

# Synthesis and Characterization of Semiconductor Nanostructures for Possible Use of Photo Splitting of Water

Sangeetha V. S.<sup>1\*</sup> A. Priya<sup>2</sup>

<sup>1</sup> Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

<sup>2</sup> Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

---

## ABSTRACT

*Among the distinctive energy choices for future, the one that holds an unequivocal edge over others is the 'Hydrogen'. It tends to be delivered in huge sums by photograph parting of water utilizing richly accessible sunlight based radiations. With zero carbon release, hydrogen is a totally spotless and naturally generous fuel. The current proposal manages concentrates on PEC parting of water utilizing as photoelectrode four distinctive material frameworks, each addressed by a bunch of bi-layered nano-hetero-organized flimsy movies as: WO<sub>3</sub> (under layer) – ZnO (over layer); BaTiO<sub>3</sub> (under layer) – ZnO (Over layer); WO<sub>3</sub> (under layer) – TiO<sub>2</sub> (over layer) and BaTiO<sub>3</sub> (under layer) – TiO<sub>2</sub> (Over layer). Studies on PC parting of water were likewise attempted, utilizing as photocatalyst two arrangements of nano-heterostructured powder tests as: ZnO (center) – Ag doped TiO<sub>2</sub> (shell) and CuO (center) – Ag doped TiO<sub>2</sub> (shell). In the PC parting of water methanol was utilized as conciliatory specialist to search openings and forestall recombination. Tests were portrayed by X-beam Diffractometer, UVVisible Absorption Spectrometry, Scanning Electron Microscopy, Atomic Force Microscopy, Tunneling Electron Microscopy, BET Surface Area Determination, Electron Dispersive X-Ray Analysis and Flat Band Potential Determination. Contrasted with unblemished examples, the bi-layered dainty movies yielded huge addition in PEC photocurrent. Bi-layered movies with WO<sub>3</sub> under layer showed generally higher photocurrent contrasted with films with BaTiO<sub>3</sub> under layer. Center shell nano-hetero-organized powder tests likewise end up being better and more proficient photocatalyst for water parting against the immaculate examples of single metal oxide. Among the two material frameworks examined, CuO (center) – Ag doped TiO<sub>2</sub> offered moderately higher hydrogen yield. This framework was likewise examined under field conditions utilizing constant sunlight based brightening. Conceivable clarifications have been given PEC/PC execution of the considered material frameworks.*

**Keywords** – Physical Sciences, Chemistry, Chemistry Analytical

## **INTRODUCTION**

Petroleum derivatives, viz coal, oil and flammable gas, address limited and non-sustainable power holds. These have played, without a doubt, a vital job in the development and improvement of the world [Dincer, 2018; Kamat, 2017; Rosen, 2015]. Be that as it may, their quickly lessening stock is currently a reason for concern. Worldwide world energy request has been assessed to be around 13 trillion watts or 13 TW each year and it is as yet rising [Nathan, 2015]. Almost 360 quadrillion BTU (British warm unit) (for example 88%) of energy request is presently being met by devouring the petroleum products (oil, coal and flammable gas) [World Energy Council, 2015 Survey; Agugliaro et al., 2017]. Another issue related with rising utilization of petroleum derivatives, which has developed to a disturbing extent in last 3 forty years, is the arrival of immense measures of CO<sub>2</sub> and other Green House Gases (GHG) to the air. Over the most recent 20 years, the consuming of petroleum products has added to the degree of 75% in the complete GHG discharges created around the world, which has been considered answerable for a dangerous atmospheric deviation and related unfavorable climatic changes [Kreith and West, 2016; Lewis, 2016].

Albeit, world is still vigorously reliant on petroleum products to meet its energy prerequisites, however the importance and pertinence of environmentally friendly power alternatives in satisfying the world energy request is additionally developing [Edwards et al, 2018; Kudo, 2019; Vayssieres 2019]. To support the presence and development of human culture, the advancement of elective clean energy supplies alongside the utilization of contamination free innovation sustainable power is a developing need. Impelled by this developing interest of sustainable power (with zero fossil fuel byproducts) the environmentally friendly power advancements, which establish a basic segment for the acknowledgment of sans carbon worldwide energy supply frameworks of future, have likewise become vital [Hussain, 2017; Dincer, 2018; Walter et al., 2018].

