS/Ni-TiO<sub>2</sub> were prepared by hydrothermal method and followed by dip coating process. Further studied its structural, morphological and photoelectrochemical water splitting performance. Chapter 7: Summary and future scope of the thesis work, summarizes the main findings of the thesis work and future scope of the research work are discussed in this area.

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# **CHAPTER-2**

# Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> Particles and Structural, Morphological and Optical Properties

# **2.1 Introduction**

Quaternary chalcogenide semiconductors such as CuInGaSe<sub>2</sub>(CIGS) and Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) have widely explored due to its high absorption coefficient and direct band gap of about 1.3-1.5 eV [1]. However, the Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) quaternary chalcogenide group has attracted great attention due to its abundant nature and nontoxic constituents [2]. The replacement of Zn, by Fe in CZTS forms CFTS, leads to improvement in optoelectronic properties and suppresses the formation of the secondary phase [3]. Moreover, CFTS also has a high optical absorption coefficient (>  $10^4$  cm<sup>-1</sup>), optical band gaps (1.2–1.8eV), which is ideal for solar energy harvesting devices [4]. CFTS material has been utilized to develop an absorber layer for thin-film solar cells [5] and counter electrode for dye sensitized solar cell etc. [4]. Synthesis of CFTS nanoparticles with high yield and close to stoichiometry is challenging and, in this regards, various methods such as hot injection, spray pyrolysis, solvothermal method are investigated. Among them, solvothermal process shown promise, due to its low cost and environmentally friendly approach, synthesis is possible at low temperature with the prospect of obtaining higher yield. Moreover, morphological control can also be achieved by optimizing the growth parameters such as solvents, initial precursors, processing conditions etc [6,7]. The growth temperature, reaction time, solvent and surfactant in the solvothermal process are the key parameters that control the formation and phase purity of the CFTS material. Although, it is well known that temperature, reaction time, solvent and surfactant plays a dynamic role in structural and stoichiometry of the CFTS particles. Still, the effect of all process parameters on the synthesis as well as properties of CFTS particles are still required investigation for deeper understanding. In this chapter, the synthesis of CFTS particles is reported using solvothermal approach. Herein the effect of reaction parameters such as reaction temperature (160°C, 180°C, 200°C, 220°C), reaction time (6h,12h,18h,24h) and solvents (H<sub>2</sub>O, OLA, DMF, EG) on structural, morphological and optical properties of CFTS particles are studied. Varying the reaction temperature, time and solvents in

the synthesis process, significant difference in morphology (porous, flower, spherical, aggregate and flower-sheet), elemental composition and bandgap (1.32 to 1.7eV) of the CFTS particles were observed.

# **2.2 Experimental Details**

## 2.2.1 Materials and reagents

Copper acetate monohydrate  $(CH_3CO_2)_2$  Cu.H<sub>2</sub>O, SRL, AR grade), ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>, Lobachemie), Stannite chloride dehydrate (SnCl<sub>2</sub>, SRL) and thiourea (CH<sub>4</sub>N<sub>2</sub>S, lobachemie), ethylene glycol (EG, Merck), oleyl amine (OLA), Deionized water (DI), ethylenediamine (EDA), N, N-dimethyl formamide (DMF)

## 2.2.2 Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles by solvothermal method

In solvothermal process, organic solvent as a reaction medium and metal precursors are mixed to form a homogeneous solution. The reaction process generally occurred at high pressure and temperature (200°C) in an autoclave hot air oven. In this study, the stoichiometric ratio of (Cu:Fe:Sn:S) are 2:1:1:6 mmoles were dissolved in a 40ml of Ethylene glycol (EG) in a beaker. The mixture was stirred vigorously for 30 min in order to obtain a homogeneous solution. Subsequently, the solution shifted to a Teflon liner, which was then kept in an autoclave. The reaction was carried out at 160°C for 24h in the oven and then allowed to cool down naturally to room temperature. The supernatant is discarded from autoclave and remaining solution is centrifuged for 15 min at 10000 rpm with ethanol. Repeat the centrifugation process was repeated two to three times to remove the organic impurity's. Finally, the residue was vacuum dried at 60°C for 6h. The same synthesis recipe was repeated at different temperatures (180°C, 200°C, and 220°C). For another set of studies, the initial precursors, reaction temperature (200°C), Ethylene glycol (EG) as solvent all were kept the same and only the reaction time was varied (6h,12h,18h,24h). Similarly, the synthesis process was also carried out in the presence of different solvents i.e oleyl amine (OLA), Deionized water (DI), ethylenediamine (EDA), N, Ndimethyl formamide (DMF) keeping the reaction temperature  $(200^{\circ}C)$  and reaction time (24h).

## 2.2.3 Characterization of Cu<sub>2</sub>FeSnS<sub>4</sub>(CFTS) particles

The phase purity and crystal structure of synthesized CFTS particles were determined by X-ray diffraction measurement with Cu-Ka radiation ( $\lambda$ = 1.54Å) using Bruker D-8 Advance X-ray diffractometer. The impurity phases and confirmation of crystal structure were further investigated by Micro-Raman spectrometer (Horibra LABRAM-HR visible (400 - 1100 nm) laser source with an excitation wavelength of 473 nm and spot size of 1µm at 25 mW laser power. Oxidation states/chemical composition of synthesized CFTS particles were examined by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II, operating voltage:3 kV, full scan time 1 h). Scanning Electron Microscope was used to analyze morphology, and elemental composition of the synthesized CFTS particles (FEG–SEM, Supra 55 Zeiss), attached with Energy Dispersive Spectrometer (EDS) operated at 20kV. The optical absorption properties of synthesized CFTS particles were examined by using a spectrophotometer (UV-Vis, Shimadzu) at room temperature.

# 2.3 Results and Discussion

# **2.3.1** Effect of reaction temperature on structural, morphological, and optical properties of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

The XRD patterns of CFTS particles synthesized at various reaction temperature (160°C, 180°C, 200°C, 220°C) are shown in Figure 2.1. The diffraction peaks that appeared in XRD patterns such as (101), (112), (200), (220), (222), (312) are matched with stannite structure of CFTS phase (JCPDF Pattern:44-1476). At lower reaction temperature (160°C) poor crystallinity of CFTS particles is observed [8]. However, as the reaction temperature increases, the diffraction peaks' intensities also increase gradually, indicating improvement in the crystallinity of the CFTS particles. The synthesis reaction at 200°C shows the highest intensity of the diffraction peaks and lowest full width half maximum indicating the better crystalline phase of CFTS particles. Further increase in reaction temperature to 220°C, the intensity of XRD peaks decreases with wider FWHM. The lattice parameters of CFTS particles are calculated [12]. These values are agreement with reported literature values (a = 5.45, c = 10.739, PDF card no. 44-1476). The crystalline size of the CFTS particles was determined by using the Debye- Scherrer formula (D=  $K\lambda/\beta$ Cos $\theta$ , where  $\lambda$  is incident X-ray wavelength,  $\beta$  is the FWHM of the diffraction peak,  $\theta$  is the

diffraction angle). The largest crystalline size is obtained in case of 200°C and the lowest crystalline size is noticed in 220°C growth.



Figure 2.1: XRD pattern of CFTS particles synthesized using various reaction temperatures (160°C, 180°C, 200°C, 220°C).

SEM images of the CFTS particles synthesized by various reaction temperatures (180°C, 200°C, 220°C) are shown in Figure 2.2. Aggregate particles like morphology are obtained at reaction temperature (180°C) are depicted in Figure 2.2. Further, increasing temperature to 200°C leads to the formation of a sphere-sheet-like morphology was noticed. Intermixed aggregate and sheet-like morphology (1 $\mu$ m) was obtained for 220°C growth time. The change in morphology of the CFTS particles might be due to the nucleation dissolution and recrystallization process in the synthesis process [9]. The elemental composition of CFTS particles analyzed by EDX spectra, and the obtained elemental composition, as shown in Figure 2.3. At reaction temperature 180°C, *Cu* deficient and sulfur-rich CFTS observed, and near stoichiometric ratios were obtained in the case of 200°C and 220°C. The difference in elemental composition might be due to the different reactivity of the metal ions in the reaction process [10].



Figure 2.2: SEM images of CFTS particles synthesized using different reaction temperature (180°C, 200°C, 220°C).



Figure 2.3: EDX spectra (a) elemental composition (b) of the CFTS particles (synthesized different temperature).

Figure 2.4 shows the optical absorption spectra of the synthesized CFTS particles. The optical band gap is estimated using the following equation. Absorption coefficients ( $cm^{-1} mol^{-1}$ ) were calculated using the following formula [2].

Absorption coefficient(
$$\alpha$$
) =  $\frac{A}{C \times I}$  (2.1)

Here: A – Absorbance,  $\alpha$  = Molar absorption coefficients, C = concentration (0.001 mol ml<sup>-1</sup>),

L = path length (1cm). The relationship between molar absorption coefficient ( $\alpha$ ) and wavelength for CFTS is shown in Figure 2.4a. The band gap was calculated by extrapolation of the liner portion of ( $\alpha$ hv)<sup>2</sup> and hv plot see Figure 2.4b. The band gap of CFTS particles is 1.5 eV(180°C), 1.48 eV(200°C), 1.42 eV(220°C) found respectively. The obtained band gap values are close to the optical value reported in the literature values [2,11,12]. A better crystalline CFTS phase is observed when the reaction temperature (200°C). While, varying the reaction

temperature in the synthesis process, a significant change in the morphology of CFTS particles is noticed. Also band gap of the CFTS particles varied from 1.42eV to 1.5eV.



Figure 2.4: Optical –absorption spectra (a) Tauc,s plot (b) of CFTS particles synthesized using (different reaction temperatures).

# 2.3.2 Effect of reaction time on structural, morphological, and optical properties of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

The measured XRD patterns (Figure 2.5a) of the as prepared samples exhibit various diffraction peaks, such as (101), (112), (200), (220), (222), and (312) matches with the tetragonal structure of CFTS phase (ICDD No: 44-1476). The CFTS particles synthesized in 6 h reaction time have a slightly lower intensity and broader peaks (for example: (112) peak). The peak intensities in XRD patterns increase with an increase in the reaction times (12 h and 18 h), which represents the improvement in the crystallinity of the CFTS particles. The average crystalline size of the CFTS particles is estimated using Scherrer formula [13] to be 2.04 nm, 5.23 nm, and 7.12 nm for 6 h, 12 h, and 18 h, respectively. Raman analysis was carried out to confirm the phase purity and identify impurity phases (CuS, Cu<sub>2</sub>SnS<sub>3</sub>) present in the synthesized particles (Figure 2.5b). All synthesized CFTS particles show a strong peak at 320.5 cm<sup>-1</sup>, verifying the pure CFTS phase formation. The strong peak is ascribed to the symmetric vibration bond of sulfur atoms [14].



Figure 2.5: XRD patterns and (b) Raman spectra of the CFTS particles solvothermal synthesized at 200 °C for 6 h, 12 h, and 18 h, respectively.



Figure 2.6: (a) Scanning survey XPS spectrum of  $Cu_2FeSnS_4$  particles synthesized at 200°C for 6 h (b) carbon spectrum, high resolution core levels spectrum of (c) Cu2p, (d) Fe2p, (e) Sn3d and (f) S2p respectively.

The elemental composition and oxidation states of the constituent elements in the Cu<sub>2</sub>FeSnS<sub>4</sub> particles synthesized at 200 °C for 6 h are investigated using XPS and data is shown

in Figure 2.6. Figure 2.6a depicts the survey spectrum evidence for constituent elements (Cu, Fe, Sn, and S) of CFTS, and C additional elements. The binding energies were corrected by referencing the C1s peak to 284.5 eV (Figure 2.6b). The core-level XPS spectrum of the constituent elements of CFTS is fitted with XPS PEAK 41 software (Figure 2.6c - Figure 2.6f). The fitted core level XPS spectrum of Cu2p has displayed two peak splits (932.14 eV (2p<sub>3/2</sub>) and 951.94 eV  $(2p_{1/2})$ , and the separation between peak splits calculated to be 19.8 eV, thus attributed to the Cu<sup>1+</sup> state configuration (Figure 2.6c) [5]. The fitted core level XPS spectrum of Fe2p is showing two peaks at 710.23 eV( $2p_{3/2}$ ) and 723.56 eV ( $2p_{1/2}$ ); the difference between these two peaks is estimated to be 13.33 eV, which confirms the Fe<sup>2+</sup> state in the prepared sample (Figure 2.6d) [5,15]. Similarly, the core level spectrum of Sn3d has exhibited two peaks at 486.47 eV (Sn3d<sub>5/2</sub>) and 494.86 eV (Sn3d<sub>3/2</sub>). The separation between these two peaks is found to be 8.34 eV, thus indicating the presence of  $Sn^{4+}$  state in CFTS (Figure 2.6e) [37][38]. Other peaks also appears at 486.97, and 495.26eV is attributed to the SnO<sub>2</sub> phase presence on the CFTS surface [16]. The core-level spectrum of S2p has displayed the two peaks located at 161.66 eV (2p3/2) and 162.84 eV (2p1/2); the gap between the two splits is 1.1eV, which is consistent with sulfur (2-) state presence the CFTS compound [16]. All fitted parameters of constituent elements are tabulated in Table 2.1. We can conclude that the standard oxidation states present in the compound are agreed with  $Cu_2^+Fe^{2+}Sn^{4+}S_4^{2-}$  in the material.

Elements		Peak position(eV)	FWHM (eV)
Cu	Peak1	932.14	1.284
	Peak2	951.94	2.350
Fe	Peak1	710.73	11.121
	Peak2	722.56	1
Sn	Peak1	486.47	1.016
	Peak2	486.971	2.877
	Peak3	494.86	0.901
	Peak4	495.265	2.023
S	Peak1	161.66	0.863
	Peak2	162.84	2.494

Table 2.1: Peak position and their FWHM values of porous CFTS particles.

FTIR analysis confirms the functional groups present (OH<sup>-</sup> groups) on synthesized CFTS particles (Figure 2.7). The O–H stretching band (3170 cm<sup>-1</sup>) is usually assigned to the water molecules in all synthesized CFTS particles for different reaction times [17–19]. Further, a peak at 1624 cm<sup>-1</sup> attributed to the NH<sub>2</sub><sup>-</sup> stretching vibrations in all CFTS samples [20–22]. The other peaks at 610 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> is corresponding to the sulfate peaks (SO<sub>4</sub> group) [17] and peak at 770 cm<sup>-1</sup> belonging to C–H vibration, which indicates the functional groups present in all synthesized CFTS particles [23]. The FTIR analysis concludes that functional groups present on the surface of all synthesized CFTS particles.



Figure 2.7: FTIR spectra of the CFTS particles synthesized at 200 °C for 6 h, 12 h, and 18 h, respectively.

Morphologies of the CFTS particles synthesized at different reaction times (6 h, 12 h, and 18 h) are shown in Figure 2.8 (a<sub>1</sub>,b<sub>1</sub>,c<sub>1</sub>). The porous spheres (approximately 200 nm) are obtained for 6 h (Figure 2.8a<sub>1</sub>). Further increase in reaction time (12 h) resulted in sheet-flake-like morphology (Figure 2.8b<sub>1</sub>). The mixture of the flower and sheet morphology is observed for 18 h (Figure 2.8c<sub>1</sub>). According to the reported literature, chemical composition, amount of solvent, surfactants/complexing agent, initial precursors, and concentration, reaction temperature/ time influences the morphology of quaternary chalcogenides particles [25, 29–32]. In the present study, the change in morphology with reaction time might be due to the variation

of the chemical composition of synthesized CFTS particles [26]. The mixed morphology of flowers with sheets together might be due to the adsorption of hydroxyl groups of ethylene glycol over the surface of CFTS particles [9]. The OH<sup>-</sup> groups on the surface of CFTS particles were corroborated by FTIR analysis (Figure 2.7). The morphology variation might be due to the kinetically controlled nucleation - dissolution - recrystallization mechanisms [27,28].



Figure 2.8: SEM imaging, energy-dispersive X-ray spectroscopy, and elemental color mapping of the CFTS particles (a<sub>1</sub>-a<sub>3</sub>) CFTS-6h, (b<sub>1</sub>-b<sub>3</sub>) CFTS-12h and (c<sub>1</sub>-c<sub>3</sub>) CFTS-18h.

The composition analysis of CFTS particles synthesized at various reaction times is analyzed using the EDS technique. Four different spots were analyzed for each sample, and the resulted average elemental composition of prepared CFTS particles is summarized in Table 2.2. The particles grown at 6 h have shown the stoichiometric ratio, and the corresponding EDS spectrum and elemental mapping are shown in Figure 2.8 ( $a_2\&a_3$ ). The Fe - rich and S - deficient particles are obtained for 12 h reaction and elemental mapping represented in Figure 2.8b<sub>3</sub>. Further, a longer reaction time (18 h) results in Cu - rich and Sn - deficient particles, and related EDS spectrum and mapping are depicted in Figure 2.8( $c_2\&c_3$ ). The stoichiometric ratio difference might be due to the difference in the metal ions' chemical reactivity (cations and anions) [29].

Reaction time	Elemental composition (atomic %)						
	Copper (Cu)	Iron (Fe)	Tin (Sn)	Sulphur (S)			
Ideal	25	12.5	12.5	50			
CFTS-6h	26.9	10.8	12.6	49.7			
CFTS-12h	24.65	14.1	13.15	48.10			
CFTS-18h	28.6	11.10	9.05	51.25			

Table 2.2: Elemental composition of CFTS particles synthesized at 200 °C for 6 h, 12 h, and 18h.



Figure 2.9: (a) Nitrogen adsorption-desorption isotherm curves and (b) pore size of CFTS particles synthesized at 200 °C for 6 h, 12 h, and 18 h.

The adsorption-isotherm curves of CFTS particles exhibit hysteresis loops (Figure 2.9(ab)), which are the porous structures' main characteristics. The specific surface area and pore size of prepared CFTS particles are (obtained from multipoint BET) found to be 53.50 m<sup>2</sup>g<sup>-1</sup> and 4.301 nm for porous-CFTS, 33.10 m<sup>2</sup>g<sup>-1</sup> and 3.822 nm for flakes- CFTS and, 20.99 m<sup>2</sup>g<sup>-1</sup> and 3.72 nm for flowers-CFTS morphology, respectively. FEG-SEM and BET analysis conclude that CFTS particles synthesized at 6 h have shown the porous surface, high specific surface area with larger pore size among the other two samples with sheet-flake and intermixed the flower-sheet morphologies.

# **2.3.3** Effect of solvents on structural, morphological, and optical properties of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

Figure 2.10 (a,b) shows XRD analysis of CFTS particles synthesized using different solvents at 200°C for 24h. The diffraction peaks obtained in XRD analysis such as (112), (101), (200), 220), (312) are matched with stannite structure of CFTS phase (JCPDF No:44-1476) and also observed impurity phases (i.e SnS) are also noticed in all solvents based CFTS particles. In case of DMF and EDA (as solvents) the diffraction peaks (112), (220) are sharper and less broadness; it indicates the large crystalline grains and better crystallinity. Moreover, the particles synthesized using DI water and OLA exhibits broader diffraction peaks corresponding to (112), (220). The average grain size of the as synthesized CFTS particles was calculated using Scherrer equation varies from 18.23 nm to 23.13nm. The highest grain size (23.13nm) is observed in case of OLA and lowest (18.23) in case of DMF as solvents, respectively. The lattice parameters were also calculated from the XRD data (a=b=  $5.43-5.52 \text{ A}^{\circ}$ , c= 10.63-10.75), which are found to be in good agreement with the literature values [10]. The pure crystalline phase is obtained when the CFTS particles heat-treated at 450°C for 30 min in argon ambiance (Figure 2.10b). All samples show sharper peaks, the FWHM of the peaks is also reduced, indicating that the CFTS particles' crystallinity is enhanced. The grain size (after heat treatment) samples are in the range of 19.80 nm to 23.89 nm and lattice parameters are varied  $a=b=5.32-5.75 \text{ A}^{\circ}$ , c=10.73 to 10.93 A°. The highest grain size (23.89nm) in the case of OLA and lowest (19.80nm) in case of DMF as a solvents. We can conclude that after heat-treatment of particles can be used to obtain the pure stannite structure of CFTS phase.