Sun powered energy is one type of environmentally friendly power accessible on earth that holds enormous potential for its use both in metropolitan just as country portions. Truth be told, sun powered radiations got by the earth comprise a lasting and practically non-thorough wellspring of energy that can be saddled to meet the energy needs of the world. The earth gets almost  $1.3 \times 10^5$  TW of energy, which is around four significant degrees to the current worldwide energy utilization [Wilke et al., 2019; Murphy, 2016]. Further, sunlight based energy is broadly disseminated and effectively storable to other energy structures. The photovoltaic (PV) cell innovation for changing sun based energy over to power has just arrived at the business level [Khaselev et al., 2019; Bisquert et al., 2018]. Notwithstanding, the establishment and upkeep cost of PV cell/boards, combined with repeating cost on batteries, have end up being a significant obstruction in their huge scope uses. For the effective reaping of sun oriented energy, three significant issues of its catch, change and capacity should be settled [Bak et al. 2018; Balat, 2018].

The capacity is even more critical to handle the shaky and occasional inconstancy in the accessibility of daylight. In such manner the choice of putting away sun oriented energy by changing it over to a reasonable synthetic energy structure has its own benefits. Hydrogen produced by separating water atom is a high energy material that has colossal potential for its utilization as fuel (instead of petroleum derivatives) in various areas of energy utilization. The

crude materials required for hydrogen age for this situation would be water and sun based energy, the two of which are boundlessly accessible on earth [Steinfeld, 2015; Lewis, 2016]. Significant exploration endeavors are guided everywhere on the world to develop an effective interaction through which sun based energy can be used to break the water atoms and produce hydrogen as fuel [Walter et al., 2015; Dresselhaus, 2019].

Hydrogen is a high energy material that can be utilized as energy transporter for assorted applications. Being totally carbon free, it is an earth considerate fuel for what's to come. Further, utilizing 4 hydrogen as energy transporter offers a more productive energy transportation and circulation framework where the energy misfortunes during transmission and dispersion would be generously limited [Nowtony, 2015; Tseng, 2018; Zou and Zhang, 2015]. The fuel characteristics of hydrogen are introduced, which plainly features that it is certainly a far better fuel looked at than oil.

Ordinarily hydrogen is delivered in huge amounts for modern and different applications through coal gasification and steam improving of methane. As of now, both the techniques offer over 95% towards business hydrogen age. Just 4% of the hydrogen is acquired by electrolysing water, especially in those regions where power is accessible in adequate amount at less expensive rates. Both the above courses for hydrogen age depend upon the immediate or aberrant (by means of power) utilization of non-renewable energy sources and can't be feasible for a really long time under the developing emergency of petroleum derivatives [Serrano, 2017]. An elective course for hydrogen creation that isn't just inexhaustible but at the same time is economical would be the point at which it is gotten by photosplitting of water, utilizing sunlight based energy [Wolcott et al., 2019; Dusastre, 2019]. With both the crude materials, 5 water and sunlight based energy being accessible in wealth on earth, it offers a suitable course for putting away sun oriented energy in compound energy structure (for example hydrogen), which can be used later advantageously on need premise. Basically, hydrogen creation by this course requires productive gathering of the bit of sun powered obvious light ( $400\text{ nm} < \lambda < 760\text{ nm}$ ) where main part of the energy of sun oriented range falls. As the water is non-retaining in the noticeable area, an appropriate material is required that can ingest the sun oriented light and move the consumed energy to water atoms to start the water parting cycle and age of hydrogen and oxygen [Aloney et al., 2018; Zou and Zhang, 2019].

## **OBJECTIVE OF THE STUDY**

1. To research the characterization of nanostructures in semiconductors.
2. To research the use of synthesis in photo splitting of water

## **EXPERIMENTAL**

### **Sample Synthesis: Thin films**

**Blend of WO<sub>3</sub> – ZnO bilayered slim movies:** ITO (Sn:In<sub>2</sub>O<sub>3</sub>) glass sheets, of size 1.5 cm × 1.5 cm and electrical resistivity ~ 8 Ω cm, were utilized as substrate for film union. These were pre-washed by splashing for 2 min in cleanser arrangement followed by 4-5 washings with a liberal portion of water and hot air-drying at 110 °C for 5 min. Cleaned substrates were put away, away from dampness and residue, in a hermetically sealed glass holder. Utilizing sol-gel

measure, a progression of bi-layered nanostructured flimsy movies, involving WO<sub>3</sub> (under layer) and ZnO (over layer) were orchestrated. The forerunner utilized in the amalgamation of WO<sub>3</sub> under layer was Sodium Tungstate Dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), a fixed amount of which was broken down in 10 ml water and afterward hastened by adding HNO<sub>3</sub>. The subsequent yellowish encourage of H<sub>2</sub>WO<sub>4</sub> was broken up in 6 ml of H<sub>2</sub>O<sub>2</sub>. The expansion of 0.5 g of polyethylene glycol (PEG) in it yielded a thick sol, which was mixed for 2 h with the expansion of 25 ml of ethanol.

Arrangement, consequently got, was saved over ITO substrate (in 4 coats) and the film was sintered at 450 °C for 1 h [Jiao et al., 2017]. To store the ZnO over layer on the highest point of WO<sub>3</sub> under layer, following strategy was followed. Zinc acetic acid derivation dihydrate, (CH<sub>3</sub>COO)<sub>2</sub> Zn·2H<sub>2</sub>O, was broken up in 2-propanol under blending (for around 20 min.) to yield 0.5 M arrangement. To this arrangement, 1 ml of di-ethanolamine was added as restricting specialist and the substance was blended for ~ 4 h and kept for the time being at 28 ± 3 °C, which yielded a reasonable arrangement [Sharma et al., 2016]. They got arrangement was turn covered over recently acquired movies of WO<sub>3</sub>. The ZnO layer contained different coatings (2, 3, 4, 5, and 6), with progressive coats being interspaced by a drying period of 5 min. at 45-60 °C. After the last coat, the movies were sintered in air, first at 250°C for 30 min. and afterward at 600°C for 60 min. Step sintering saved the examples from any conceivable warmth stun and furthermore guaranteed the total crystallization, evacuation of natural pollutions, and underlying/compound consistency in movies incorporated. All through the movies were stored by utilizing a Milman Photoresist Spinner at 2200 rpm. The arrangement utilized per coat was 1 ml. Movies were kept uniquely on almost 3/4 length of substrate plates. From the uncovered bit of the substrate, electrical contact was set up that encouraged the utilization of movies as working terminal in PEC contemplates.

### **Sample synthesis: Powders**

Two arrangement of tests, involving ZnO (center) – Ag doped TiO<sub>2</sub> (shell) and CuO (center) – Ag doped TiO<sub>2</sub> (shell) were blended. The acquired powder tests were described and examined for use as photocatalyst in PC parting of water. Progressed portrayals viz. EDX, XPS and HR-TEM examinations for this situation were limited to just not many agent tests (for the most part the one that yielded great PC reaction).

### **Synthesis of CuO Nanoparticles**

To the fluid arrangement of copper (II) acetic acid derivation monohydrate, Cu(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, arranged alongside the expansion of 1 mL frigid acidic corrosive, controlled expansion of NaOH arrangement at 80°C yielded an encourage. The substance was mixed at room temperature and the expansion of NaOH arrangement proceeded till pH expanded to ≈ 7. Following it the substance was blended for 2 h and the came about accelerate was washed utilizing water and dried for 1 h at 60°C. To finish the pattern of crystallization, tests were sintered in air at 450°C for 1 h that yielded a dark hued item.