In order to further analyze, the crystallinity and impurity phases, Raman spectroscopy is performed. Figure 2.10c shows Raman peaks at 285 and 319cm<sup>-1</sup>, which suggest the formation of CFTS phase [11]. The peak at 319cm<sup>-1</sup> it corresponds to the asymmetry vibration of a pure anion mode. The peak at 285 cm<sup>-1</sup> attributes to a pure anion mode around the Cu cation [30]. The impurity phases are not detected i.e. Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>2</sub>S phases. In addition, when the solvents are OLA, EDA case the Raman peaks are very sharp compared to the other two solvents due to the precursors being dissolved properly in the solvents ( i.e. boiling point of the EDA, OLA is

higher) [31]. When the DMF and DI water are used as a solvent the raman peaks are broad and asymmetry in nature.



Figure 2.10: XRD pattern of CFTS particles (a) As synthesized (b) Heat-treated at 450°C for 30 min with argon ambience sample (c) Raman analysis.

It might be due to the different vibrational excitation in a sample [32]. The elemental composition of CFTS particles was examined by using EDS analysis. The elemental composition of CFTS particles with different solvents is summarized in Table 2.3. The deficiency of iron, tin and copper in rich, were observed in the synthesis of CFTS particles (DMF is used as a solvent), it is due to difference in chemical reactivity of different metal precursors as well as a difference in ionic radius of the metal ions [33]. However, near stoichiometric ratio of CFTS was noticed when the EDA and OLA used as a solvent. The copper, iron and sulphur are near stoichiometric ratio, Sn - deficiency are found in solvent used as a DI water. It might be due to lower reactivity of the Sn with DI water [29].

Tal	ble	2.	3:	E	lemental	compo	sition	of	the	CF	TS	nanoparticles.	
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Different	Elemental composition (%)								
solvents	Cu	Fe	Sn	S					
DMF	28.50	10.85	10.69	49.96					
OLA	21.97	11.24	13.66	53.13					
DI water	26.22	13.05	9.69	51.03					
EDA	23.24	13.43	10.38	52.99					



Figure 2.11: SEM images of CFTS particles for different solvents (a) DMF (b) EDA (c) DI water (d) OLA.

Figure 2.11 shows the SEM images of CFTS particles synthesized at 200°C for different solvents. A flower like morphology is observed when the DMF is used as a solvent (particles size 200 nm). Irregular shape large size particles are observed with size of 1µm when EDA is used as a solvent, it might be due to the its lower viscosity and boiling point [33]. In addition, DI water is used as a solvent in the synthesis of CFTS particles, intermixed with a sheet and aggregate particle morphology. Agglomerated particle morphology is observed with 300 nm, when OLA is used as a solvent, due to high boiling point and viscous nature of OLA. It results in a relatively lower reaction rate, which provides an ideal condition for an anisotropic growth. Similarly, these properties slow down the growth rate [33].

Optical –absorption spectra of CFTS nanoparticles have shown in Figure 2.12. In the case of DMF, higher absorption is observed as compared to other solvents, it might be due to the larger surface area of the flowers like structure compared to other solvents. The optical band gap is found by extrapolating the linear portion of Tauc plots (Figure 2.12) and procedure adopted in the appendix A1. The optical band gap of the CFTS nanoparticles synthesized by using various

solvents (DMF, DI water, OLA, EDA) is found to be, 1.43eV, 1.5eV, 1.65eV, and 1.7eV, respectively. Variation in the bandgap might be due to the varied particle size of CFTS particles (synthesized CFTS particles with different solvents). The estimated optical band gap value matches well with the literature value [2].



Figure 2.12: Optical absorption of CFTS particles, insert figure shows tauc plots of CFTS particles.

# 2.4 Summary

Stannite structure of CFTS phase has been synthesized by varying the temperature, reaction time, and solvents, in solvothermal synthesis. In the temperature-controlled synthesis, a better crystalline CFTS phase was observed at 200°C. While varying the reaction time in the synthesis process, improvement in the crystalline phase of CFTS and numerous morphologies was observed with increasing reaction time. The as-grown particles have some impurity phases and pure crystalline phase particles have achieved after heat treatment. A significant difference in morphology of the CFTS particles is also noticed due to changes in solvents. If the changing the solvent in the synthesis process varies the elemental composition of the CFTS particles and varies the band gap values from 1.43 eV to 1.7 eV, was observed, respectively. The better crystalline phase of CFTS particles is obtained after sulfurization, which are suitable for

photovoltaic and photocatalytic applications. Overall, the results of this study show the synthesis of CFTS particles and reaction parameters such as temperatures, reaction times, and solvents are optimized in solvothermal methods.

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# **CHAPTER-3**

# Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> Particles Using Various Sulphur Precursors and Structural, Optical and Photocatalytic Properties

# **3.1 Introduction**

Quaternary chalcogenide semiconducting materials are intensively investigated for solar energy conversion devices [1]. One of the quaternary chalcogenides semiconductor,  $Cu_2ZnSnS_4$ (CZTS) has shown excellent potential for energy devices due to its several fascinating properties such as suitable bandgap, high absorption coefficient, earth abundant elements etc. [1–4]. The  $Cu_2FeSnS_4$  (CFTS) also has similar properties like CZTS, i.e. high absorption coefficient, earth abundant elements and bandgap in range of visible light [5–7]. The CFTS has also demonstrated its potential application in photovoltaic [8–11] and photocatalytic area [12,13]. The formation of CFTS may lead to better stoichiometry and lesser chance to form secondary phases as compared to CZTS. It has been reported that the replacement of '*Zn*' by '*Fe*' rendered better stoichiometric ratio in CFTS particles. The synthesis of CFTS particles have been performed using variety of techniques such as hot injection, solvothermal process and mechanical grinding etc. [5]. Among these processes, solvothermal technique is widely considered due to several benefits such as high yield, low cost, low-temperature and environmental friendly process [14–16].

In solvothermal synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS), the role of different solvents, capping agents and process parameters has been investigated by various researchers to optimize the structural and optical properties. In most of the studies, the thiourea was used as sulphur precursor [16–20] and there are only few studies in which sodium sulphide was also considered as sulphur precursor [7,19]. The synthesis of phase pure CFTS compound in solvothermal process, the sulphur precursor plays an important role in structural and stoichiometry properties of the CFTS particles [20]. However, the effects of different sulphur precursors on structural and optical properties of CFTS particles are not investigated systematically. Thus, this study is conducted to understand the effect of different sulphur precursors on structural, morphological and optical properties of CFTS particles. Herein, four different sulphur precursors named as *thiourea, thioacetamide, sulphur powder* and *sodium sulphide* is used individually with ethylene

glycol (as a solvent) for the synthesis of CFTS particles. The stannite structure of CFTS particles is obtained in all sulphur precursors. In as-synthesized CFTS particles, binary/impurity phases are also present and has poor stoichiometry ratio. The use of thioacetamide or sodium sulphide as sulphur precursor results in poor crystallinity and binary phases. The crystallinity improves in the case of thiourea or sulphur powder. The use of distinct sulphur precursors renders significant variation in the morphology (spherical shape mixed particles, agglomeration of random size particles, mixture of sheet and flower, agglomerated random particles) of the CFTS particles.

In addition, the photocatalytic properties of the grown CFTS particles are also investigated because photocatalytic properties depend upon structural, compositional and morphological properties of the catalyst. It is well known that the different metal-oxides such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and other binary/ternary semiconductors were sincerely investigated and extensively reported [21–27]. However, most of them are required UV light for excitation which is not favorable for large scale degradation process. The visible light active photo catalysts are preferable for direct degradation under solar light. The quaternary semiconductor such as CFTS has also been demonstrated as good photocatalyst for degradation of organic contamination of water under visible light excitation. For example, the CFTS nanoparticles synthesized by ball milling process has shown around 89% degradation of Rhodamine dye within 2 h time period under white light illumination [12]. J. Zhong and his group have reported 70% degradation of rhodamine dye within 3h using CFTS microspheres synthesized by solvothermal method [28]. The CFTS nanoparticles synthesized by hot injection method was also investigated for degradation of methylene blue dye [29]. There are many reports available, in which the degradation of organic contamination is reported using CFTS particles under white light excitation [12,13,28]. However, the sulphur source dependent change in the structural and compositional properties of CFTS and its effect on photo catalytic properties is not investigated thoroughly. In this study, it is observed that the CFTS particles grown using thiourea has highest photo degradation rate and more than 70% dye is degraded within 1hour excitation of white light.

## **3.2 Experimental Details**

#### 3.2.1 Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles

In a typical synthesis, a mixture of 2mmol (0.399g) copper acetate monohydrate (Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O), 1mmol (0.404g) ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O), 1mmol (0.225g) stannous chloride dihydrate (SnCl<sub>2</sub>.2H<sub>2</sub>O), and 8mmol (0.608g) thiourea (CH<sub>4</sub>N<sub>2</sub>S) was added into a beaker with 40 ml of ethylene glycol ( $C_2H_6O_2$ ) [10]. The precursor's mixture was vigorously mixed for half an hour to get the homogeneous solution. Then, the prepared solution was shifted into the Teflon liner (100 ml) of autoclave. The autoclave was placed in a laboratory oven to conduct the solvothermal reaction. The reaction was carried out at 200 °C for 24h time. After reaction, the autoclave was naturally cooled down to the room temperature. The supernatant was discarded by centrifugation at 10000 rpm for 15 min in ethanol. The centrifugation was repeated three to four times to remove the organic impurities. Then after, grown sample was kept in a vacuum oven at 60 °C for 6 h to get the powder of CFTS particles. Further, to improve the crystallinity of CFTS particles, the particles were sulphurized at 450°C for 30 min in argon atmosphere. To investigate the effect of different sulphur precursors on structural and optical properties, the synthesis was also carried out using thioacetamide (TTA), sodium sulphide (Na<sub>2</sub>S) and sulphur powder (Su) in place of thiourea (Tu). In all synthesis, the ratio of metal precursor was fixed (2:1:1:8) and same amount of solvent was also used. All the synthesis reactions were carried out at optimized temperature 200°C for 24 h time. In the manuscript, CFTS particles synthesized using thiourea, thioacetamide, Na<sub>2</sub>S and sulphur powder are denoted as CFTS-Tu, CFTS-TTA, CFTS-Na<sub>2</sub>S, and CFTS-Su, respectively.

### 3.2.2 Characterization of Cu<sub>2</sub>FeSnS<sub>4</sub> particles

The phase purity and crystal structure of synthesized CFTS particles were determined by X-ray diffraction measurement with Cu-Ka radiation ( $\lambda$ = 1.54Å) using Bruker D-8 Advance X-ray diffractometer. The impurity phases and confirmation of crystal structure were further carried out by Micro-Raman spectrometer (Horibra LABRAM-HR visible (400 - 1100 nm) laser source with an excitation wave-length of 473 nm and spot size of 1µm at 25 mW laser power. Morphology and elemental analysis of the synthesized CFTS particles was analyzed by Scanning Electron Microscope (FEG–SEM, Supra 55 Zeiss), attached with Energy Dispersive Spectrometer (EDS) operated at 20kV. Surface oxidation states/elemental compositions were

analyzed by X-ray photoelectron spectroscopy (monochromatic Al X-ray source and Ar ion gun). The carbon 1s line corresponding to 285 eV was used for the calibration of the binding energies in X-ray photoelectron spectroscopy. The specific surface area of CFTS particles was investigated by the nitrogen adsorption - desorption isotherm measurement at 77K using Accelerated Surface Area and Porosimetry (ASAP) 2020 Micro-metrics (Quantchrome Autosorb IQ2) system. The optical absorption properties of synthesized CFTS particles were examined by using spectrophotometer (Cary 100 Bio UV-Vis, PerkinElmer) at room temperature.

#### 3.2.3 Photocatalytic properties of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

The photocatalytic activities of CFTS particles were determined by studying the degradation of methylene blue (MB) dye in an aqueous solution, exposed to 500 W halogen lamp. The distance between the light source to sample was 30 cm. The schematic representation of photocatalytic measurement test is given in Figure 3.1. The intensity of the light source was measured using Lux meter (Lutron/LX-101A model) and it was 16150 lux (~9 mW/cm<sup>2</sup>). A 50 mg CFTS powder was added in a 100 ml of Methylene blue dye with a concentration of 10<sup>-4</sup> mol/L. The solutions were stirred for 30 min to get the adsorption and desorption equilibrium between the catalyst and Methylene blue dye solution. Then the solution was exposed to presence of light under continuous stirring. A small amount of solution at the different time interval was taken and centrifuged at 5000 rpm for 5 min to remove the catalyst. Further, the solution was filtered to do the analysis on UV-Visible spectroscopy. The catalytic performance of CFTS sample is also conducted in dark light.



Figure 3.1: Schematic representations of photocatalytic measurement test.

# **3.3 Results and Discussion**

#### 3.3.1 Structural properties of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

The XRD patterns of CFTS particles synthesized using different sulphur precursors are shown in Figure 3.2a. The XRD diffraction pattern of all the samples have peaks of planes (112), (200), (222), (312) in accordance with the stannite structure of CFTS (JCPDF No:44-1476). Apart from this, a tiny peak at 52.5° is also there which is related to Cu<sub>2</sub>S phase. The CFTS particles synthesized using thiourea and sulphur show high intensity peak of (112) and relatively less broadness; it indicates the better crystallinity and large crystallite size of CFTS particles. In other hand, the particles synthesized using thioacetamide and sodium sulphide results in less intense and wider (112) peak. The crystallite size of CFTS particles are calculated using Debye-Scherer formula with the full width at half maximum (FWHM) of the (112) diffraction peak [30]. The crystal parameters and average crystallite size (9.22 nm) and the CFTS- TTA particles have the smallest (4.27 nm) crystallite size. The lattice parameters of CFTS particles are extracted from XRD data using interplanar spacing formula and Bragg's equation [16]. A noticeable change in XRD pattern is observed after heat treatment of CFTS particles



Figure 3.2: XRD patterns of CFTS particles (synthesized using different types of sulphur precursors) (a) As-synthesized (b) sulphurized at 450 °C for 30 min in Argon ambiance.

under sulphur atmosphere, the sulphurized CFTS particles (at 450°C for 30 min in argon atmosphere with sulphur) have sharp peaks and reduce FWHM. It indicates the improvement in crystallinity of the CFTS particles as well as size of the crystallites after sulphurization. Such improvement in crystallinity might be due to reduction in organic impurities and residual solvents that has evaporated during heat-treatment. The crystallite size of CFTS particles also increases after heat treatment [31] possibly due to the recrystallization process [32].

Table 3.1: Crystallite size and lattice parameters of the as synthesized and sulphurized CFTS particles, synthesized using different precursors of sulphur.

	As-synthesiz	ed CFTS p	articles	Sulphurized CFTS Particles			
Sulphur Precursors	Crystallite size (nm)	Lattice parameters		Crystallite size (nm)	Lattice parameters		
		a (Å)	c (Å)		a (Å)	c (Å)	
Thiourea	9.05	5.458± 0.025	10.826 ± 0.181	18.78	5.362± 0.031	10.791± 0.238	
Thioacetamide	4.27	5.369± 0.001	10.961 ± 0.105	18.33	5.373± 0.071	$10.632 \pm 0.182$	
Sodium sulphide	4.62	5.393± 0.003	10.711 ± 0.016	19.01	5.372± 0.023	10.582± 0.059	
Sulphur powder	9.22	5.363± 0.003	10.651 ± 0.079	19.49	5.361± 0.044	10.603± 0.032	

The formation of binary phases or other impurity phases could not be distinguished using XRD analysis due to similarity in crystal structure of CFTS and binary phases. Therefore, Raman spectroscopy is performed to investigate such differences. The CFTS particles show an intense peak at 319 cm<sup>-1</sup> in Raman spectrum due to symmetric vibration motion of sulphur ions [33]. In addition, presence of pure '*S*' anion around the '*Cu*' cation results a peak at 285 cm<sup>-1</sup> corresponds to crystalline phase [33]. While, the peak at 472 cm<sup>-1</sup> in Raman spectra of CFTS indicates the formation of Cu<sub>2</sub>S phase [10,33,34]. The CFTS -Tu and CFTS-Su samples show strong Raman peak at 319 cm<sup>-1</sup>, confirm the formation of CFTS phase. However, a low intensity peak at 472 cm<sup>-1</sup> is also present in CFTS-Tu sample which- indicates the partial presence of Cu<sub>2</sub>S phase. The CFTS crystalline peak is observed at 319 cm<sup>-1</sup> in CFTS-TTA or CFTS-Na<sub>2</sub>S samples, but they have strong peaks at 472 cm<sup>-1</sup> that mean Cu<sub>2</sub>S phase is dominating in these two samples

(Figure 3.3a). Further, a low intensity Raman peak at 285 cm<sup>-1</sup> is present in all the samples which indicates formation of crystalline CFTS. In case of CFTS-Su, a peak at 214 cm<sup>-1</sup> appears that indicate the presence of partial FeS binary phase (Figure 3.3a) [34,35]. The formation of such secondary phases is observed in as-synthesized CFTS particles due to the different reactivity of sulphur sources in same organic media at same reaction temperature [36]. The reactivity (the rate of diffusion) of constituent elements of Cu<sub>2</sub>FeSnS<sub>4</sub> can be changed by varying the reaction or annealing temperature [35]. At high temperature annealing the binary phases are usually diffused to form pure crystalline phase due to the change in reactivity of constituent elements [37,38]. Therefore, the Raman spectra of sulphurized (annealed) CFTS particles show significant change, here all the samples have strong crystalline peak at 319 cm<sup>-1</sup> and 285cm<sup>-1</sup> (Figure 3.3b). It indicates that the secondary phases are disappeared/reduced after sulphurization and crystallinity of the CFTS particles is improved.



Figure 3.3: Raman spectra of (a) as-synthesized CFTS particles, (b) Sulphurized CFTS particles at 450 °C for 30 min in Argon ambience.



Figure 3.4: FTIR spectra of CFTS samples (synthesized using different Sulphur source).

FTIR spectroscopy has been studied to get the information about the organic impurities of CFTS powder samples as shown in Figure 3.4. The band around 3170 cm<sup>-1</sup> is usually assigned to water molecules and O-H stretching band [39–41]. Further, it is presented that the peak at 1624 cm<sup>-1</sup> attributed to the NH<sub>2</sub> group that is assigned to the metal- complex in CFTS-Tu and CFTS-TTA samples [42–44]. Moreover, in CFTS-Su, CFTS-Na<sub>2</sub>S sample, the low intensity peak appears at 1624 cm<sup>-1</sup> due to the bending vibration of hydroxyl groups from the water (here water is producing from the metal salts)[45,46]. The other peaks such as 610 cm<sup>-1</sup> and 1087 cm<sup>-1</sup> belong to sulfate peaks (SO<sub>4</sub> group) [47] and peak at 760 cm<sup>-1</sup> belonging to C-H group attributed to the aromatic C-H in-plane bend are noticed in all cases i.e. means that organic compound present in the all samples and less intensity peak is appeared in CFTS-Tu [48].

The structural properties of CFTS particles are further investigated using XPS. The binding energy of '*Cu*' in CFTS are shown in Figure 3.5a, narrow and symmetric peaks at 931.5 eV and 951.36 eV are observed in all CFTS particles that are attributed to the Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub> states, respectively. The separation between these peaks (Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub>) is 19.86 eV that indicate Cu (+1) state in CFTS particles [49–51]. However, another shoulder peak in Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub> are also noticed that belong to the oxide phase of copper (CuO), indicated

the partial presence of CuO in all the CFTS particles. The binding energy peak of '*Fe*' in CFTS appears at 710.4 eV and 723.9 eV corresponding to Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  peaks with the separation of 13.52 eV for Fe (+2) configuration [49,50]. In three samples, CFTS-Tu, CFTS-Na<sub>2</sub>S, CFTS-TTA, the Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  peaks are observed at designated positions (Figure 3.5b), however, all these peaks are asymmetric. A satellite peak at 715.16eV is also noticed, which is very prominent in all four samples. The satellite peak is highly intense in the case of CFTS-Su particles is attributed to the Fe (+2) state [52,53]. The binding energy peak of '*Sn*' in CFTS particles appeared at 486.3 and 494.9 eV, corresponds to Sn (+4) with  $3d_{5/2}$  and  $3d_{3/2}$  states [49,51]. All four samples have shown intense peaks of crystalline '*Sn*' in XPS analysis.



Figure 3.5: XPS analysis of as synthesized  $Cu_2FeSnS_4$  particles grown using different sulphur precursors (a) Cu2p3/2 and Cu2p1/2 peaks (b) Fe 2p3/2 and Fe 2p1/2 (c) Sn 3d5/2 and Sn 3d3/2 (d) S 2p3/2 and S2p1/2.

The CFTS-TTA and CFTS-Na<sub>2</sub>S samples results in doublet peaks at 487.3 eV and 495.37 eV, attributing to the SnO<sub>2</sub> phase [54–56]. The asymmetric and peak splitting might be due to the impurity phase presence in the CFTS particles (in TTA, and Na<sub>2</sub>S). The binding energy of *S*' in CFTS, S2P<sub>3/2</sub> and S2P<sub>1/2</sub> peaks appear at 161.59 eV and 162.65 eV (Figure 3.5d), with the peak separation of 1.06 eV, indicating the presence of sulphur in (-2) state [7]. However, CFTS particles synthesized using sulphur powder, has significant difference in peaks S2P<sub>3/2</sub> and S2P<sub>1/2</sub> positions, it indicates the presence of some unbounded/residual sulphur. Thus, XPS analysis of as-synthesized CFTS particles suggests that out of four samples, the CFTS-Tu particles have better crystalline properties. It also has better stoichiometric ratio and standard oxidation state of all elements. While, *Cu*, *Fe* and *S* are in standard oxidation states in CFTS-TTA and CFTS-Na<sub>2</sub>S particles, but *Sn* is having slight variation. However, in CFTS-Su the only *Cu* and *Sn* are in standard oxidation state and *Fe* and *S* has a large variation.

Sulphur source	Elemental composition (Atomic%)							
	As- synth	ticles	Sulphurized CFTS particles					
	Си	Fe	Sn	S	Си	S		
Ideal	25	12.5	12.5	50	25	12.5	12.5	50
Sulphur	25.79	11.94	10.24	52.03	24.01	13.62	10.39	51.98
ТТА	26.43	12.03	10.32	51.22	23.81	12.23	10.98	52.98
Tu	24.76	14.07	13.02	48.15	23.33	13.85	12.21	50.61
Na <sub>2</sub> S	28.76	13.65	8.96	48.63	24.52	11.37	12.08	52.03

Table 3.2: Elemental composition of the CFTS particles synthesized using different sulphur precursors.

In further structural investigation, elemental compositions of synthesized CFTS particles are determined using EDX analysis are shown in Table 3.2. The Copper is found in close to ideal stoichiometric ratio in only CFTS- Tu particles but other samples (CFTS-Na2S, CFTS-TTA, CFTS-Su) has copper-rich composition. The iron rich composition is found in CFTS-Na<sub>2</sub>S and CFTS-Tu, other samples have slightly lower amount of iron. The *Sn*- deficiency is observed in CFTS-TTA, CFTS-TTA, CFTS-Na<sub>2</sub>S, CFTS-S sample but Sn-rich composition is noticed in CFTS-Tu sample. The *S*-deficiency was observed in CFTS-Na<sub>2</sub>S, CFTS-Tu but high content of sulphur is

measured in CFTS-S, CFTS-TTA samples. The different elemental composition in the synthesized CFTS particles leads to formation of secondary phases along with as synthesized CFTS particles [5]. After sulphurization, the amount of sulphur is increased in CFTS-Tu and CFTS-Na<sub>2</sub>S samples. The distribution of other metallic elements also changes and slight variation in their composition is noticed after sulphurization process.

# **3.3.2** Morphological properties and surface area of $Cu_2FeSnS_4$ (CFTS) particles

The shape and surface morphologies of as-synthesized CFTS particles are shown in Figure 3.6. The CFTS-Su particles are having spherical shape with variation in their size (Figure 3.6a). The agglomerated (random size) particles are obtained in CFTS-TTA (Figure 3.6b). The CFTS-Tu sample is having intermix sheets-flower like morphology (Figure 3.6c). While, the CFTS-Na<sub>2</sub>S samples results in the formation of agglomerate mixed size-shape particles (Figure 3.6d). The specific surface area of the as-synthesized CFTS particles is also calculated using BET measurement to understand the active surface area in all the CFTS samples.



Figure 3.6: SEM images of as- synthesized CFTS particles grown using (a) Sulphur powder (b) Thioacetamide (c) Thiourea (d) Sodium sulphide as sulphur precursor.

The N<sub>2</sub> adsorption-desorption isotherm data of the as-synthesized CFTS particles are presented in Figure 3.7. The specific surface area of the CFTS particle are calculated to be 55.91  $m^2/g$ , 48.67  $m^2/g$ , 40.56  $m^2/g$ , and 28.02  $m^2/g$ , in CFTS-Tu, CFTS-Na<sub>2</sub>S, CFTS-TTA, and CFTS-Su, respectively. Figure 3.7b shows the pore size distribution of CFTS particles which are examine by using the Barrett-Joyner-Halenda (BJH) method. The pore size of the CFTS particles is 3.80 nm in CFTS-Na<sub>2</sub>S), 3.83 nm in CFTS-Tu), 3.82 nm in (CFTS-TTA) and 3.64 nm in CFTS-Su samples. Thus, out of four samples, CFTS-Tu sample has high surface area as well pore size which might be due to flower-nanosheets mixed morphology.



Figure 3.7: (a) N<sub>2</sub> adsorption-desorption isotherms (b) Pore diameter distribution examine the desorption branch using the BJH method of CFTS sample.

#### 3.3.3 Optical properties of Cu<sub>2</sub>FeSnS<sub>4</sub>(CFTS) particles

All CFTS samples have shown optical absorption in the visible region, as shown in Figure 3.8. The change in absorption might be induced by light scattering due to different morphology and size of the particles. As per the reported literature, change in structural properties such as crystallinity, crystallite size, and morphology etc. affect the optical absorption [57]. Herein, change in sulphur source changes the reaction process during the growth of CFTS particles and results in the variation of structural and morphological properties that leads to significant change in optical properties [32]. The optical band gap of CFTS particles is estimated after calculating molar absorption coefficients [6]. The band gap of the CFTS particles is found to be 1.48 eV (CFTS-Su), 1.53 eV (CFTS-Tu), 1.72 eV (CFTS-TTA), 1.81 eV (CFTS-Na<sub>2</sub>S) when sulphur powder, thiourea, TTA and Na<sub>2</sub>S are used for growth, respectively.–In CFTS compound semiconductor, the conduction band minima is composed of anti-bonding state of Fe

3s/Sn 5s and S3p orbitals whereas the valance band maxima is the consequence of hybridization of Cu3d and S3p orbitals [58,59]. It has been reported that the change in elemental content in ternary and quaternary chalcogenide compounds can affect the p-d, s-p and d-p hybridization (for example Cu-S bond (p-d), Sn-S bond (s-p), Fe-S (d-p) bond) which influences the optical bandgap [8,51].



Figure 3.8: Optical absorption of CFTS particles synthesized using different sulphur precursors; inset figure shows Tauc plot and bandgap.

## 3.3.4 Photocatalytic performance of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

The industrial revolution is good in one sense, but it is also polluting our natural resources day by day. The water contamination by organic dyes, such as methyl orange, rhodamine B, methylene blue, methyl red, azo dye, acid red G and eosinY, is the common issue in textile industries, dye industries and biological tagging. It causes adverse effect on our environment and human being [60–62]. Therefore, the degradation of such organic pollutants is essential before discharging contaminated water into the environment [60]. TiO<sub>2</sub> is the most studied materials for degradation of organic and inorganic pollutants due to its nontoxicity, chemical and biological stability and low cost availability [61]. However, TiO<sub>2</sub> applicable only under UV light excitation that limits its usage. Therefore, the development of highly efficient visible-light active photocatalysts for degradation of organic/inorganic pollutant is an essential

task. In this direction, the bismuth based compounds such as  $Bi_2WO_6$ ,  $Bi_2MoO_6$ ,  $BiVO_4$  etc., have been reported to demonstrate high degradation rate of organic dye under visible-light excitation [63]. CTAB/BiOCl composite material have also shown an excellent adsorptive capacity and highly efficient photocatalytic activity [62]. Recently, graphene (GR)- wrapped rose- like  $Bi_2O_2CO_3$  core- shell structures and layered structure of bismuth Oxychloride were reported which has shown photocatalytic activities in white light source [64,65]. Similarly, g- $C_3N_4$  [66] has shown visible light photocatalytic activities [67]. Hierarchical porous titania spheres were also reported to show high photocatalyst activity on the degradation of organic dyes [68]. The chalcogenides semiconductors such as CZTS and CFTS etc. were also extensively investigated for visible light driven photocatalytic activities [12,13,28].



Figure 3.9: The photocatalytic degradation of Methylene blue in the presence of CFTS particles (As- synthesized) under visible light irradiation; (a) CFTS-Tu, (b) CFTS-TTA, (c) CFTS-Su, (d) CFTS- Na<sub>2</sub>S.

The photocatalysis refers to the oxidation and reduction reactions on the surfaces of photocatalyst material, intermediate by the valence band (VB) such as holes (h<sup>+</sup>) and conduction band (CB) such electrons(e<sup>-</sup>) generated by the absorption of UV-Vis light radiation. Such photogenerated pairs (e<sup>-</sup>-h<sup>+</sup>) induces the formation of aggressive species such as hydroxyl (OH<sup>-</sup>).

These species are strong enough to oxidize and decompose organic materials [69]. To study the photocatalytic activity, the optical absorption spectra of methylene blue dye are recorded (peak at 667nm, Figure 3.9) during degradation process (with different CFTS particles). The percentage of photocatalytic activity was calculated using the following formula as:

Photocatalytic activity (%) =  $((C_o - C_t)/C_o) \times 100$  (3.1)

Where  $C_o$  was the initial concentration of methylene blue dye and  $C_t$  was the concentration of methylene blue dye when it is reacted with CFTS for a certain time (t) [70,71]. The maximum photocatalytic activity obtained for CFTS-Tu particles is 80% for 90 min which is accredited to the highest active surface area (55.91 m<sup>2</sup>/g), pore size (3.83nm) and its superior crystallinity. The photocatalytic activity of methylene blue dye for CFTS-Su, CFTS-TTA and CFTS-Na<sub>2</sub>S particles is 70%, 65% and 55% in 90 min, respectively (Figure 3.10). Among CFTS-Su, CFTS-TTA particles, and CFTS-Na<sub>2</sub>S, although the surface area of CFTS-Na<sub>2</sub>S has high surface area but the photocatalytic performance is the lowest might be due to the poor crystallinity and high optical bandgap. Because photocatalytic properties depend upon active surface area as well as light harvesting capability/bandgap, photo charge generation-separation properties of photocatalyst [72]. In addition, the catalytic performance of CFTS samples is also tested in dark and only slight decrease in the intensity of dye peak is observed, this small change may be possible due to dye absorption at CFTS surface (Figure 3.10). The photo-degradation performance of sulphurized samples (annealed) is also investigated, however, there is only slight improvement (approximate 5%) in degradation rate is measured are shown in Figure 3.11.

Further, the presence of impurity phases in CFTS plays a significant role on photocatalytic properties because the impurity phases affect the band gap, photo charge generation and life time of electron-hole pair and recombination rate etc.[73–75]. As per structural analysis, the as- synthesized CFTS-TTA, CFTS-Na<sub>2</sub>S and CFTS-Su have high order of secondary phases than CFTS-Tu sample, therefore, they result in poor photocatalytic performance. The impurity phase act as photo charge carriers (electron-hole) trapping states, which increases the carrier's recombination rate and lower the photocatalytic performance.



Figure 3.10:The photocatalytic degradation rate of Methylene blue in the presence of CFTS particles (synthesized using different Sulphur precursor).



Figure 3.11: The photocatalytic degradation rate of Methylene blue in the presence of annealed CFTS particles (synthesized using different Sulphur precursor).

# **3.4.** Summary

Cu<sub>2</sub>FeSnS<sub>4</sub> particles were successfully synthesized using solvothermal method and effect of different source of sulphur on structural, optical and photocatalytic properties are investigated. Source of sulphur (precursors) has an important role to decide the morphology, crystallanity and optical properties of CFTS particles. Crystalline properties, stoichiometry and morphology can significanly be tuned by selecting the right sulphur precursor. Post growth heat treatment further improved the crystalline properties of CFTS particles. The bandgap tunning is also demonstrated by replacing the source of sulphur precursors, a variation from 1.48 eV to 1.81 eV in the case of Su, Tu, TTA, Na<sub>2</sub>S source are achieved. The CFTS particles grown using thiourea as a source of sulphur demonstrated better photocatalytic activity.

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# **CHAPTER-4**

# Porous Cu<sub>2</sub>FeSnS<sub>4</sub> Particles for Removal of Organic Acid Fuchsin Dye from Wastewater by Adsorption Process

# **4.1 Introduction**

Acid fuchsin (AF) dye is broadly used in textile fabrics, silk, nylon, wool, and leather [1,2]. The water pollution due to the synthetic dye pollutants (for example, AF dye) releases from textiles, paper, rubber, and plastic production which has a direct effect on the environment and human health [3,4]. The industry's wastewater release should be purified to reduce the adverse effects before mixing into natural resources [3,4]. Water purification has been performed using several techniques such as electrochemical reactions [5], biodegradation [6,7], adsorption [8], and other methods [4,8]. Among these processes, the adsorption technique for water purification is gaining popularity due to a smooth, less energy consumption, economically feasible process. It does not need any light source with reasonable efficiency [8]. For efficient removal of pollutants from water, the adsorbents should have a large surface area, porosity, hollow and layered structures [4,8]. Numerous materials such as carbon (carbon nanotubes and graphene/magnetite) [9–11], graphene-TiO<sub>2</sub> [12], metal-organic frameworks (MOFs) [13], inorganic materials (oxides such as Fe<sub>3</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO [14–17]) and chalcogenides (MoS<sub>2</sub> [18], NiS [19],  $Cu_3SnS_4@C$  [20] and  $Cu_2FeSnS_4$  [21]) and biomaterials (chitosan and peat) have been reported as an adsorbent for the extract of dyes from the aqueous solution/ industrial wastewater [22-24]. Among these materials, earth-abundant and non-toxic quaternary chalcogenide Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) has received great attention owing to outstanding physicochemical and optoelectronic properties such as non-toxicity nature of constituent elements, large absorption coefficient (>10<sup>4</sup> cm<sup>-1</sup>), suitable bandgap (1.0 eV - 1.5 eV), and excellent electrical properties [25–28]. It has been explored in numerous applications such as solar cells, gas sensors, optical devices, and photocatalysis [26-28]. Hierarchical porous hollow CFTS microspheres exhibited superior capability to remove methyl orange dye pollutants in water via the adsorption process [21]. CFTS particles have also been investigated for photodegradation of rhodamine (RhB) and methyl orange (MO) under visible light [29,30]. However, the removal of acid fuchsin (AF) dye

pollutant from the water solution with CFTS adsorbent is not yet reported in the literature. Thus, it will be exciting to synthesis porous CFTS particles and utilize them to remove acid fuchsin (AF) dye pollutants from the aqueous solution.

Non-toxic quaternary chalcogenide CFTS particles have been synthesized in various methods such as thermal decomposition [26], microwave [21], solvothermal/ hydrothermal method [25,27], hot injection method, and others [27]. Among them, the solvothermal process is facile, high yield and has good control over crystal phase, morphology, and chemical composition of CFTS particles while varying process parameters such as reaction temperature, time, surfactants, and an initial precursor and their concentrations [29,31,32]. It is essential to the synthesis of porous CFTS particles and their application towards efficient dye adsorbent. In this article, solvothermal synthesis of CFTS particles and their application towards adsorbent for the adsorption (degradation) of acid fusion (AF) dye from the aqueous solution are reported. The role of surface morphology of CFTS particles on dye adsorption properties is studied. (97.12  $\pm$  0.76)% of AF dye is adsorbed by the porous spheres of CFTS particles within 60 min. The CFTS particles have shown recyclable nature and can be repeatably used for adsorption of dye. The obtained results indicate that porous CFTS particles have a higher adsorption capacity.

# 4.2 Experimental details

## 4.2.1 Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

Cu<sub>2</sub>FeSnS<sub>4</sub> particles were synthesized at 200 °C for 6 h, 12 h, and 18 h via solvothermal method. The synthesized CFTS particles using different reaction times are represented as CFTS-6h (porous), CFTS-12h (flakes), CFTS-18h (sheet-flower) in the manuscript. Details experimental procedure was discussed in the chapter-2, section-2.2.2.

#### **4.2.2 Dye adsorption experiments**

Adsorption is a physicochemical surface interaction between the adsorbate and the adsorbent. The adsorbents should have a high surface area, desirable textural and surface features for fast and efficient performance to remove the organic pollutants from the wastewater. Synthesized CFTS particles were utilized as an adsorbent to remove acid fusion (AF) dye from aqueous solution in the absence of light. The schematic diagram represented in Figure 4.1. To remove acid fuchsin (AF) dye from aqueous solution: 20 mg of prepared CFTS particles were

added in 100 ml of AF dye solution (initial dye concentration: 20 mgL<sup>-1</sup>, pH ~ 5.6, and room temperature). The dye solution was stirred continuously at 400 rpm in a dark room. A small amount (4 ml) of the dye solution was taken at a specific time interval, and the adsorbents were separated by centrifugation at 4000 rpm for 5 min. The concentration of AF dye in the supernatant solution was analyzed using UV-visible spectroscopy. The following equations estimate the percentage of dye removal and adsorption capacity [8,33].

$$Dye\ removal(\%) = \left(\frac{c_o - c_t}{c_o}\right) \times 100 \tag{4.1}$$

Adsorption capacity 
$$(q_e) = (C_o - C_e) \times \frac{V}{M}$$
 (4.2)

Where  $C_o$  initial concentration of the adsorbate solution, C<sub>t</sub> final concentration of the adsorbate solution at a particular time interval, C<sub>e</sub> equilibrium concentration of adsorbate solution (mgL<sup>-1</sup>) and V is the volume of AF dye solution (L), M is the mass of the adsorbent (g) respectively.



Figure 4. 1: Schematic diagram of the adsorption process.

# 4.3 Results and discussion

# 4.3.1 Structural and morphological characteristics of $Cu_2FeSnS_4$ (CFTS) particles

The detailed structural and morphological properties are discussed in chapter-2, section 2.3.2. The crystallinity of CFTS particles analyzed by XRD technique confirms the tetragonal crystal structure of CFTS phase. Raman spectroscopy has also used to analyze the impurity phases present in the CFTS particles. Raman technique reveals that pure crystalline phase of CFTS particles was noticed. In addition, oxidation states of CFTS particles (6h grown sample) analyzed by XPS technique demonstrate that all constituent elements are standard oxidation states ( $Cu^{+1} Fe^{2+}Sn^{4+}S^{-}$ ) present in the CFTS compound. The functional groups (for example, OH<sup>-</sup> groups) of synthesized CFTS particles confirms by FTIR analysis. The FTIR analysis concludes that functional groups present on the surface of all synthesized CFTS particles. The morphological study of CFTS particles (grown with different reaction times) was estimated by SEM. The 6h grown sample reveals porous sphere (200nm), 12h growth sample sheet-flake like morphology, and a mixture of flower-sheet for 18h grown CFTS sample were observed. The surface area prepared CFTS particles are (obtained from multipoint BET) found to be 53.50 m<sup>2</sup>g<sup>-1</sup> for porous-CFTS, 33.10 m<sup>2</sup>g<sup>-1</sup> for flakes- CFTS and, 20.99 m<sup>2</sup>g<sup>-1</sup> for flowers-CFTS morphology, respectively.