## HYDROGEN GENERATION THROUGH PEC AND PC SPLITTING OF WATER

Inexhaustible hydrogen got through sun based light initiated photosplitting of water is a suitable and reasonable substitute for non-renewable energy sources [Honda and Fujishima, 2015; Bard et al., 2019; Aroutiounian et al., 2015]. There are high possibilities of utilizing hydrogen in future to fulfill the energy needs of the world. Nonetheless, in the progress from petroleum product to hydrogen, it is needed to streamline the advances for age, stockpiling, circulation and end-utilizations of hydrogen created [Zhang, 2015; Li et al., 2018]. The as a matter of first importance step in this is develop appropriate techniques/innovations through which huge scope creation of hydrogen from sun powered energy would be conceivable. These are various courses accessible for sun powered water parting, viz. photovoltaic-electrolysis, sun powered warm, photobiological, photochemical, photoelectrochemical and photocatalytic. [Turner, 2018; Licht et al., 2017; Gratzel, 2019; Bak et al., 2016; Ager, 2016]. In any case, the last two in the above rundown, for example photoelectrochemical (PEC) and photocatalytic (PC) courses are the most encouraging by virtue of their simplicity of activity and ease of hydrogen creation. Also, the transformation of sun powered energy to hydrogen in both the PEC and PC measures happens in one stage, henceforth their proficiency of energy change is required to be high [Nowtony, 2015; Walter, 2010; Hisatomi, 2015].

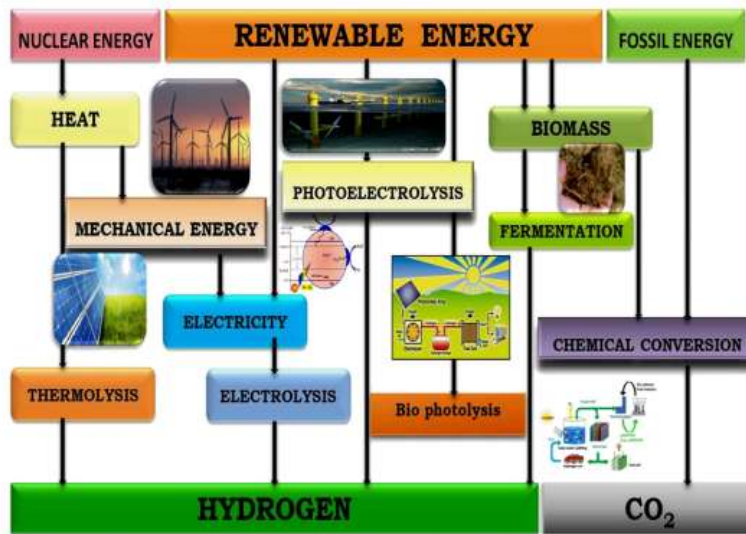


Fig. 1.1

Various potential ways/courses to create hydrogen [Turner, 1999] the critical angle in the plan of hydrogen age reactor framework for PEC/PC water parting is the determination of a reasonable semiconductor material for use as photograph cathode/photograph impetus.

## HYDROGEN GENERATION: INTERNATIONAL/NATIONAL INITIATIVES

In both the PEC and PC frameworks for sun oriented water parting, the sun powered energy catch and hydrogen age measures are coordinated in one stage. A photoactive semiconductor material structures the center part in the plan of above frameworks; henceforth for proficient water parting, it needs to meet certain prerequisites. Other than the coordinating band hole of

with the energy required driving water parting response, when a solitary semiconductor photoelectrode is utilized in a fair-minded condition in a PEC cell, its band edges should likewise ride the hydrogen and oxygen advancement redox possibilities [Kale et al., 2019].