## 4.3.2 Adsorption of AF dye molecules by Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles

Removal of organic pollutants (i.e., AF dye) from aqueous solution using adsorbent depends on the following parameters: pH of the solution, a contact time of adsorption, adsorbent dosage, temperature, and initial dye concentration [34]. The effect of pH of the solution, adsorbent dosage, temperature, and initial dye concentration on percentage of dye removal and dye adsorption capacity was investigated. The obtained results are discussed in the following section.

#### 4.3.2.1 Effect of contact time for removal of AF dye using various morphology of CFTS

Removal of toxic AF dye from wastewater using various morphology of CFTS particles as adsorbent was used in the adsorption process. Figure 4.2(a-d) shows the dye adsorption behavior and dye removal percentage of the various morphology (porous sphere, sheet-flake, and flower-sheet) of CFTS particles. The highest (89.25  $\pm$  2.21)% of AF dye adsorbed (removal) within 10 min for porous spheres of CFTS particles (Figure 4.2a) and this value reaches (97.12  $\pm$  0.76)% within 60 min due to porous nature and high surface area of CFTS particles. Further, CFTS particles with flakes and flower-sheet-like morphology exhibit 86% and 79% of AF dye removal within 10 min, and adsorption reaches more than 90% of AF dye (Figure 4.2b & 4.2c) after 60 min respectively. The absorption spectra and inset photograph (inset, Figure 4.2a) confirm the complete removal of AF dye from the water within 60 min. The higher dye adsorption (removal) might be due to the electrostatic interaction between negatively charged AF dye and positively charged CFTS particles, and the high surface area of porous sphere CFTS particles [8]. It also depends on functional groups of the adsorbent (confirmed by FTIR analysis), the structure of the adsorbate, the surface area of the adsorbent, and interaction among adsorbent and adsorbate [3,8].



Figure 4.2: Time-dependent adsorption study of CFTS particles (a) CFTS-6h, (b) CFTS-12h, (c) CFTS-18h and (d) dye removal percentage of porous CFTS particles. Error bars show the standard deviations.

The adsorption properties of CFTS for methylene blue (MB) and rhodamine blue (RhB) dye to understand the diverse dye's effect. The 50% for MB dye and 57% for RhB dye removal is obtained in 4 h contact time, as shown in Figure 4.3. Due to the presence of positive charges on both dyes (MB and RhB) [35] and adsorbent (CFTS), the same charges repel each other, leading to a slower removal rate of dye than AF dye (negatively charged) from an aqueous solution. According to previous studies, the positively charged dyes and negatively charged adsorbents interact with each other due to electrostatic attraction, leading to a better removal percentage of dye and vice versa [33].



Figure 4.3: (a) Removal of Methylene blue dye (b) Rhodamine blue using CFTS as adsorbent.

#### 4.3.2.2 Effect of pH of solution for the removal of AF dye

The isoelectric point or point of zero charge (PZC) of adsorbent plays a vital role in identifying the optimum pH value required for the adsorption experiment [36]. The PZC of porous CFTS particles was examined by salt addition method. In, a series of experiments containing 50 ml of 0.01M NaCl solution was adjusted to pH in the range of 2.0-10.0. The pH values were calibrated using aqueous 0.1M HNO<sub>3</sub> or 0.1M NaOH. In all experiments, the initial pH (pH<sub>i</sub>) was measured. A 20 mg of CFTS particles were added to each 50 ml beaker separately. The solution was mixed properly and stirred for 24 h. After that, a solution was filtered and the final pH (pH<sub>f</sub>) of the solution was measured. The  $\Delta$ pH (difference between initial and final) values plotted against the initial pH values. Figure 4.4a shows that  $\Delta$ pH is equal to zero represents the PZC of the adsorbent [37–39]. The determined PZC value of porous CFTS adsorbent is 5.80 (calculated from Figure 4.4a), indicating the adsorbent surface is neutral.

Nevertheless, the surface of the porous CFTS is positively charged for the solution pH < 5.80, while it is negatively charged for the solution pH > 5.80. The adsorption mechanism between the adsorbent and adsorbate depends on the pH of the solution. Further, the percentage of AF dye removal using porous CFTS adsorbent was investigated in the range of pH values from 3 to 9 (Figure 4.4 b).  $(96.5 \pm 1.29)$  % of the dye removal was obtained in the range of pH values from 5 to 5.6. It can be justified under the following reasons: acidic pH, positively charged porous CFTS surface, consequence from the protonation of its amine groups results in attracting the anionic AF dye due to the strong electrostatic interaction [2,40,41].  $(89 \pm 2.58)$  % of the dye removal is observed for pH = 3, which could be due to the strong acidic nature. The sulfonate groups of the AF start deprotonating, finally diminishing the anionic nature of dye [2]. From FTIR result confirm the sulfonate group's presence in the AF dye as shown in Figure 4.5. Further, dye removal percentage decreases significantly while increasing pH values from pH = 7 to pH = 9(towards alkaline media). From the PZC analysis (Figure 4.4a), porous CFTS adsorbent negatively charges alkaline solution media. With the presence of negative charges on both dye (AF) and adsorbent (CFTS), the same charges repel each other, leading to a slower removal rate of AF dye from an aqueous solution.



Figure 4.4: (a) Point of zero charge measurement of porous CFTS particles (b) dye removal (%) in presence of various pH value (dosage: 20 mg, dye concentration: 20 mg/L, contact time: 60 min).



Figure 4.5: FTIR spectra of the Acid fuchsin (AF) dye.

#### 4.3.2.3 Effect of porous Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) dosage for removal of AF dye

The dye adsorption capacity and percentage of dye removal performance were investigated by changing the initial dosages of porous CFTS adsorbent (5 mg to 25 mg taken in 100 ml of aqueous AF dye solution) with fixed contact time = 60 min, dye concentration = 20 mg/L, pH = 5.60. The percentage of dye removal increases with an increase in adsorbent dosage upto 20 mg, and behind this point, it maintains constant dye adsorption with an increase in adsorbent dosage (Figure 4.6a). A minimum of  $(81.45 \pm 1.61)$  % dye removal is noticed for 5 mg and (97.65 ± 1.00) % for 20 mg, respectively. This phenomenon may be due to the increase in adsorbent surface area and adsorption of binding sites in the porous CFTS. Besides, adsorption capacity decreases with increasing adsorbent dosage (5 mg to 25 mg) are depicted in Figure 4.6a, which might be due to the aggregation of porous sites and increases diffusion path length, attributed to the decrease of the total available surface area [42].

#### 4.3.2.4 Effect of dye concentration for removal AF dye using porous CFTS adsorbent

The dye adsorption capacity and percentage dye removal performance were investigated by varying the initial dye concentration (20 mg/L to 80 mg/L), with fixed adsorbent dosage (20 mg), contact time (60 min), and pH= 5.6. Figure 4.6b depicted that the percentage dye removal decreased with increasing initial AF dye concentration, which may be ascribed to the saturation of active binding sites of the porous CFTS surface by the AF molecules [33]. However, the equilibrium adsorption capacity increases with an increasing dye concentration of adsorbate (Figure 4.6b). Therefore, it might be a stronger interaction between the adsorbent and AF dye at a higher concentration. Mass transfer driving force is also enhanced by increasing the dye concentration at the adsorbent's active site [54]. The adsorbent's surface occupies AF dye molecules until reaching adsorption equilibrium via mass transfer driving force [54].



Figure 4.6: Effect of adsorbent dosages, dye concentrations, and temperatures on dye removal (%) and adsorption capacity of the porous CFTS: (a) using various adsorbent dosages, (b) initial dye concentration, (c) temperatures.

#### 4.3.2.5 Effect of temperature for removal of AF dye

The effect of temperature on the AF dye adsorption process and percentage of dye removal was examined in the various temperatures such as 25 °C, 30 °C, 40 °C, 50 °C with fixed adsorbent dosage (20 mg), dye concentration (20 mg/L), pH=5.6, and contact time of 60 min. Figure 4.6c shows that (97.38  $\pm$  0.85) % of dye removal is observed at an initial temperature (25 °C). More than (98.87  $\pm$  0.49) % is noticed at 30 °C. Further, decreasing in the percentage of dye removal was observed in a rise in temperature from 30 °C to 50 °C. At lower temperature, the adsorbent porosity is higher which adsorb the more dye molecules thus increasing the percentage of dye adsorption. However, at high temperatures, desorption may occur due to increased thermal motions of adsorbent, which results in a lower percentage of adsorption [33].

#### **4.3.3** Adsorption kinetics studies

The adsorption capacity calculation details are in section 4.2.2. Figure 4.7a shows that the equilibrium adsorption capacity of the porous sphere, sheet-flake, and flower-sheet is determined to be 48.4 mg/g, 46.83 mg/g, and 46.21 mg/g, respectively. Adsorption kinetics was evaluated to understand the adsorption mechanisms. The various kinetic models, specifically pseudo-first-order, pseudo-second order, and intraparticle diffusion models, were studied to understand the adsorption process. The pseudo-first-order kinetic model assumes that the rate of change of

solute adsorption is directly proportional to the difference in saturation concentration and solid adsorption, which generally occurs at the initial stage of an adsorption process [43]. The pseudo-second-order kinetic model assumes that the adsorption rate is determined by the interaction between the adsorbent and adsorbate, such as ion sharing and transferring [42]. The liner form of pseudo-first-order and pseudo-second-order kinetics equations (3) and (4) are as follows [33,40].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
(4.3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(4.4)

Where  $q_t$ ,  $q_e$  are the amount of dye adsorbed (mg/g) at different time intervals (min), equilibrium adsorption capacity, and  $k_1$ ,  $k_2$  are the rate constants for pseudo-first order(min<sup>-1</sup>) and pseudo-second order (g.mg<sup>-1</sup>.min<sup>-1</sup>) adsorption, respectively. The experimentally observed adsorption capacities exhibit very close to the calculated values obtained from equation 4.2 for the various morphology of CFTS, and the raw data is given in Table 4.1. For the pseudo-first-order model, the liner graph between  $log(q_e - q_i)$  vs. t is shown in Figure 4.7b. The extracted intercept and slope of  $log(q_e - q_i)$  vs. t plots (Figure 4.7b) represent the  $q_1$  and  $k_1$  values. The obtained  $q_1$  and  $k_1$  values are summarized in Table 4.1. Further, for the pseudo-second-order model, the values of  $k_2$  and  $q_e$  are obtained from the plot of  $t/q_t$  vs. t (Figure 4.7c) are shown in Table 4.1. The correlation coefficients (R<sup>2</sup>) value for all three cases is 0.99, which indicates a better fit for the pseudo-second-order model than the pseudo-first-order model. Thus, the adsorption of AF dye onto the surface of CFTS follows the pseudo-second-order kinetics. The experimental and calculated values are very close ( $q_e$  (cal) = 50.76 mg/g and  $q_e$ (exp) = 48.4 mg/g) for porous sphere CFTS, and it also confirms that the adsorption process follows pseudo-second-order kinetic model.

To further identify the diffusion mechanism, the kinetic data were analyzed with the help of Weber and Morris's intraparticle diffusion model is given by the equation (5) [33].

$$q_t = k_i t^{0.5} + C \tag{4.5}$$

Where  $k_i (mg g^{-1} min^{-1/2})$  is the intraparticle diffusion rate constant, and C is the boundary layer thickness, respectively. The  $q_t$  vs.  $t^{1/2}$  plots shows two linear regions for all three morphologies (Figure 4.8). The first region demonstrates boundary layer diffusion due to the mass transfer from the dye solution to the outer surface of the CFTS particles [33,43]. The second linear segment corresponds to the intraparticle diffusion of dye molecules throughout the adsorbents



Figure 4.7: (a) Equilibrium adsorption  $capacity(q_e)$ , (b) pseudo-first-order kinetic plot, (c) pseudo-second-order kinetic plot for the adsorption of AF dye using various morphology of CFTS.

porous surface [43]. In Figure 4.8, all three cases, the  $k_i$  and *C* for both segments, are indexed in Table 4.2.-Figure 4.8(a-c) depicts that the first region passes through the origin, which indicates the rate-controlling step diffusion of AF dye from the aqueous phase to the CFTS boundary layer, which is clear that higher intraparticle diffusion has taken place [44]. In all three cases, the second segment (0.6206 mg.g.min<sup>-1/2</sup>) has a lower value of diffusion rate constant compared to that of the first segment (13.61 mg.g.min<sup>-1/2</sup>), which exhibits that the intraparticle diffusion of AF dye molecules takes place into the pores of CFTS [43].

Table 4.1: Kinetic parameters	obtained from the	e fitting of pa	seudo-first ord	ler and pseu	do-second-
order equations of various mo	orphology of CFTS	S.			

Adsorbents	Experimental	Pseudo-first order			Pseudo-second order		
	value	<b>k</b> <sub>1</sub>	q <sub>e1</sub>	$\mathbb{R}^2$	<b>k</b> <sub>2</sub>	qe2	R <sup>2</sup>
	q <sub>e</sub> (mg/g)	(min <sup>-1</sup> )	(mg/g)		(g.mg <sup>1</sup> .min <sup>-1</sup> )	(mg/g)	
Porous-	48.4	0.122	4.250	0.822	0.0107	50.76	0.999
CFTS							
Flakes-	47.35	0.094	3.750	0.777	0.0086	50.25	0.998
CFTS							
Flowers-	46.21	0.079	4.281	0.697	0.0053	49.56	0.996
CFTS							



Figure 4.8: Intraparticle diffusion models (a) Porous-CFTS (b) flakes-CFTS and (c) flower-CFTS, respectively.

Adsorbents	Intraparticle diffusion kinetic model						
	K <sub>i1</sub> (mg.g <sup>-1</sup> .min <sup>-1/2</sup> )	$K_{i2}(mg.g^{-1}.min^{-1/2})$ and	R <sub>1</sub> <sup>2</sup> and R <sub>2</sub> <sup>2</sup>				
	and C <sub>1</sub>	C2					
Porous-CFTS	13.61 and 0.1976	0.6206 and 43.77	0.988 and 0.8914				
Flakes-CFTS	12.96 and 0.210	0.726 and 42.01	0.9878 and 0.932				
Flowers-CFTS	11.89 and 0.194	1.240 and 37.02	0.988 and 0.845				

Table 4.2: Intraparticle diffusion kinetic parameters for various morphology of CFTS.

#### **4.3.4 Adsorption isotherms**

Isothermal adsorption models such as Langmuir and Freundlich were determined by fitting the experimentally obtained adsorption data to understand the dye adsorption process. The Langmuir isotherm adsorption analysis suggests that adsorption took place on the homogeneous surface of adsorbent with identical binding sites and no interaction between adsorbed substances [45,46]. The Langmuir isotherm mathematical expressions are given by the following equations (4.6) and (4.7) [47,48].

$$C_{e}/q_{e} = C_{e}/q_{max} + 1/q_{max} * K_{L}$$
(4.6)

$$R_{\rm L} = 1/(1 + K_{\rm L}C_{\rm o}) \tag{4.7}$$

 $C_e$  and  $q_e$  represent the equilibrium concentration (mg/L) and adsorption capacity (mg/g).  $q_{max}$  is the maximum adsorption capacity (mg/g),  $K_L$  is Langmuir constant (L/mg) related to the adsorption's energy,  $C_o$  is the initial dye concentration, dimensionless separation factor ( $R_L$ ), the
$R_L$  value represents feasibility of the adsorption process. The isotherm to be favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ) or unfavorable ( $R_L > 1$ ).

Isotherm model	Parameters	Values
	q <sub>max</sub> (mg/g)	128.20
Langmuir	K <sub>L</sub> (L/mg)	1.18
	$\mathbb{R}^2$	0.956
	$K_F(L/g)$	6.110
Freundlich	n	0.2671
	R <sup>2</sup>	0.91

Table 4.3: Langmuir and Freundlich isotherm constants.

Figure 4.9a shows the linear relation between  $C_e/q_e$  and  $C_e$  of the Langmuir adsorption isotherm model fitted with experimental data. The obtained regression factor value ( $R^2$ ) was estimated to be 0.95, and other fitting parameters ( $K_L$ , slope, and intercept) are listed in Table 4.3. The maximum adsorption capacity was found to be 128.20 mg/g. The adsorption capacity of AF dye using CFTS adsorbents and other adsorbents reported in the literature is given in Table 4.4. The calculated  $R_L$  values are estimated to be in the range of 0.01 to 0.04 for different initial dye concentrations of 20 mg/L to 60 mg/L, representing a favorable adsorption process. Similarly, the Freundlich adsorption isotherm model can suggest information about heterogeneous multilayer adsorption process and analyzed by the following equation (4.8) [47].

$$\log q_e = \log K_f + 1/n (\log C_e)$$
(4.8)

Where  $K_f$  (L/g) is Freundlich constant and *n* is the heterogeneous factor, respectively. If n value (0 < 1/n < 1) is favorable, (1/n > 1) is unfavorable or (1/n = 0) is irreversible of adsorption isotherm. Figure 4.9b shows the linear relation between  $log(q_e)$  vs.  $log(C_e)$  of a Freundlich adsorption isotherm model fitted with experimental data. The correlation coefficient R<sup>2</sup> is 0.91 and other relevant fitting parameters are summarized in Table 4.3. The isothermal model exhibited that the experimental data fitted well to the Langmuir model compared to the Freundlich model. These results suggested that adsorption of AF dye onto the porous CFTS

particles followed homogeneously with a uniform active site. Besides, 1/n values lie between 0 to 1, suggesting a favorable adsorption process.

Adsorbents	Surface	Poresize	Adsorption	References
	area $(m^2/g)$	(nm)	ability (mg/g)	
Carboxymethyl-chitosan	- (m /g)	-	253.2	[1]
(CMC)/bentonite composite				
De-oiled biomass	2.119	0.1398	9.9	[49]
		pore volume		
Magnetic Chitosan/Al <sub>2</sub> O <sub>3</sub> /	33.69	11.36	1666.67	[38]
Fe <sub>3</sub> O <sub>4</sub> nanocomposite				
Laccase-modified Zeolite	40.80	-	31mg/g	[50]
MgO-SiO <sub>2</sub> -TEPSIC-ATet	58.99	3.77	775.6	[2]
(MSNT)				
Chemically modified cellulose	-	-	105.71	[51]
CSNPs/PA6 membrane	-	-	1679	[52]
CFTS	53.50	4.301	128.18	This work

Table 4.4: Comparison of adsorption capacity of AF dye using various adsorbents.



Figure 4.9: Isotherm models for the adsorption of AF; (a) Langmuir isotherm (b) Freundlich isotherm; (c) thermodynamic parameters for the adsorption of AF dye using porous CFTS.

### 4.3.5 Adsorption thermodynamics

Thermodynamic parameters such as Gibbs free energy ( $\Delta G^{\circ}$ ), Enthalpy ( $\Delta H^{\circ}$ ), and Entropy ( $\Delta S^{\circ}$ ) were calculated by experimental data using the following equations (4.9-4.13) [33,36].

$$\Delta G^{\circ} = -RT \ln K_c \tag{4.9}$$

$$\mathbf{K}_{\mathbf{c}} = \mathbf{Q}_{\mathbf{e}}/\mathbf{C}_{\mathbf{e}} \tag{4.10}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{4.11}$$

$$-RT \ln K_{c} = \Delta H^{\circ} - T \Delta S^{\circ}$$
(4.12)

$$\ln K_c = \Delta S^{\circ}/R - \Delta H^{\circ}/RT$$
(4.13)

Where R is the ideal gas constant, T is the temperature (K), Kc is the adsorption equilibrium constant,  $Q_e$  is the equilibrium adsorption capacity (mg/g), and  $C_e$  represents the concentration of adsorbate (mg/L).

The enthalpy and entropy values of the adsorption process were obtained from the slope and intercept of the linear plot between lnKc vs. 1/T (Figure 4.9c), and the obtained values are given in Table 4.5. The negative values of  $\Delta G^{\circ}$  decrease with increasing temperature at 30 °C to 50 °C indicate the feasible and spontaneous adsorption process [33,42,47]. The enthalpy value is -30.645 KJ/mole, representing the exothermic adsorption process [53]. Entropy value was found to be negative (-60.214 J/mol.K), which suggested reducing randomness nature during AF dye adsorption at porous CFTS/ dye molecules interface [42,54].

Table 4.5: Thermodynamic parameters for adsorption of AF dye using porous CFTS.

Temperature	ΔG°	ΔH° (KJ/mol)	ΔS° (J/mol. K)
	(KJ/mol)		
25 °C	-13.095		
30 °C	-16.93	-30.645	-60.214
40 °C	-12.257		
50 °C	-10.876		

#### 4.3.6 Dye adsorption mechanism

The adsorption mechanism depends on several fundamental factors: porosity and surface area of the adsorbent, pH of the solution, and electrostatic interaction. The adsorbent's surface charge is the opposite of the charge of the dye molecules [33,34]. The possible interaction involved in the adsorption process is the electrostatic interaction between the positive charge of the adsorbent (porous CFTS) and the negative charge of the AF dye molecule. Apart from the above-stated reason, dipole-dipole H bonding interaction between the -OH groups present on the

adsorbent surface (-OH groups confirmed by FTIR analysis) and AF dye molecules is also an important factor [33,55]. The adsorption mechanisms can also be described by sequential dye diffusion, consisting of intraparticle diffusion and surface adsorption [56]. It was noticed that the removal of AF dye is initially rapid, and after that, equilibrium is reached slowly. It might be taken place through a surface adsorption process. The fast adsorption is usually due to the hydrophilic nature of the adsorbent and surface mass transport. However, the porous CFTS facilitate the diffusion process as the amine and OH<sup>-</sup> functional groups are hydrophilic and can swell in the aqueous dye solution due to the fast diffusion of dyes [3]. Therefore, the intraparticle diffusion process might also take place for the adsorption process of anionic dye. Langmuir isotherm confirmed that the homogeneous nature of porous CFTS surface with equal identical binding sites. Finally, the adsorption isotherm model reveals that the negative  $\Delta G^{\circ}$  value leads to spontaneously in the adsorption process.

#### 4.3.7 Reusability study

The dye adsorption experiment was conducted with the porous Cu<sub>2</sub>FeSnS<sub>4</sub> adsorbent for four cycles to check reusability. The CFTS adsorbent is taken out and centrifuged at 4000 rpm for 5 min, then re-utilized for the next cycle of adsorption study after completing the first cycle. The efficiency of AF dye adsorption using porous CFTS is estimated to be 98%, 94%, 90%, and 87% within 60 min for 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd,</sup> and 4<sup>th</sup> cycles, respectively (Figure 4.10). The efficiency of AF dye adsorption of CFTS decreases from the first cycle to the next cycle. It might be due to a portion of the AF dye located deep within the pores of CFTS particles that are not easily washed out [3].

The stability of CFTS particles, used in recycling the adsorption measurement, are characterized by XRD and EDX analysis. The diffraction peaks in the measured XRD patterned match with a tetragonal crystal structure of the CFTS phase (Figure 4.11a). The EDX analysis reveals that a near stoichiometric ratio is observed (Figure 4.11b). Both XRD and EDX analysis confirms that the CFTS particles are stable after reutilized for AF dye adsorption.



Figure 4.10: Reusability experiments of AF dye removal by porous CFTS-6h particles (in % adsorption).



Figure 4.11: Characterization of reusability porous CFTS particles (a) XRD pattern (b) EDX spectrum.

# 4.4 Summary

The change in solvothermal reaction time has shown significant impact on the surface morphologies of  $Cu_2FeSnS_4$  particles. The reaction time has a clear impact on the chemical composition and surface morphology of synthesized CFTS particles. The porous spherical CFTS particles have a higher dye removal percentage (90% within 10 min) and dye adsorption capacity properties than other sheet-flake and intermixed flower-sheet morphologies. The adsorption isotherms fitted well with the Langmuir isotherm indicating monolayer adsorption, and adsorption kinetic studies follow the pseudo-second-order kinetic model. The obtained experimental results concluded that the earth-abundant and non-toxic quaternary porous CFTS

particles could be utilized as low-cost, highly efficient adsorbent to remove toxic acid fuchsin (AF) dye pollutants from wastewater.

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# **CHAPTER-5**

# Surface Controlled Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> Particles for Enhanced Hydrogen Evolution Reaction

## **5.1 Introduction**

Hydrogen gas (H<sub>2</sub>) is considered alternative fuel to provide clean and sustainable energy [1]. The production of the  $H_2$  gas includes biomass gasification, steam methane reforming, thermolysis, pyrolysis, photolysis, electrolysis, and others [2,3]. Electrolysis or electrochemical water splitting is a more accessible, low-cost, and greener approach to efficiently producing H<sub>2</sub> gas [4]. In general, nobel metals, such as Pt, Rh, and Ir, were used as electro-catalyst to generate  $H_2$  gas [4]. The use of these expensive metals and their scarcity leads to an increase in production costs. To overcome this issue, various electro-catalyst materials, including metal oxides and their composites [5–7], carbides [8,9], metal hydroxides [10,11], phosphides [12–15], nitrides [16], multimetallic alloy [17,18], metal-organic frameworks (MOFs) based composites [19,20], binary chalcogenides [14,15,21,22], ternary chalcogenides and their hybrid materials [23,24], and earth-abundant quaternary chalcogenides have been investigated for the generation of H<sub>2</sub> gas via electrocatalytic process [3,4]. Among these, earth-abundant quaternary chalcogenide materials such as Cu<sub>2</sub>XSnS<sub>4</sub> (CXTS, X= Zn, Ni, Co, Mn) have chemically shown stable and better catalytic performance for HER [25]. Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) is another earth-abundant chalcogenide semiconductor has high absorption coefficient ( $\geq 10^4$  cm<sup>-1</sup>), narrow optical bandgap (1.2 eV- 1.8 eV) and excellent electrical properties [26,27]. It has structural and optoelectronic properties similar to CXTS materials [28]. CFTS has been reported as cost-effective and efficient electrocatalysts for oxygen evolution reaction (OER) [29]. However, CFTS has not been found as electro-catalysts for hydrogen evolution reactions (HER).

The Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) material was synthesized using vacuum-based (sputtering, e<sup>-</sup>beam evaporation) and solution-based methods (solvothermal, hydrothermal, sol-gel, hot injection method) [28,30–32]. Among solution methods, the solvothermal process has revealed higher crystallinity, better stoichiometric ratio, and low temperature [26,33]. The role of different solvents, surfactants, reaction temperature/time is critical to control the properties of CFTS

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material [26,34]. The morphology of materials plays a vital role in electrocatalytic performance [35–37]; hence control over the morphology of the CFTS particles has attracted several attentions in the recent past. The formation of the aggregated particles with an average size of the particles about 200 nm was reported using dimethylformamide (DMF) as solvent [38]. Sphere and flower-like morphology (200 nm), when the polyvinylpyrrolidone (PVP) as surface ligand and ethylene glycol (EG) as a solvent was used in the synthesis of CFTS particles [33]. The PVP and EG as a surface ligand, a solvent, were used to control the size and shape of the CFTS particles [39]. PVP was commonly used as a surfactant in the synthesis of CFTS particles, and that has shown the formations of various shapes, sizes, and variations in band gaps (1.28 eV to 1.8 eV) [33]. Similarly, the effect of different surfactants on structural and morphological properties of CFTS nanoparticles and their consequences on electro-catalyst water splitting is an open issue and has excellent scope for further investigations.

Herein, different surfactants named TGA, PVP, and PVA are used in the synthesis, and the effect of surfactants on structural, morphological, and electrocatalytic properties of CFTS particles is investigated. The stannite crystal structure of the CFTS phase is obtained in all three cases; however, there is some variation in the degree of crystallinity and presence of binary phases. Diverse morphology (i.e., aggregate-porous, porous-sheets, and uniform spherical) of CFTS particles is observed using different surfactants. The overpotential of PVP-based CFTS particles is the lowest as  $\eta = 421$  mV at 10 mA/cm<sup>2</sup> compared to the other two samples synthesized using PVA and TGA. The Tafel slope of CFTS-PVP is 54 mV dec<sup>-1</sup> which is also the lowest among all three samples. These results indicate that CFTS particles synthesized using PVP have shown better electro-catalyst performance and stability than the other two CFTS samples.

## **5.2 Experimental details**

## 5.2.1 Synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles

The stoichiometric ratio of Cu: Fe: Sn: S (2:1:1:6) precursors were added into 40 ml of DMF solvent in the beaker. Then 50  $\mu$ l of TGA was added to the above solution, and a detailed synthesis process has been reported [26]. The solution was stirred for 30 min get a homogeneous solution. Further, the solution is transferred to a Teflon liner (autoclave) and kept in a hot air

oven at 200 °C for 24 h. After completing the reaction, the hot air oven is allowed to cool down to room temperature naturally. The bottom supernatant in the Teflon liner was collected in a centrifuge tube. Then, methanol was added to the supernatant and centrifuged at 10000 rpm for 10 min to remove the organic impurities and the sample by-products. The centrifugation process was repeated two to three times to get the product and dried in a vacuum oven at 70 °C for 6 h to obtained CFTS powder. The synthesis was performed for other samples using PVP (0.2 g) and PVA (0.2 g) as a surfactant while other parameters were the same. In this manuscript, synthesized CFTS particles using different surfactants (TGA, PVP, PVA), the sample codes are denoted as CFTS-PVA, CFTS-PVP, CFTS-TGA. The synthesized CFTS particles were annealed at 450°C for 30 min in the Ar atmosphere to improve the crystallinity and eliminate impurity phases present in the samples. The schematic representation of the synthesis of CFTS particles shown in Figure 5.1.



Figure 5.1: Schematic diagram of CFTS particles synthesized by solvothermal process using different surfactants.

## 5.2.2 Characterization of Cu<sub>2</sub>FeSnS<sub>4</sub> particles

XRD (Bruker D-8 Advance X-ray diffractometer) analysis confirms the phase purity of the synthesized CFTS particles. Raman spectroscopy (Horibra LABRAM-HR) was used to identify the impurity phases of CFTS particles (laser source with an excitation wavelength of 532 nm). The elemental composition and morphology of the CFTS particles were measured using an energy dispersive spectrometer (EDS, Oxford instrument INCA, X-sight 7557) and field– emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II) to identify the valence states of synthesized CFTS particles. All binding energies were calibrated using carbon 1s line corresponding to 285 eV as a reference. The surface area of prepared CFTS samples was studied using accelerated surface area and porosimetry (ASAP) 2020 micro-metrics (Quantchrome, Autosorb IQ2) system.



Figure 5.2: The schematic diagram of the three-electrode system.

### 5.2.3 Electrochemical measurements of Cu<sub>2</sub>FeSnS<sub>4</sub> Particles

The electrochemical properties were measured in a three-electrode cell using an electrochemical analyzer (Auto-Lab, PG start 204A). The schematic diagram of the three-electrode system is depicted in Figure 5.2. 10 mg Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particle was dispersed in 1 ml of ethanol and Nafion solution (1:10), and the mixture was ultrasonicated for 30 min to form a homogeneous solution. Then, the small CFTS solution is coated on a 3mm glassy carbon electrode (GCE) and dried overnight at room temperature. The coated GCE act as a working electrode, Pt electrode, and Ag/AgCl was used as a counter and reference electrode. The electrocatalytic activity was studied via linear sweep voltammetry (LSV) measurement in an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte within the potential window of 0.2 to -0.6 V with a sweep rate

range of 1 mV/s to 100 mV/s. All the measured potential were converted to reversible hydrogen electrode,  $E_{RHE} = E_{Ag/AgCl} + 0.244$  V. The cyclic voltammetry (CV) was carried out for 1000 cycles for CFTS-PVP catalyst in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte within the potential window of 0.2 to -0.7 V at a scan rate of 20 mV/s. The electrochemical impedance spectroscopic (EIS) measurements were conducted in the range of 0.1 Hz - 100000 Hz at a DC bias potential with an amplitude adjustment in the 10 mV range.

### **5.3 Results and Discussion**

#### 5.3.1 Surface Morphology and Structural Properties of Cu<sub>2</sub>FeSnS<sub>4</sub> Particles

The variation in surface morphology of synthesized Cu<sub>2</sub>FeSnS<sub>4</sub> particles is evident in the scanning electron micrograph given in Figure 5.3. A noticeable change in surface morphology is observed when the different surfactants are used in synthesis. The mixture of aggregate and porous particles (1µm) is obtained when PVA is used as a surfactant to synthesize CFTS particles, shown in Figure 5.3a. The magnified image of CFTS particles (PVA) is given in Figure 5.3b, which shows that surface of the particles is constituted with a thin nanosized sheet and offers a porous structure. While, when PVP is used as a surfactant, the formation of porous particles is observed in Figure 5.3c. The magnified image of these porous particles reveals ultrathin nanosheets with a larger area compared to Figure 5.3b. Further, the tiny nanoparticles (~10nm) are deposited over the nanosheet of the CFTS particles (Figure 5.3d). Thus, PVP as a surfactant result in the formation of highly porous CFTS particles with ultrathin sheets and nanoparticles on the surface. Whereas spherical particles approximate1µm size is obtained when TGA is used as surfactant are depicted in Figure 5.3(e-f). The differences in surface morphologies of the CFTS particles can be correlated with the function of the respective surfactant. Here, PVA is used as a stabilizer to control the growth of CFTS particles in the reaction and reduce nanoparticle aggregation [40,41]. Similarly, PVP might play two different roles in the growth process; i.e., prevent the aggregation of CFTS particles by steric hindrance during the initial growth stage; another is selective adsorption on specific facets of CFTS particles and kinetic control growth rates of these facets [42,43]. The TGA can prevent the aggregation of CFTS particles by capping on the grown particles to reduce the surface energy during the synthesis process [44,45] and form uniform spherical particles.



Figure 5.3: SEM images of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles synthesized using different surfactants (a) low and (b) magnified image of PVA–CFTS, (c) low and (d) magnified image of PVP-CFTS, and (e) low (f) magnified image of TGA-CFTS.



Figure 5.4: EDX spectra (a) elemental composition (b) of CFTS particles (synthesized using different surfactants).

The elemental compositions of the  $Cu_2FeSnS_4$  (CFTS) particles are analyzed by the EDS technique (results are shown in Figure 5.4). The *Cu* and *S* have a near stoichiometric ratio, while *Fe* deficient and *Sn* rich particles are obtained when PVA is used as a surfactant. In the case of PVP, a near stoichiometric ratio was observed. While, in the case of TGA, *S* and *Sn* are observed in near stoichiometric ratio with *Cu*-rich and *Fe* deficiency. The difference in chemical composition is due to the different reactivity of the metal ions (ions and cations) in the reaction

process [46,47]. Figure 5.5 shows the XRD pattern of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles, the diffraction peaks (112), (200), (220), (312), (400), and (316) are tetragonal crystal structure of CFTS phase are matching with standard JCPDF data No (44-1476) in all three as-synthesized samples (Figure 5.5a). In the PVA, TGA case, the binary peaks (SnS) are also noticed along with the crystalline phase of CFTS. While PVP results in a pure crystalline phase of CFTS- The crystalline size of CFTS particles calculated using the Debye Scherrer formula is tabulated in Table S1[48]. PVA has resulted in the highest crystalline size (11.94 nm), and the PVP leads to having the lowest crystalline size (10.44 nm). The synthesized CFTS particles were annealed at 450°C for 30 min reduces the binary phases and improves the crystallinity of particles (Figure 5.5b).



Figure 5.5: XRD patterns of CFTS particles synthesized using different surfactants (TGA: thioglycolic acid, PVA: Polyvinyl alcohol, PVP: Polyvinyl pyrrolidone), (a) as-synthesized, (b) annealed samples.

Raman spectra of annealed CFTS particles (synthesized using different surfactants) are given in Figure 5.6. The strong and broader peaks appear at 319 cm<sup>-1,</sup> and 285 cm<sup>-1</sup> belongs to the crystalline CFTS particles. The peak at 319cm<sup>-1</sup> attributes to the asymmetry vibration of a

pure anion mode [26]. The peak at 285 cm<sup>-1</sup> corresponds to a pure anion mode around the Cu cation [49]. Therefore, no secondary phases are detected in all three cases, which indicates that the pure crystalline phase of the CFTS particles is noticed.



Figure 5.6: Raman spectra of annealed CFTS particles synthesized using PVA, PVP, and TGA as surfactants in the solution process.

XPS analysis was carried to evaluate valence states of constituent elements of annealed CFTS particles synthesized using PVA, PVP, and TGA as a surfactant (Figure 5.7). The corelevel XPS spectrum was fitted with XPS peak41 software (Figure 5.7). The binding energy of the  $Cu2p_{3/2}$  and  $Cu2p_{1/2}$  are located at 931.9 eV and 951.74 eV, respectively. The peak separation of 19.84 eV between the  $Cu2p_{3/2}$  and  $Cu2p_{1/2}$  indicates the presence of  $Cu^{(+1)}$  state in all three CFTS samples [27,50,51]. The asymmetry in peaks indicates the presence of additional peaks at 933.4 and 953.68 eV (as fitted), which refers to the partially CuO phase present in all CFTS samples (Figure 5.7(a<sub>1</sub>,b<sub>1</sub>,c<sub>1</sub>)) [26]. Similarly, the core level spectra of Fe peaks appeared at binding energies of 711.8 eV (2p3/2) and 723.3eV (2p1/2) with peak separation of 11.44 eV, which strong evidence to the Fe<sup>(+2)</sup> state presence in all three samples are shown in Figure 5.7(a<sub>2</sub>,b<sub>2</sub>,c<sub>2</sub>) [50,52]. A strong satellite peak was noticed at 716.47 eV, which corresponds to the Sn2p<sub>3/2</sub> [53]. The binding energy of Sn 3d peaks located at 486.96 eV (Sn3d<sub>5/2</sub>) and 495.38 eV(Sn3d<sub>3/2</sub>) with separation between peaks is of 8.42 eV which indicate the presence of  $Sn^{(+4)}$  state in all samples (Figure 5.7(a<sub>3</sub>,b<sub>3</sub>,c<sub>3</sub>)) [26,27].



Figure 5.7:  $(a_1-a_4)$  fitted core level XPS spectrum of constituent elements of annealed CFTS particles synthesized using PVA.  $(b_1-b_4)$  Fitted core level XPS spectrum of constituent elements of annealed CFTS particles synthesized using PVP.  $(c_1-c_4)$  fitted core level XPS spectrum of constituent elements of annealed CFTS particles synthesized using TGA.

In XPS spectra of CFTS-PVA, CFTS-TGA case, the doublet peaks are noticed at 488.58 eV and 496.65 eV, corresponding to the partially  $SnO_2$  phase present in these CFTS samples [54,55]. The peak splitting and asymmetric might be due to the impurity phase present in the CFTS particles (PVA and TGA). The S2p core level spectrum (Figure 5.7(a<sub>4</sub>,b<sub>4</sub>,c<sub>4</sub>)), the binding energy peaks are noticed at 161.18 eV(S2p<sub>3/2</sub>) and 162.34 eV (S2p<sub>1/2</sub>), with a peak separation of 1.16 eV, which indicates the S<sup>-2</sup> state presence in all three samples [31]. Another shoulder peaks also appeared at 163.49 eV, which belongs to the SO<sub>4</sub><sup>-</sup> phase present in all three samples [56].