## **STRATEGIES TO ENHANCE THE EFFICIENCY OF PEC/PC SPLITTING OF WATER**

Semiconductor material, utilized as photograph anode/photograph impetus in the parting of water, establishes the most imperative and a center segment in the plan and capacity of the PEC/PC gadgets utilized for the reason. Likewise, a large portion of the investigates in this field are coordinated towards recognizing better and more effective semiconductors for the cycle and improving the photoresponse of the promising semiconductors. There are numerous procedures in such manner that have been explored by various analysts lately [Khaselev and Turner, 2019; Maeda and Domen, 2017; Lewis, 2018; Gratzel, 2017; Bak et al., 2018; Alexander et al., 2018; Walter et al., 2018]. Not many of these, which are pertinent for the current work, are momentarily referenced beneath. As would be seen, a large portion of these techniques rotate around presenting appropriate alterations in the material properties of the semiconductor by changing the material amalgamation convention and the material microstructure/morphology [Wang et. al., 2018]

### **Doping**

The utilization of semiconductors like  $\text{TiO}_2$  and  $\text{ZnO}$  for sunlight based water parting has been restricted because of their moderately high band hole, which restricts the ingestion of just the UV and a little bit of noticeable segment of the sun powered range. To grow the retention to the noticeable locale, their band hole should be brought down. Pollutant doping is one of the procedures to accomplish this, as it might produce transitional contamination levels between the conduction and valence band of the semiconductor [Aroutiounian et al., 2017; Huang et al., 2018]. The two sorts of doping, by metals just as non-metals, can prompt a move in the ingestion edge to the obvious scope of light [Upadhyay et al., 2016; Yang, 2018]. Other than the move in the band hole, doping has additionally been accounted for to make a few other miniature underlying changes in the semiconductor materials that can expand transporter thickness and encourage better charge transport,

## **PEC SPLITTING OF WATER**

As referenced before, the current proposition fuses considers relating to PEC parting of water for hydrogen age. In this setting the utilization of bilayered nano-hetero-organized slim movies of few imminent semiconductors, viz.  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{TiO}_2$  and  $\text{BaTiO}_3$  have been investigated. The past part introduced results acquired with bi-layered flimsy movies, involving  $\text{WO}_3$  or  $\text{BaTiO}_3$  under layer and  $\text{ZnO}$  over layer. Introduced in this section are the outcomes acquired with bi-layered slight film tests, including  $\text{WO}_3$  (under layer) –  $\text{TiO}_2$  (over layer) and  $\text{BaTiO}_3$  (under layer) -  $\text{TiO}_2$  (over layer). Leading glass (ITO) sheets were utilized as substrate for this situation too; for developing slender movies by sol-gel turn covering. A portrayal of the examples arranged is given. For correlation, slim movies of perfect  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{BaTiO}_3$  were likewise arranged and researched.

## **Characterization**

In order to explore the essence of the evolved crystalline phase(s) and its microstructure and surface and optical characteristics, the prepared thin film samples were characterized.

## **General Characteristics**

The films stick well to the surface of the substrate. These films did not peel off even when they were used as photo electrodes in PEC cells. Using a Surface Profilometer, film thickness was calculated, while density was estimated by the method mentioned elsewhere [Sharma et al., 2017]. From the current-potential map, electrical resistivity was calculated using the method stated earlier [Singh et al., 2019].

## **X-Ray Diffraction Analysis**

The observed pattern of X-ray diffraction of thin film samples is portrayed. In the samples, the XRD data helped to distinguish major crystalline phases. In addition, the knowledge was also used to estimate the average crystallite size, micro strain and dislocation density (through Debye-computations). Scherer's