Thus, all three samples have valence states of constituent elements (Cu, Fe, Sn, and S) in the CFTS particles that match the standard valence states (+1,+2,+4, and -2) Cu<sub>2</sub>FeSnS<sub>4</sub> compound. However, in the case of PVA, TGA case, few elements are the standard oxidation states observed along with partially CuO and SnO<sub>2</sub> phases on the surface of CFTS particles [57,58].



Figure 5.8: Nitrogen adsorption/desorption isotherms curves and (b) pore size of CFTS particles synthesized using different surfactants.

The porous nature of CFTS particles is further investigated to determine the specific area and porosity using Brunauer-Emmett-Teller (BET) method. The N<sub>2</sub> adsorption-desorption isotherm data of the synthesized CFTS particles were depicted in Figure 5.8. The BET surface area and pore size of the CFTS particles are 19.883 m<sup>2</sup>/g, and 3.74 nm for CFTS-PVA, 27.621 m<sup>2</sup>/g, and 3.92 nm for CFTS-PVP, 19.363 m<sup>2</sup>/g and 3.69 nm for CFTS-TGA observed, respectively. CFTS-PVP shows a higher surface area than the other two samples due to the porous nature of CFTS particles confirmed by SEM analysis. The availability of large surface areas in the CFTS particles (synthesized using PVP) could be very beneficial for electro-catalytic and surface-related applications.

#### 5.3.2 Effect of high surface area on hydrogen evolution reaction

The electro-catalytic activity measurement is conducted using three-electrode systems. The CFTS particles coated on GCE as working electrode and Pt electrode as a counter electrode, Ag/AgCl electrode as a reference electrode. The linear sweep voltammetry (LSV) of all three CFTS samples is conducted to measure the overpotential (Figure 5.9a). The overpotential of CFTS-PVP is the lowest as  $\eta = 421$  mV at 10 mA/cm<sup>2</sup> compared to the other two samples 451 mV for CFTS-PVA, 470 mV for CFTS-TGA. The lower over-potential of the CFTS-PVP sample is related to the higher surface area and porous morphology than the other two samples. The recent development in different quaternary chalcogenides and their relevant composites-based catalyst materials for hydrogen evolution reaction (HER) is summarized in Table 5.1. From Table 5.1, the experimentally obtained over potential values and Tafel slopes of CFTS-based electrodes are similar to the previously reported values of quaternary chalcogenides. Tafel analysis was performed to predict the mechanism responsible for HER activity (Figure 5.9b). The slope of the Tafel plot (Tafel slope) determines the probable mechanism responsible for HER according to the following reactions (1-3); [59–61]

Volmer: 
$$H_3O + CFTS + e^- \rightarrow CFTSH_{ads} + H_2O$$
 (5.1)

Heyrovsky: 
$$H_3O + CFTSH_{ads} + e \rightarrow CFTS + H_2O + H_2$$
 (5.2)

Tafel: 2 CFTS 
$$H_{ads} \rightarrow 2CFTS + H_2$$
 (5.3)

Here CFTS denoted an active site of the species, and CFTS  $H_{ads}$  determines an H adsorbed intermediate. The HER reaction occurs either by Volmer-Heyrovsky or Volmer-Tafel reactions depending upon the value of the Tafel slope. If the value of the Tafel slope approximate from the Tafel plot is close to 120 mVdec<sup>-1</sup>, the reaction is taking place by the combination of Volmer-Heyrovsky reaction steps (equation 1 & 2) [59]. A Tafel slope value close to 40-30 mVdec<sup>-1</sup> indicates the Volmer-Tafel combination (equation 1 & 3) [61].

The Tafel plot is for the understanding of the mechanism of the electron transfer. The Tafel plot for CFTS is linearly fitted by the Tafel equation  $\eta = b \log (j + a)$  [62]. where 'a' is the exchange current density, 'b' is the Tafel slope, 'j' is the current density, and ' $\eta$ ' is the overpotential. As for Tafel slope of CFTS-PVP (54 mV dec<sup>-1</sup>) is lower than those of CFTS-PVA (112 mV dec<sup>-1</sup>) and CFTS-TGA (153 mV dec<sup>-1</sup>), respectively. The lower Tafel slope and lower over-potential value indicate the higher HER activity in CFTS-PVP samples than other samples. The CFTS-PVP sample shows the smaller Tafel slope (54 mV dec<sup>-1</sup>), indicating the Volmer-Tafel combination, which means reaction kinetics is faster than other samples. The Tafel slope of the CFTS-TGA is 153 mVdec<sup>-1</sup>, which demonstrates that the surface desorption is slow, and the rate-determining step is the Volmer step (equation (1)). The obtained value of the Tafel slope is

lower and shows better charge kinetics than the recently reported chalcogenide catalysts [3,25,63].



Figure 5.9: (a) LSV polarization curves of CFTS-PVP, CFTS-PVA, and CFTS-TGA based catalysts for (HER) at a scan rate of 20 mV/s and (b) their corresponding Tafel plots. (c) EIS spectra of CFTS-PVP, CFTS-PVA, and CFTS-TGA based catalysts. (d) Stability measurement of CFTS-PVP based catalysts with cyclic voltammetry curve of 1<sup>st</sup> and 1000<sup>th</sup> cycle.

The linear sweep voltammetry of CFTS-PVP based catalyst was measured in sweep rate range from 1mV/s to 100 mV/s, and the measured LSV polarization curves are shown in Figure A.1 in appendix. A small change in the characteristics of LSV polarization curves with an increase in scan rate from 1 to 100 mV/s Vs. RHE is observed, which suggests that the catalytic

activity of CFTS-PVP based catalyst toward HER is less impacted by the scan rates and is well agreed with similar CZTS catalyst reported in the literature [62].

Table :	5.1:	Comparison	table	of	recently	developed	catalyst	material	for	hydrogen	evolution
reactio	n.										

Catalyst materials	Over potential (mV)	Tafel slope (mV/dec)	References
Cu <sub>2</sub> ZnSnS <sub>4</sub> (CZTS)	985	155	[25](2020)
Cu <sub>2</sub> NiSnS <sub>4</sub>	369	76	
$Cu_2MnSnS_4$	705	119	
$Cu_2CoSnS_4$	689	103	
Co-CZTS	200	73	[63] (2018)
CZTS	442	125	[3] (2019)
Fe-CZTS	300	110	
Ni-CZTS	214	100	
CZTS	300	85	[62] (2017)
CZTS/MoS <sub>2</sub> -RGO	50	68	[64] (2021)
Heterostructures			
Core-shell	190	151.6	[23] (2018)
NiCo <sub>2</sub> S <sub>4</sub> @NiCo <sub>2</sub> S <sub>4</sub>			
Ni-Mn-S	400	81	[65](2021)
CDs/Pd NPs composite	291	141	[66] (2021)
WO <sub>3</sub> -TiO <sub>2</sub> nanocomposite	120	98	[67] (2021)
CFTS-TGA	470	153	
CFTS-PVA	451	112	This work
CFTS-PVP	421	54	

We further investigated charge transfer resistance at the electrode/electrolyte interface of CFTS particles via electrochemical impedance spectroscopy (EIS). The Nyquist plot (Figure 5.9c) in EIS shows a small semicircle in the case of CFTS-PVP compared to the other two samples, indicating the lower charge transfer resistance ( $R_{ct}$ ). The EIS spectra were fitted with Z-VIEW software. The charge transfer resistance of CFTS–PVA, CFTS–TGA, and CFTS-PVP are calculated to 450  $\Omega$ , 500  $\Omega$ , and 320  $\Omega$ , respectively. The CFTS-PVP reveals lower  $R_{ct}$  values (320  $\Omega$ ), suggesting that a faster electron transfer process occurred during the electrochemical HER at the interface of CFTS-PVP. This might be due to the porous structure and the high

surface area leading to the favorable charge and mass transport, thus better HER electro-catalytic performance. The stability of the catalyst is a critical parameter for practical application towards hydrogen generation. The stability study CFTS-PVP catalyst is conducted by cyclic voltammetry measurement in 0.5 M H<sub>2</sub>SO<sub>4</sub> within the potential window of 0.2 to -0.7 V at a scan rate of 20 mV/s for 1000 cycles. The slight change in features of the CV curves is observed after scanning 1000 cycles suggesting that the CFTS-PVP catalyst degraded in the electrolyte solution. The degradation of catalyst activity might be due to change in chemical composition, morphology, and formation of secondary phase (Cu<sub>2</sub>S), which consists of previously reported literature [26,68–73]. The series of characterizations such as XRD, RAMAN, SEM, EDS, and XPS analysis was carried further to examine CFTS–PVP-based catalyst after post stability test.

#### **5.3.3 Post CFTS-PVP based catalyst characterization**

The XRD, RAMAN, SEM, EDS, and XPS analysis was carried further to examine the crystal phase, morphology, chemical composition, and surface properties of the CFTS–PVP-based catalyst after 1000 cycles of cyclic voltammetry test. The XRD and RAMAN analysis reveals that the impurity phase (Cu<sub>2</sub>S) is appeared along with the crystalline CFTS phase (Figure 5.10a and Figure 5.10b). The morphology of the catalyst shows aggregate particles after 1000 cycles (Figure 5.11a and 5.11c), which indicates that the surface of the catalyst is reacted with electrolyte (aqueous H<sub>2</sub>SO<sub>4</sub> acidic conditions). Furthermore, the EDS analysis reveals that change in chemical composition is noticed after 1000 cycles (Figure 5.11b and 5.11d), which might influence the overpotential and Tafel slope of CFTS–PVP-based catalyst [71,73].

The XPS technique analyzed the valence states and surface properties of the CFTS-PVP particles catalyst (Figure 5.12). The peak broadening and asymmetric peaks of core-level XPS spectra of Fe, Sn, and S are noticed, representing the presence of the impurity phase on the surface of the CFTS catalyst. Overall, the change in crystal phase, morphology, and chemical composition might be potential causes for the degradation of CFTS-PVP particles catalyst properties after the stability test [26,68–73].



Figure 5.10: (a) XRD spectra and (b) Raman spectra of fresh and recovered CFTS-PVP catalyst.



Figure 5.11: (a, b) SEM and EDX analysis of fresh CFTS-PVP catalyst and (c, d) SEM and EDX analysis of recovered CFTS-PVP catalyst.



Figure 5.12: Core level XPS spectra of fresh and recovered catalyst of CFTS-PVP: (a) Cu 2p, (b) Fe 2p, (c) Sn 3d, and (d) S 2p, respectively.

## **5.4 Conclusion**

Stannite phase of Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles were successfully synthesized by solvothermal method, and the role of different surfactants (PVA, TGA, PVP) on the surface morphology was investigated. Synthesis has resulted in the crystalline phase of CFTS particles with some impurity phases in PVA and TGA surfactants. Post-synthesis sulphurization improved the crystallinity and reduced the impurity phases. The divergent morphology, such as intermix of aggregate with porous particles, highly porous particles having nanosheets and nanoparticles at the surface, and uniform spherical particles of CFTS particles, was obtained when PVA, PVP, and TGA were used as surfactants. The CFTS particles synthesized using PVP have shown the

highest surface area, leading to lower onset potential (~410 mV) for hydrogen evolution reaction and Tafel slope around 54 mV/dec<sup>-1</sup> with reasonably good stability hydrogen evolution reaction.

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# **CHAPTER-6**

# Cu<sub>2</sub>FeSnS<sub>4</sub> Decorated Ni-TiO<sub>2</sub> Nanorods Heterostructured Photoanode for Enhancing Water Splitting Performance

## **6.1 Introduction**

Harvesting of the solar energy to produce environmental friendly fuel is one of the ongoing demand of present era [1]. Solar energy can be harvested using a semiconducting electrode to drive a water splitting reaction that produces useful hydrogen fuel [2,3]. The performance of photoelectrochemical based water splitting cell majorly depends upon the semiconducting material used as a working electrode [4]. TiO<sub>2</sub> has been in the prime focus as working electrode materials due to high chemical stability and suitable electronic band positions for photoelectrochemical water splitting [5–7]. However, TiO<sub>2</sub> working electrodes are a wide bandgap materials, leads to partial or no absorption of wider segment of solar energy and also shows higher recombination of photo-generated charge carriers [8]. To overcomes these limitation and improve the visible light harvesting such as doping of metal, non-metal, surface modification, quantum dot/dye sensitization, and composite formation have been adopted with TiO<sub>2</sub> [9]. The doping has shown very effective results and is considered as a suitable strategy to enhance photoelectrochemical performance of TiO<sub>2</sub> [10]. TiO<sub>2</sub> has been doped by metal and nonmetal elements such as Sn [11], Nb [12], Bi [13,14], nitrogen [15], sulfur [16], fluorine [17] etc. and doping has induced a redshift in the band edge absorption. The high surface area in nanostructures improves the light absorption, provide direct electrical pathways for the excited electrons, and demonstrate higher charge transportation properties [18,19]. Hence, nanostructures of doped and undoped TiO<sub>2</sub> such as nanotubes [20,21], nanorods [8,22], and nanowires were also investigated [10]. Tae-Lee et al. have reported the effect of the Fe doping concentration on the photoelectrical properties of TiO<sub>2</sub> NRs [23,24]. Similarly, higher photocurrent density were achieved in Fe, Mn, and Co-doped TiO<sub>2</sub> nanorods (NRs) and nanotubes [8,25]. Kardas et al. have reported gadolinium doped TiO<sub>2</sub> nanorods that results in reduction of the surface recombination of electron and hole [26]. Nickel (Ni) was also explored as one of the ideal dopant element for enhancing the photocatalytic and photoelectrochemical

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properties of TiO<sub>2</sub> [27]. It has been demonstrated that Ni forms the 3d states in band gap leads to improve the light absorption properties of the material [27–29]. Recently, Dong et al. have prepared TiO<sub>2</sub> (Ti-Ni-O) nanotubes doped with Ni via anodizing process which had shown improvement in light absorption and assist separation of photo-generated electron-hole pair [10]. Further, surface doped TiO<sub>2</sub> have synergistically boosted the PEC performance due to Sn ions are implanted into the outer surface of TiO<sub>2</sub> [30].

Photoelectrochemical performance of doped TiO<sub>2</sub> nanowire is further improved by surface decoration/modification using narrow bandgap materials. Earth-abundant, low-cost chalcogenide materials have been designed for surface modification to develop heterostructures based photoanode [31-33]. Formation of CZTS nanocrystal on the surface of the TiO<sub>2</sub> nanorods developed using in-situ deposition technique have shown reduction in recombination of photoexcited electron and hole pairs leads to higher PEC performance [33,34]. Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) also have similar optical properties with lesser probability of forming secondary phases and offers better stoichiometry [35]. In 2015, Yin wong et al, demonstrated that Au/Cu<sub>2</sub>FeSnS<sub>4</sub> core/shell nanostructure exhibit photocatalytic activity for hydrogen generation [36]. CFTS has demonstrated high absorption coefficient for sunlight and has good scope to investigate the PEC water splitting by developing  $TiO_2$  nanorods -  $Cu_2FeSnS_4$  heterostructure. Herein, Ni-doped  $TiO_2$ nanorod is developed to investigate the optical and photoelectrochemical properties. The structural characterization indicates that the Ni-doped TiO<sub>2</sub> NRs are single-crystalline rutile structure. Then, CFTS layer is coated on Ni doped TiO<sub>2</sub> NRs via the dip-coating process. The newly developed CFTS/Ni-TiO<sub>2</sub> photoelectrode shows a significant improvement in visible light harvesting and significantly enhance the photocurrent conversion efficiency.

## **6.2 Experimental details**

#### 6.2.1 Synthesis of TiO<sub>2</sub> Nanorods film

TiO<sub>2</sub> nanorods were directly grown on fluorine-doped tin oxide (FTO) substrate via hydrothermal method [37]. In typical procedure, 20 ml of HCl (SRL grade, 37% purity) and 20 ml of DI water were added in the Teflon liner and mixed for 10 min, then 0.6 ml of titanium butoxide (Sigma Aldrich) added to the HCl and DI water solution [38]. The prepared mixture was further stirred for 30 min to get a homogeneous solution. Simultaneously, the FTO substrate was cleaned by ultrasonication in soap water, DI water, ethanol, and acetone for 10 min in each.

Then, prepared solution was transferred in Teflon liner and cleaned FTO was immersed in solution. The Teflon liner was then transferred to a 50 ml autoclave, and hydrothermal reaction was performed in a hot air oven at 150 °C for 9 h (schematic diagram of fabricated TiO<sub>2</sub> film as shown in Figure 6.1a). After cooling down to room temperature, the coated FTO was taken out and rinsed with DI water for several times to remove the loosely connected particles from the FTO substrate. Further, hydrothermally grown TiO<sub>2</sub> nanorods films were annealed at 450 °C for 30 min in a muffle furnace to improve the crystallinity.



Figure 6.1: Schematic representation of (a) fabricated  $TiO_2$  film (b) Ni-doped  $TiO_2$  nanorods by hydrothermal method.

#### 6.2.2 Surface doping of TiO<sub>2</sub> nanorods by nickel

5 mM nickel nitrate and 0.5 g urea were dissolved in a 20 ml of DI water in Teflon liner, mixed to form a homogeneous solution. The TiO<sub>2</sub> nanorods film is kept in the prepared nickel solution. The teflon liner was kept at 100 °C for 1 h in a hot air oven, and then after cooling down to ambient temperature. The Ni coated TiO<sub>2</sub> nanorods were extracted and washed using DI water. Further, Ni doped TiO<sub>2</sub> films were annealed at 200 °C for 1 h in an oven to improve the crystallinity of the Ni doped TiO<sub>2</sub> NRs. The schematic representation of the Ni- TiO<sub>2</sub> nanorods are shown in Figure 6.1b.The same synthesis protocol is conducted for 10 mM and 20 mM of nickel nitrate solution to prepare Ni doped TiO<sub>2</sub> NRs.

#### 6.2.3 Coating of Cu<sub>2</sub>FeSnS<sub>4</sub> layer on Ni-TiO<sub>2</sub> nanorods

A precursor solution containing 3.75 mmol copper chloride, 2.4 mmol ferric nitrates, and 2.4 mmol tin chloride were prepared in 25 ml of ethanol in a beaker. The solution was stirred at 50 °C for 30 min to get a homogeneous cations precursor solution [39]. Simultaneously, 13 mmol thioacetamide was added in 25 ml of ethanol in another beaker and stirred at 50 °C for 30 min to make anions precursor solution. Then after, the cations and anions precursor solutions were mixed and stirred at 50 °C for 20 min on hot plate to prepare CFTS precursor solutions. Subsequently, 1 ml of monoethanolamine was added to the CFTS precursor solution and further stirred at 50 °C for 60 min to the dissolution of precursors in the solvent properly and to stabilize the solution. Ni-TiO<sub>2</sub> NRs films and TiO<sub>2</sub> NRs film were dipped in a CFTS precursor solution for 30 sec and then soft baked at 220 °C for 15 min on hot plate inside fume food. The soft baked films were further annealed at 350 °C for 30 min in tubular furnace in continues flow N<sub>2</sub> gas to remove by products and an increase in the crystallinity of CFTS films.

#### 6.2.4 Structural and morphological characterization techniques

Crystalline properties were analyzed using XRD analysis (Bruker D-8 Advance X-ray diffractometer). The elemental composition and morphology of the TiO<sub>2</sub> NRs and Ni doped TiO<sub>2</sub> NRs were examined using by energy dispersive spectrometer (EDS) and a scanning electron microscope (FEG-SEM, JEOL JSM-6500F). The optical properties of hydrothermal synthesized TiO<sub>2</sub>, Ni doped TiO<sub>2</sub> NRs and CFTS/Ni doped TiO<sub>2</sub> NRs were obtained by a UV-visible spectrophotometer (Shimadzu, UV-2600) at room temperature. The chemical states and composition were examined using a high-resolution X-ray photo-electron spectroscopy (XPS, PHI 5000 Versa Probe II, operating voltage (3 kV), full scan time 1 h). All binding energies were calibrated using carbon as reference.

#### **6.2.5** Photoelectrochemical measurements

The photo-electrochemical properties were measured in a three-electrode system using an electrochemical system (Auto-Lab, PG start 204A). The schematic diagram is given in the Figure 6.2. The fabricated electrodes (TiO<sub>2</sub> NRs, Ni doped TiO<sub>2</sub> NRs, and CFTS/Ni-TiO<sub>2</sub> NRs) were used as a working electrode with an active surface area of 1 cm<sup>2</sup>, Pt electrode and Ag/AgCl were used as a counter and reference electrode, respectively. An aqueous electrolyte 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 5.8) was used as an electrolyte to test the PEC measurement. The N<sub>2</sub> gas was bubbled into
the electrolyte solution for 30 min to eliminate the dissolved oxygen (O<sub>2</sub>) in the solution. The working electrode potential (*vs* Ag/AgCl) was converted to the reversible hydrogen electrode (RHE) by the Nernst equation:  $E_{RHE} = E_{Ag/AgCl} + 0.059*pH + 0.199$ . A 150 W full spectrum Xenon light source (model No. HSN Code 9027, Holmarc Opto-Mechatronics Pvt. L) with wavelength range UV to IR (250 nm to 2500 nm) were used, and light source was calibrated to 100mW/cm<sup>2</sup>. The Linear sweep voltammetry (LSV) measurement under the chopped light on/off illumination was performed with a scan rate 10 mV/s and scan range was from -0.5 to 1.8 V (*vs* Ag/AgCl). To evaluate the electrode resistance, the electrochemical impedance spectroscopy (EIS) of the samples was measured in the same electrochemical configuration and electrolyte. The frequency ranged from 0.1 Hz to 100 kHz, with an amplitude adjustment in 10 mV range.



Figure 6.2: Schematic representation of photo-electrochemical measurement setup.

#### 6.3 Results and Discussion

# 6.3.1 Structural, morphological and optical properties of TiO<sub>2</sub> and Ni-TiO<sub>2</sub> nanorods

All the X-ray diffraction peaks of undoped  $TiO_2$  and Ni doped  $TiO_2$  NRs were corresponding to the tetragonal rutile phase (JCPDS No: 21-1276) and additional peaks are attributing to the FTO substrate (Figure 6.3a). The diffraction peaks at 36.01°, 62.8° and 70.1°

are assigned to the (101), (002), and (112) crystal planes of the rutile phase of the TiO<sub>2</sub> NRs and Ni-TiO<sub>2</sub> NRs. The peak (002) dominating over the (101) peak suggested that the nanorods grow along the c-axis <001> direction [8]. No impurity peak was observed in XRD patterns when 'Ni' is doped in the TiO<sub>2</sub> crystal. The inset in Figure 6.3a, the diffraction peaks (002) shifted to lower angles slightly when the increasing of Ni<sup>2+</sup> concentration implies the occupation of Ni<sup>2+</sup> at the substitutional sites of Ti<sup>4+</sup> in the TiO<sub>2</sub> crystal lattice. This might be resulting from Ni doping since the radius of Ni<sup>2+</sup> was more extensive than that of Ti<sup>4+</sup> [20, 27].



Figure 6.3:(a) XRD spectra of the TiO<sub>2</sub> NRs and Ni doped TiO<sub>2</sub> NRs with varying concentration of Nickel dopant (b-d) core level spectrum constituent of element of (b) Ti, (c) O, and (d) dopant of Ni for 10mM Ni-TiO<sub>2</sub> nanorods respectively.

Further, XPS measurement was conducted to confirm the elemental analysis and oxidation state of the elements of Ni doped  $TiO_2$  nanorods are shown in Figure 6.3(b-d). The core-level XPS spectra of Ti, O, and Ni elements are fitted with XPS peak 41 software. The fitted core level spectrum (Figure 6.3b) of Ti is shown symmetrical peaks at 458.2 eV and 464.1

eV and which are attributed to be Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> states, respectively [33,40]. The difference between symmetrical peaks is found to be 5.9 eV, which indicate that the Ti<sup>4+</sup> oxidation state is present in the TiO<sub>2</sub> lattice. The binding energy position of O1s appeared at 529.16 eV peak belongs to the core level of the oxygen (2<sup>-</sup>) state, and 530.30 eV might be to the hydroxide or oxygen vacancy in the TiO<sub>2</sub> lattice [7,41]. The core level spectrum of Ni shows two splitting of peaks appear at 855.1 eV and 873.43 eV, corresponding to the Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub> states, which indicate that successful Ni<sup>2+</sup> doping in the TiO<sub>2</sub> structure [20]. The additional peaks appears at 861.07 eV, and 880.24 eV are belonging to the satellite peaks in the sample [42]. These peaks are attributed to Ni in the form of oxide and hydroxide phases [43].

SEM images reveal the vertically aligned nanorods growth that is uniformly deposited on the FTO substrate as shown in Figure 6.4. These nanorods are uniform with a rectangular surface and the diameters of the nanorods are in the range of 100 nm - 150 nm, and the length of nanorods is around 400 nm. Figures (6.4b and 6.4c) shows, no significant change in the nanorod morphology is noticed after Ni doping (using lower concentration of Ni solution). The higher concentration (20 mM) of Ni doping solution renders Ni particles formations on the top of the TiO<sub>2</sub> NRs are observed (Figure 6.4d). Figures (6.4e and 6.4f) shown that cross-sectional SEM images of TiO<sub>2</sub> NRs and 10 mM Ni-TiO<sub>2</sub> NRs demonstrate that the nanorods are grown vertically on the FTO substrate. Figures (A.2&A.3) depicted the cross - sectional elemental mapping of the TiO<sub>2</sub> NRs and 10 mM Ni-TiO<sub>2</sub> NRs. Elemental mapping of 10mM Ni-TiO<sub>2</sub> was confirmed that Ni is deposited on the entire surface of the TiO<sub>2</sub> NRs. Here Sn, Fe, and Si are detected from the FTO substrate. EDS pattern and elemental mapping of the Ni-doped TiO<sub>2</sub> NRs are shown in Figure 6.5. The atomic weight (%) of Ni is obtained by EDS found to be from 0.5%, 0.9%, 1.3% for 5 mM, 10 mM, and 20 mM Ni precursor respectively (Figure 6.5a1 to Figure 6.5c<sub>1</sub>). The elemental mapping confirms uniform distribution of Ni particles on the  $TiO_2$ NRs films (Figure 6.5).



Figure 6.4: SEM images of (a) hydrothermally grown TiO<sub>2</sub> nanorods (b) TiO<sub>2</sub> nanorods treated using 5mM Ni solution to achieve Ni doped TiO<sub>2</sub> nanorod (c) TiO<sub>2</sub> nanorods treated using 10 mM Ni solution (d) TiO<sub>2</sub> nanorods treated using 20 mM Ni solution; cross-sectional image of (e) TiO<sub>2</sub> NRs (f) 10 mM Ni-TiO<sub>2</sub> NRs.



Figure 6.5: EDS pattern and elemental mapping of  $(a_1-a_4)$  TiO<sub>2</sub> nanorods treated using 5 mM Ni solution and  $(b_1-b_4)$  TiO<sub>2</sub> nanorods treated using 10 mM Ni solution  $(c_1-c_4)$  TiO<sub>2</sub> nanorods treated using 20 mM Ni solution to achieve Ni doped TiO<sub>2</sub> nanorods.

UV-visible spectra shown in Figure 6.6 depict that the optical absorption capacity of the Ni-doped TiO<sub>2</sub> NRs exceeds then the undoped TiO<sub>2</sub> NRs. It can be indicated by the excitation to the bandgap states over the fermi level from the lower energy states [44,45]. The Ni-TiO<sub>2</sub> samples prepared using 20 mM Ni solution show high absorption in visible range due to coated Ni particles on the surface of TiO<sub>2</sub> nanorod film. Figure 6.6b shows Tauc plot ( $\alpha$ hv<sup>2</sup> vs hv) for calculating the band gaps were evaluated to be 3 eV (TiO<sub>2</sub>), 2.93 eV (5 mM Ni/TiO<sub>2</sub>), 2.84 eV (10 mM Ni/TiO<sub>2</sub>) and 2.79 eV (20 mM Ni/TiO<sub>2</sub>), respectively. The reduction in bandgap is observed due to the impact of Ni doping in the crystal of TiO<sub>2</sub> NRs that might create impurity states underneath the conduction position framed because of the hybridization of metal (Ti and Ni) 3d and O2p orbits [20,28].



Figure 6.6: UV-visible absorption spectra of the Ni doped TiO<sub>2</sub> NRs (a) Tauc plot (b).

# 6.3.2 Photoelectrochemical performance of $TiO_2$ and $Ni\text{-}TiO_2$ nanorod electrodes

Linear sweep voltammetry (LSV) graph of the Ni doped TiO<sub>2</sub> NRs photoanodes (with variation in Ni amount) in chopped light excitation are shown in Figure 6.7a. The photocurrent density of the undoped TiO<sub>2</sub> NRs is measured 0.730 mA/cm<sup>2</sup> at 1.23 V vs RHE, while the enhancement in photocurrent density is observed for Ni doped TiO<sub>2</sub> NRs. The photocurrent densities are obtained for 1.11 mA/cm<sup>2</sup>, 1.56 mA/cm<sup>2</sup>, and 1.35 mA/cm<sup>2</sup> at 1.23 V vs RHE for 5 mM, 10 mM, and 20 mM Ni doped TiO<sub>2</sub> film, respectively. Thus, results show TiO<sub>2</sub> nanorods doped using 10 mM Ni solution has higher PEC performance in the visible light region. Such increase in the PEC performance is related to high absorption of visible light, the increased electrical conductivity of materials, even passivation of surface defects, etc.[8]. This also suggested that Ni doping assists the separation process of the photo-excited  $e^{-}h^{+}$  pairs, as the Ni 3d states in the energy band could serve as trap sites for photo-generated electrons from the valence band (VB) [20,44]. The lower photocurrent in the 20 mM Ni samples could be attributed to the NiO particles and Ni particles on the top of TiO<sub>2</sub> nanorods films that might partially block the light to reach the TiO<sub>2</sub> layer. Metal oxide particles may improve optical absorption, in any way; they likely carry on as recombination centers, which would prevent electron-hole pairs moving to the surface [8]. Subsequently, there exists an ideal concentration of doped metal oxide, underneath which the enhancement of optical absorption is insignificant, and over which the PEC performance decreases due to an increment in recombination. Figure 6.7b shows the current (I)- time(t) response was measured at 0V vs the reference electrode (Ag/AgCl), during

which light was rapidly switched on and off. The time of photo-generated electron lifetime was calculated by the following kinetic equation [46,47]:

$$D = \exp\left(\frac{-t}{\tau}\right) \tag{6.1}$$

$$D = \frac{I_t - I_f}{I_i - I_f} \tag{6.2}$$

Here t indicates time, I is the photoanode current, the index 'i' and 'f' indicate the starting and last steady-state. Based on the calculation strategy of Radecka's work [22], the calculated  $\tau$  values to be 10.87 s, 11.16 s, 14.97 s, and 13.23 s for the undoped, 5 mM-Ni/TiO<sub>2</sub>, 10 mM-Ni/TiO<sub>2</sub> and 20 mM-Ni/TiO<sub>2</sub> electrodes, respectively. It means recombination rate of the doped TiO<sub>2</sub> NRs is lower than that of un-doped TiO<sub>2</sub> NRs electrode. The longer recombination time means lesser recombination of e<sup>-</sup>-h<sup>+</sup> pairs in the PEC system due to which higher photo response of 10 mM Ni/TiO<sub>2</sub> NRs is observed. Photo-electrode stability as a function of illumination time is also essential for stable PEC water splitting. Figure 6.7c appears the *I-t* response of all four samples (TiO<sub>2</sub> and Ni doped TiO<sub>2</sub>) recorded for approximately 30 min continuous illumination of light. It can be observed that there is no noteworthy rot of the photocurrent density during long-term light, indicating that TiO<sub>2</sub> and Ni doped TiO<sub>2</sub> NRs photoanode shown better PEC stability. To determine the conversion of solar energy to hydrogen fuel efficiency, it can be found by using the following equation [10]:

$$\eta = \frac{I(1.23 - V_{RHE})}{J_{light}} \tag{6.3}$$

here  $V_{RHE} = V_{Ag/AgCl} + 0.059pH + 0.199$ , where J is the illumination intensity (100 mW/cm<sup>2</sup>) and I is the photocurrent density,  $V_{Ag/AgCl}$  and  $V_{RHE}$  is the applied potential and reversible hydrogen electrode potential and pH value is 5.85 (Na<sub>2</sub>SO<sub>4</sub> electrolyte). The photoconversion efficiencies of the TiO<sub>2</sub> and Ni-doped TiO<sub>2</sub> NRs are calculated and shown in Figure 6.7d. The photoconversion efficiency of 0.7% (undoped TiO<sub>2</sub>), 1.31% (5 mM Ni/TiO<sub>2</sub>), 1.55% (10 mM Ni/TiO<sub>2</sub>) and 1.42% (20 mM Ni/TiO<sub>2</sub>) at 0.3 V *vs* V<sub>RHE</sub>, are observed, respectively, it is noticed that the doped TiO<sub>2</sub> NRs electrode have two times higher efficiency than that of undoped TiO<sub>2</sub> NRs. The improvement in PEC efficiency for Ni-doped TiO<sub>2</sub> NRs based photoanode because of less trapping sites for photo-generated electrons that suppress the charge carriers from quick recombination [44,48].



Figure 6.7:(a) Linear Cyclic Voltammetry with chopped light excitation, (b) Photocurrent density vs time (I-t) plot at 0 V *vs* Ag/AgCl (c) electrode stability measurement in the presence of light (d) Photoconversion efficiency of undoped TiO<sub>2</sub> and Ni-doped TiO<sub>2</sub> NRs.

To investigate the electrochemical behavior of the fabricated photoanodes using the Electrochemical impedance spectroscopy technique. EIS results are depicted in Figure 6.8a represented in the form of Nyquist plots. The Lower-frequency region in Nyquist plots (Figure 6.8a) is attributed to the photoanode/electrolyte charge transfer resistance ( $R_{ct}$ ). The interfacial charge transfer resistance ( $R_{SC}$ ) and space charge resistance ( $C_{SC}$ ) are occurring at the counter electrode/electrolyte interface due to higher frequency phenomena [31,49]. Impedance measurements for four different photoanodes (undoped, Ni-doped TiO<sub>2</sub>) were determined using a standard three-electrode system under the dark condition in the frequency range of 0.1 Hz to 100 kHz. The equivalent circuit and fitted parameters are given in Figure A.4 &Table A.2. The undoped TiO<sub>2</sub> NRs photoanode exhibits higher  $R_{ct}$  values (2.28 k $\Omega$ ) compared to Ni doped TiO<sub>2</sub> NRs. After Ni doping, the  $R_{ct}$  value was significantly decreased, and 10 mM Ni/TiO<sub>2</sub> indicates

the lowest  $R_{ct}$  value as 480  $\Omega$ , suggesting that faster charge transfer process occurring at the photoanode interface.



Figure 6.8:(a) EIS Spectra of and (b) Mott-Schottky plot of undoped  $TiO_2$  NRs and Ni doped  $TiO_2$  NRs.

The charge carrier density of the undoped and Ni-doped TiO<sub>2</sub> NRs was measured by Mott-Schottky (MS) plots are shown in Figure 6.8b. The M-S plots shown the positive slope of all four samples, which is attributed to the n-type semiconducting nature of TiO<sub>2</sub> NRs. After doping Ni into the rutile structure of TiO<sub>2</sub> NRs also showing n-type nature. The flat band potential ( $V_{FB}$ ) of -0.69, -0.68, -0.77 and -0.70 were obtained for undoped TiO<sub>2</sub>, 5 mM Ni/TiO<sub>2</sub>, 10 mM Ni/TiO<sub>2</sub> and 20 mM Ni/TiO<sub>2</sub> NRs electrodes, respectively. Higher negative flat band potential of 10 mM Ni/TiO<sub>2</sub> NRs photoanodes indicated more efficient charge separation and transportation compared to the other three samples. Consequently, the 10 mM Ni/TiO<sub>2</sub> NRs photoanode could exhibit higher photocurrent density. From the Mott-Schottky plot, charge carrier densities (N<sub>d</sub>) of the doped TiO<sub>2</sub> NRs electrode were calculated using the following equation [23].

$$N_d = \left(\frac{2}{e\varepsilon\epsilon}\right) \left[\frac{d\left(\frac{1}{c^2}\right)}{dv}\right]^{-1} \tag{6.4}$$

The charge carrier density (N<sub>d</sub>) of the un-doped TiO<sub>2</sub> NRs is  $1.04 \times 10^{18}$  cm<sup>-3</sup>. While  $1.53 \times 10^{18}$  cm<sup>-3</sup> for 5 mM Ni/TiO<sub>2</sub>,  $2.529 \times 10^{18}$  cm<sup>-3</sup> for 10 mM Ni/TiO<sub>2</sub> and  $1.235 \times 10^{18}$  cm<sup>-3</sup> for 20 mM Ni/TiO<sub>2</sub>, respectively. Significantly, 10 mM Ni doped TiO<sub>2</sub> NRs leads to higher donor density,

which could raise the fermi level near the conduction band, promoting the charge separation at the  $TiO_2$  photoanode/electrolyte interface [8]. The 10 mM Ni-doped  $TiO_2$  NRs electrode has effective charge separation, transportation, and improvement of visible light absorption, resulting in significant enhancement of the overall PEC performance.

#### 6.3.3 Cu<sub>2</sub>FeSnS<sub>4</sub> coated Ni-TiO<sub>2</sub> nanorods photoelectrode

XRD pattern confirm the coating of Cu<sub>2</sub>FeSnS<sub>4</sub> on TiO<sub>2</sub> and Ni-TiO<sub>2</sub> NRs as shown in Figure 6.9a. The additional peaks at 28.5°(112), 47.5°(220) and 56.2°(312) belongs to tetragonal crystal structure of CFTS phase (JCPDF no:44-1476) [35,50] and along with rutile structure of TiO<sub>2</sub> NRs. The high resolution XPS spectra of Ti2p, O1s, Ni2p, Cu2p, Fe2p, Sn3d and S2p noticed in the CFTS/Ni-TiO<sub>2</sub> electrode as shown in Figure 6.9(b-h), respectively. Figure 6.7e shows that the spectrum of Cu2p is split into two peaks are noticed at 931.3 eV and 951.14 eV which can be assigned to Cu2p1/2 and Cu2p3/2 respectively, thus indicate of Cu(1+) state with a spin orbit separation of 19.84 eV [35]. The Fe spectrum shows two peaks at 710.8 eV and 723.14 eV, attributed to the Fe2p3/2 and Fe2p1/2 respectively, which is assigned to the Fe (2+) state [35,51–53]. The binding energy peak of 'Sn' in the spectrum reveals that symmetrical peaks at 486.1 and 494.4 eV shown in Figure 6.9g, which is attributed to the Sn<sup>4+</sup> oxidation state with binding energies of Sn3d<sub>5/2</sub> and Sn3d<sub>3/2</sub>. However, additional peaks at 487.04 and 495.5 eV are attributed



Figure 6.9: (a) XRD spectra of CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> NRs (b-h) XPS analysis of CFTS/Ni-TiO<sub>2</sub> NRs (Ti2p, O1s, Ni2p, Cu2p, Fe2p, Sn3d, and S2p).

to the presence of SnO<sub>2</sub> phase on the surface of CFTS [54,55]. The S2p peaks (Figure 6.9h) located at 161.6 eV (2p3/2) and 162.3 eV (2p1/2) are consistent with binding energy of S in the sulfide (-2) state in CFTS [56]. Therefore, XPS analysis of CFTS coated on Ni-doped TiO<sub>2</sub> NRs signifies that, the fabricated electrodes have standard oxidation states of all elements and confirm the coating of Cu<sub>2</sub>FeSnS<sub>4</sub>.



Figure 6.10: SEM images of CFTS/Ni-TiO<sub>2</sub> NRs electrode (a) top view, (b) magnification image of a, (c) cross-sectional view of the image a, ( $c_1$  to  $c_9$ ) cross-sectional elemental mapping of image c of Ti, O, Ni, Si, Cu, Fe, Sn, and S respectively.

The surface morphology of CFTS/Ni-TiO<sub>2</sub> NRs electrode shows a uniform coating of CFTS on the entire surface area of the Ni-doped TiO<sub>2</sub> NRs (Figure 6.10a). Further, the crosssectional elemental mapping of CFTS/Ni-TiO<sub>2</sub> NRs is represented in Figure 6.10c. Figure 6.10c clearly shown that the CFTS layer deposited on the surface of the Ni-TiO<sub>2</sub> NRs. Figure 6. 10(c<sub>1</sub> to c<sub>9</sub>) confirmed that the CFTS layer is noticed in the cross-sectional images of the CFTS/Ni-TiO<sub>2</sub> NRs electrode. EDS spectra and elemental mapping of the CFTS/Ni-TiO<sub>2</sub> NRs electrode reveals the atomic weight percentage of 1.5% (Ni), 1.2% (Cu), 2.9% (Fe), 1.2% (Sn), and 0.2% (S) for CFTS/Ni-TiO<sub>2</sub> NRs electrode is shown in Figure 6.11, respectively.



Figure 6.11: EDS spectra and elemental mapping of the CFTS/Ni-TiO<sub>2</sub> NRs electrode.



Figure 6.12: (a) absorption spectra (d) Tauc plot of CFTS/Ni-TiO<sub>2</sub> NRs electrodes.

The absorbance of the CFTS/Ni-TiO<sub>2</sub> NRs electrode is enhanced from 400 nm to 500 nm is noticed after CFTS coated on TiO<sub>2</sub> NRs are shown in Figure 6.12a. The CFTS/TiO<sub>2</sub> NRs shows an absorption edge at 430 nm, suggesting that the energy level created by valence band (VB) upshift after CFTS particle coating. Significantly, the absorption edge is extended to the visible region at a wavelength of 500 nm when the CFTS particles coated on Ni-TiO<sub>2</sub> NRs, respectively, which appears from the strong visible-light harvesting by the CFTS particles (1.5

eV bandgap). These studies clearly imply that the changing of optical properties is observed when Ni doping and CFTS particle coated on the surface of TiO<sub>2</sub> NRs. The bandgap values are calculated by tauc plot (depicted in Figure 6.12b) which are found to be 2.9 eV (CFTS/TiO<sub>2</sub>), 2.84 eV (Ni/TiO<sub>2</sub>), 2.5 eV (CFTS/Ni-TiO<sub>2</sub>), respectively.



Figure 6.13: (a) Linear scan voltammetry plot (b) I-t plot (c) photocurrent conversion efficiency (d) stability measurement (e) EIS Spectra (f) Mott-Schottky plot of CFTS/TiO<sub>2</sub>, Ni/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> NRs.

The photocurrent density of 2.09 mA/cm<sup>2</sup> and 1.14 mA/cm<sup>2</sup> at 1.23 eV *vs* RHE is obtained in case of CFTS/Ni-TiO<sub>2</sub> and CFTS/TiO<sub>2</sub> based electrodes (Figure 6.13a), respectively. Figure 6.13b shows the photo-generated charge carrier lifetime of CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> electrode, calculated using the kinetic equation discussed in section 6.3.2. The charge carrier lifetime of CFTS/TiO<sub>2</sub> is 12.93 sec, and CFTS/Ni-TiO<sub>2</sub> is 15.36 sec, respectively. Figure 6.13c shows the photoconversion efficiency of CFTS/TiO<sub>2</sub> is 1.31% at 0.13V *vs* RHE and 2.55% at 0.13V *vs* RHE for CFTS/Ni-TiO<sub>2</sub> respectively. Photoelectrode stability measurement of CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> NRs electrodes show no significant decay of the photocurrent density in the presence of long-term illumination, suggesting that CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> photoelectrode exhibited better stability in PEC application. Figure 6.13e shows the impedance spectra for fabricated electrodes such as CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> NRs under dark illumination, which have been plotted as the form of Nyquist plots. The equivalent circuit (EC)

to simulate the Nyquist plot is shown in the Figure A.4. The calculated parameters of the EC elements are shown in Table A.2. When CFTS particles are decorated on Ni-doped TiO<sub>2</sub> NRs, the Rct value (330 $\Omega$ ) for CFTS/Ni-TiO<sub>2</sub> electrode decreases significantly. It contrasts with the CFTS/TiO<sub>2</sub> electrode (i.e.1.77 k $\Omega$ ), which indicates the rapid charge transfer occurs at the photoanode interface, resulting in increased PEC performance. Figure 6.13f shows Mott-Schottky (M-S) plots of the CFTS/TiO<sub>2</sub> and CFTS/Ni-TiO<sub>2</sub> electrodes. The M-S plots shown the positive slope is attributed to the n-type semiconducting nature of the material. The charge carrier density (N<sub>d</sub>) for CFTS/Ni-TiO<sub>2</sub> and CFTS/TiO<sub>2</sub> electrodes is 3.27 \* 10<sup>18</sup> cm<sup>-3</sup> and 0.92 \*10<sup>18</sup> cm<sup>-3</sup> respectively. Significantly, higher charge carrier density implies lower recombination of electron-hole pair, which facilitates higher performance of the PEC devices.

The knowledge of band structure of TiO<sub>2</sub>, Ni-doped TiO<sub>2</sub>, and CFTS is essential to understand the charge transfer process, the calculated band edge values are given in Table A.3 in appendix (section A4). Both the Conduction band (CB) edge and the Valence band (VB) edge of the CFTS are higher than the TiO<sub>2</sub>. Thus, supporting the type II semiconductor heterojunctions are formed between the CFTS and TiO<sub>2</sub>. When, the sunlight is illuminated on the heterostructure device i.e CFTS/Ni-TiO<sub>2</sub>, electron and holes pairs are generated at the heterostructure due to inner electric field at the interface of TiO<sub>2</sub> and CFTS as depicted in Figure 6.14. Further, electron is excited from the VB of the CFTS to conduction band of the CFTS, and finally injected to the CB of the Ni doped TiO<sub>2</sub> NRs (here Ni impurity states created in band gap of the TiO<sub>2</sub> lattice act as trapping sites) to reach FTO [28,44]. Further the electrons move to the external circuit to reach the surface of the counter electrode and these electrons are combined with H<sup>+</sup> ions to form a H<sub>2</sub> gas. Meanwhile, holes are separated on the VB of the TiO<sub>2</sub> then quickly transfer to VB of the CFTS, at the surface of the heterostructure, holes are accumulated, and these holes react with water to generate the oxygen gas at the photoanode surface. As a result, the higher photogenerated charge carrier separation occurs at the heterostructure due to the type II band alinement between CFTS and TiO<sub>2</sub>. This eventually reduces the recombination of e- and h+ pairs and improves the solar water splitting performance.



Figure 6.14: Band structure diagram and charge transfer process of CFTS/Ni-TiO<sub>2</sub> NRs heterostructure photoanode in water splitting cell.

#### 6.4 Summary

We have synthesized undoped TiO<sub>2</sub> and Ni-doped TiO<sub>2</sub> nanorods (NRs) using the hydrothermal method. The effect of Ni dopant on the PEC activity of the TiO<sub>2</sub> NRs is conducted systematically. The 10 mM Ni concentration is the most effective route to increase the photoactivity of TiO<sub>2</sub> NRs. Ni doping reduce the bandgap of TiO<sub>2</sub> NRs, which increment the optical absorption, enhanced the charge carrier density, and assisted the charge separation-transport process. The photocurrent density of 10 mM sample significantly increments with bias voltage and reaches 1.56 mA/cm<sup>2</sup> at 1.23V *vs* RHE. The optimal PEC performance is observed when 10mM Ni-doped TiO<sub>2</sub> NRs based electrode. CFTS layer was coated on Ni-TiO<sub>2</sub> NRs which has improved photocurrent density to 2.09 mA/cm<sup>2</sup> at 1.23 V *vs* RHE. The CFTS/Ni-TiO<sub>2</sub> heterostructure formation leads to better charge carrier density, effective charge carrier separation, transportation, and a relatively long electron lifetime.

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# CHAPTER-7 Summary and Conclusions

#### 7.1 Summary and Conclusions

Thesis briefly presented an overview on development of nanomaterials for water purification and splitting. Classification of water purification methods, basic principle of photocatalyst and adsorption process are discussed. Recent developments on photocatalyst and adsorbent for water purification were presented. In addition, introduction of water splitting, and the basic principle of photo-electrochemical water splitting are overviewed. Among various catalytic materials, abundant chalcogenide semiconducting materials are extensively reviewed to consider it utilization for water purification and water splitting application.

The synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles using the solution approach was examined and various synthesis parameters i.e, reaction temperature, reaction time and initial precursors were optimized. Effect of different temperatures (180°C, 200°C, 220°C), reaction time (6h,12h,18h) and various solvents (OLA, DMF, EDA, DI water) were investigated over structural, morphological, and optical properties of CFTS particles. In the temperature-controlled synthesis, a better crystalline CFTS phase was observed at 200°C. While varying the reaction time in the synthesis process, improvement in the crystalline phase of CFTS and significant difference in morphology (porous sphere, sheet-flakes, and intermixed flower-sheet), elemental composition of the CFTS particles were observed. In solvent-controlled synthesis, the CFTS particles synthesized using different i.e oleylamine (OLA), deionized water (DI), ethylenediamine (EDA), N, N-dimethyl formamide (DMF). As-grown CFTS particles have some impurity phases and pure crystalline phase particles have achieved after heat treatment. While varying the solvents in the synthesis process, significant difference in morphology (flower, larger grain structure, aggregate particles, and agglomerated particles) of the CFTS particles was also noticed. If the changing the solvent in the synthesis process varied the elemental composition of the CFTS particles and varied the band gap values from 1.43 eV to 1.7 eV, was observed, respectively. Overall, the results of this study show the synthesis of CFTS particles and reaction parameters such as temperatures, reaction times, and solvents were optimized in solvothermal methods.

Different sulphur precursors namely thiourea, thioacetamide, sulphur powder, sodium sulphide was used for the synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> particles and studies its effects on crystallinity, morphology, and elemental composition. The CFTS particles have shown noticeable variation in elemental composition when different Sulphur precursors were used in the synthesis. Further annealing in sulphur atmosphere, the stoichiometric ratio of CFTS particles improves, and the binary/ impurity phases were reduced. Among the four different sulphur precursors, the thiourea results in better crystallinity and larger size grains of CFTS particles. The use of different sulphur precursors also renders significant change in the morphology of CFTS particles. The optical band gap of CFTS particles was also varied from 1.48 eV to 1.81 eV due to substantial differences in crystallinity, composition, and morphology. Better photocatalytic performance was observed in the CFTS particles grown using thiourea, and approximately 70% methylene blue dye is degraded in 60 min under white light excitation.

The porous Cu<sub>2</sub>FeSnS<sub>4</sub> particles have developed using various reaction time in the synthesis process and studied the removal of organic acid fuchsin dye pollutant from wastewater by adsorption process. Variation in synthesis reaction time led to having a porous sphere, sheetflakes, and intermixed flower-sheet morphologies of CFTS particles synthesized at 200 °C for 6 h, 12 h and 18 h, respectively. The effect of surface morphologies of the CFTS particles on dye adsorption capability was examined. The porous spheres of CFTS particles have shown approximately (89.25  $\pm$  2.21) % of AF dye adsorption within 10 min and the value reaches  $(97.12 \pm 0.76)$  % in 60 min. The high adsorption capacity i.e  $(123.12 \pm 2.09)$  mg/g is obtained for porous spherical CFTS particles. The adsorption isotherm and kinetic studies reveal that the Langmuir isotherm and pseudo-second-order kinetic model can explain the dye adsorption. The highest adsorption capacity (128.12 mg/g) and 98% acid fuchsin (AF) dye adsorption observed within 60min when porous sphere CFTS was used as an adsorbent. Further, the porous CFTS particles exhibit good stability and reusability of the adsorbent for wastewater purification. The results indicate that porous earth-abundant and non-toxic quaternary chalcogenide particles can be low-cost, highly efficient adsorbent for removing organic acid fuchsin (AF) dye pollutants from wastewater.

In another study, the Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) particles were synthesized using different surfactants i.e. thioglycolic acid (TGA), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA). Then the

effect of surfactants on crystal structure, morphology, elemental composition and electrocatalytic properties of CFTS particles were investigated. The better crystalline phase of the CFTS particles was observed in the case of PVP (used as a surfactant) and impurity phases were observed in case of TGA, PVA (surfactants). Further annealing in the presence of sulphur improves the crystallinity of CFTS particles. The morphology of CFTS was significantly changed when a different surfactant were used in the synthesis process. The mixture of aggregate and porous (1µm) particles was observed when PVA was used as a surfactant to synthesize CFTS particles. At the same time, highly porous particles having nanosheets and nanoparticles at the surface are obtained in the case of PVP. In the TGA case, spherical particles with 1µm size were observed. The electro-catalytic ability of all CFTS particles toward hydrogen evolution reactions (HER) was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The overpotential of PVP-based CFTS particles was the lowest as  $\eta = 421$  mV at 10 mA/cm<sup>2</sup> compared to the other two samples. CFTS particles synthesized using PVP exhibited enhanced electro-catalytic performance due to higher surface area.

The fabrication of Cu<sub>2</sub>FeSnS<sub>4</sub> decorated Ni-TiO<sub>2</sub> nanorods photoanode was performed to understand the photo-electrochemical water splitting. Herein, the earth-abundant and visible light-sensitive Cu<sub>2</sub>FeSnS<sub>4</sub> layer was decorated on Ni-TiO<sub>2</sub> nanorods (CFTS/Ni-TiO<sub>2</sub> NRs) using a wet chemical approach. Ni doping was performed on hydrothermally grown TiO<sub>2</sub> nanorods to achieve Ni-TiO<sub>2</sub> nanorods. After doping of Ni, the bandgap of TiO<sub>2</sub> nanorod films changes from 3.0 eV to 2.79 eV. Once the layer of Cu<sub>2</sub>FeSnS<sub>4</sub> was decorated on the Ni-doped TiO<sub>2</sub> nanorods, the absorption edge of the photoanode further shifted toward lower energy was noticed. Mott-Schottky analysis revealed a more than 3-fold increase in photo-generated charge carrier density in CFTS/Ni-TiO<sub>2</sub> NRs. These heterostructured photoanodes demonstrated a significant increase in photocurrent from 0.730 mA/cm<sup>2</sup> to 2.09 mA/cm<sup>2</sup> (at 1.23V vs RHE) was observed. The lifetime of photo-generated charge carriers also improves from 10.87s to 15.36s for CFTS/Ni-TiO<sub>2</sub> NRs as compared to TiO<sub>2</sub> NRs. The CFTS/Ni-TiO<sub>2</sub> NRs exhibit excellent photoelectrochemical properties with high stability.

## 7.2 Future scope

Considering the different outcomes of the present study and other understanding from the reported literature numerous proposals of future work can be given, few are listed here.

- Size and shape control synthesis of the Cu<sub>2</sub>FeSnS<sub>4</sub> nanoparticles using wet chemical could be the interesting area that may significantly affect the water splitting properties.
- The large-scale synthesis of Cu<sub>2</sub>FeSnS<sub>4</sub> quantum dots with controlled stoichiometry is open-ended problem.
- Design and fabrication of nano-heterostructure photoelectrode using  $Cu_2FeSnS_4$  QDs and  $TiO_2$  nanorods via solution approach further need to investigate toward photoelectrochemical water splitting application.
- The stability and durability of the fabricated nano-heterostructure is another challenge that needs to be addressed. Measurement of hydrogen production and hydrogen storage capability is the other future direction in which extensive investigation is required.

### APPENDIX

#### A1: Band gap calculation:

The optical band gap is estimated using the following equation. Absorption coefficients (cm<sup>-1</sup> mol<sup>-1</sup>) were calculated using the following formula.

Absorption coefficient( $\alpha$ ) =  $\frac{A}{C \times I}$ 

Here: A – Absorbance,  $\alpha$  = Molar absorption coefficients, C = concentration (0.001 mol ml<sup>-1</sup>), L = path length (1cm).

#### A2: Cross - sectional elemental mapping of the TiO<sub>2</sub> NRs and 10mM Ni-TiO<sub>2</sub> NRs:



Figure A.1: Cross-sectional elemental mapping of TiO<sub>2</sub> NRs



Figure A.2: Cross-sectional elemental mapping of 10mM Ni-TiO<sub>2</sub> NRs.

R(RC)(RC)W



Figure A.3: The equivalent circuit model used to stimulate the Nyquist plots from ESI measurements.

Table A.1: Parameters obtained from the EIS fittings

Photoelectrode	Rs	Rct	Rsc
TiO <sub>2</sub>	48.8Ω	2.28KΩ	20Ω
5mM Ni/TiO <sub>2</sub>	54.7Ω	1.28 KΩ	1.07Ω
10mM Ni/TiO <sub>2</sub>	44.3Ω	0.480 ΚΩ	0.169Ω
20mM Ni/TiO <sub>2</sub>	1.02Ω	0.650 ΚΩ	0.074Ω

Table A.2: EIS Parameters obtained from the Circuit.

Photoelectrode	Rs	Rct	Rsc
TiO <sub>2</sub>	48.8Ω	2.28KΩ	20Ω
CFTS/TiO <sub>2</sub>	24 Ω	1.77 ΚΩ	10.6kΩ
CFTS/Ni/TiO <sub>2</sub>	8.02 Ω	333Ω	572Ω

#### A3: Electronic band positions calculation:

The Conduction band (CB) edge and Valence band (VB) edge position of CFTS layer and TiO<sub>2</sub> nanorods were calculated using the following equation [1][2].

$$E_{VB} = \chi - E_O + 0.5E_g$$
 (1)

and

$$E_{CB} = E_{VB} - Eg \tag{2}$$

Where,  $E_{VB}$  is the VB edge potential,  $E_{CB}$  is the CB edge potential,  $\chi$  – is electronegativity of the semiconductor, which is indicates as the geometric mean of the absolute electronegativity of the constituent atoms forming the semiconductor materials ( $\chi_{Cu} = 4.48$ ,  $\chi_{Fe} = 4.02$ ,  $\chi_{Sn} = 4.3$ ,  $\chi_{S} = 6.22$ ,  $\chi_{Ti} = 4.08$ ,  $\chi_{o} = 7.54$ )[3–5]. Using these individual electronegativity values, the  $\chi$  values of

TiO<sub>2</sub> and CFTS semiconductor are calculated to be 5.84 and 4.85eV respectively [5]. Eo is the energy of free electrons on the hydrogen scale (4.5eV), Eg is the band gap of the semiconductor. The Eg of TiO<sub>2</sub> nanorods is 3eV and CFTS is 1.47eV respectively. The CB and VB edges of TiO<sub>2</sub> and CFTS were examined from the equation 1and 2 are tabulated in the Table A.3.

Photoanode	χ values	Band gap	СВ	VB
TiO2	5.84	3eV	-0.16eV	2.84eV
CFTS	4.98	1.47eV	-0.255eV	1.215eV

Table A.3: Valence band position and conduction band position of TiO<sub>2</sub> NRs and CFTS layer

0.4 (b) (a) 0.9 CFTS CFTS Absorbance(a.u)  $(\alpha hv)^{2*10^6}$ 0.6 0.2 0.3 0.0 0.0 700 800 1.2 1.4 1.6 1.8 2.0 2.2 2.4 400 500 600 900 1.0 300 Photon Energy (eV) Wave length(nm)

Figure A.4: UV-Visible spectra of CFTS layer (a) absorption spectra (b) Tauc plot

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