## **CONCLUSION**

Two arrangement of bi-layered dainty film tests, comprising of WO<sub>3</sub> (under layer) – ZnO (over layer) and BaTiO<sub>3</sub> (under layer) – ZnO (over layer) (alluded as WZ and BZ arrangement of tests, separately), were combined and explored for use in PEC parting of water. Thickness of bilayered film was found to go 3.83-3.89 (in WZ arrangement), and 3.81-3.91 g/cm<sup>3</sup> (in BZ arrangement) against the estimation of 3.81, 3.52 and 3.78 g/cm<sup>3</sup> for immaculate WO<sub>3</sub>, BaTiO<sub>3</sub> and ZnO films, separately any remaining pattern figures appeared in later pages of this section, the focuses left detached in pattern plots have a place with perceptions recorded with unblemished examples. The bi-layered movies are marginally denser contrasted with the unblemished examples of the particular oxides associated with their union. This as a chance can't be precluded in the current case also [Beena et al, 2019; Paudel et al., 2018; Lahmer et al., 2016]. Seen in-situ electrical resistivity of perfect examples was in the request, BaTiO<sub>3</sub> (2.10 k $\omega$  cm) > ZnO (1.37 k $\omega$  cm) > WO<sub>3</sub> (0.93 k $\omega$  cm). Further with increment in thickness of ZnO over layer, resistivity diminished, arrived at the most reduced an incentive at a halfway thickness and expanded from that point. From the PEC current (I) values, recorded under obscurity and light, variety in photocurrent thickness (I<sub>ph</sub> = I<sub>illumination</sub> – I<sub>darkness</sub>) with applied potential were investigated. Open circuit potential (V<sub>oc</sub>) and short out current (I<sub>sc</sub>), under light, were additionally decided from 129 relating I-V plots. Further, in light of the I<sub>ph</sub> information, the Applied Bias Photon-to-Current Efficiency (ABPE) of PEC cell was assessed [Liu et. al., 2017; Ikram et. al., 2019; Sharma et. al., 2015; Kumari et. al., 2015]. Proposing a very much framed consumption layer, with all the examples the dim current remained just about zero till the break-point.

## **REFERENCES**

- [1]. Abd-Elkader M and Deraz N M (2015), Synthesis and characterization of new copper based nanocomposite, Int. J. Electrochem. Sci., 8, pp. 8614-8622.

- [2]. Bak T, Nowotny J, Rekas M and Sorrell C C (2018), Photo-electrochemical hydrogen generation from water using solar energy, Materials-related aspects, *Int. J. of Hydrogen Energ.*, 27, pp. 991-1022.
- [3]. Cao L, Yuan J, Chen M, Shangguan W (2019), Photocatalytic energy storage ability of TiO<sub>2</sub>-WO<sub>3</sub> composite prepared by wet-chemical technique, *J. of Environ Sci.*, 22, pp. 454- 459.
- [4]. Dang T C, Pham D L, Le H C and Pham, V H (2015), TiO<sub>2</sub>/CdS nanocomposite films: fabrication, characterization, electronic and optical properties, *Adv. in Natural Sciences: Nanosci. and Nanotech.*, 1, pp. 015002.
- [5]. Edwards P P, Kuznetsov V L, David W I and Brandon N P (2018), Hydrogen and fuel cells: towards a sustainable energy future, *Energy policy*, 36, pp. 4356-4362.
- [6]. Fichou D, Pouliquen J, Kossanyi J, Jakani M, Campet G and Claverie J (2015), Extension of the photoresponse of semiconducting zinc oxide electrodes by 3dimpurities absorbing in the visible region of the solar spectrum, *J. of electroanalytical chem. and interfacial electrochem.*, 188, pp. 167-168.
- [7]. Getoff N (2017), Basic problems of photochemical and photoelectrochemical hydrogen production from water, *Int. J. Hydrogen Energ.*, 9, pp. 997-1004.
- [8]. Heller A (2016), Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells, *Acc. Chem. Res.*, 14, pp. 154-62.
- [9]. Ikram A, Sahai S, Rai S, Dass S, Shrivastav R and Satsangi V R (2017), Synergistic effect of CdSe quantum dots on photoelectrochemical response of electrodeposited  $\alpha$ Fe<sub>2</sub>O<sub>3</sub> films, *J. of Power Sources*, 267, pp. 664-672.
- [10]. Jiao Z, Chen T, Xiong J, Wang T, Lu G, Ye J and Yingpu B (2018), Visible light driven photoelectrochemical and photocatalytic performances of Cr-doped SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructured nanotube arrays, *Sci. Rep.*, 3.
- [11]. Kaiser B, Fertig D, Ziegler J, Klett J, Hoch S and Jaegermann W (2019), Solar Hydrogen Generation with Wide-Band-Gap Semiconductors: GaP (100) Photoelectrodes and Surface Modification, *Chem. Phys. Chem.*, 13, pp. 3053-3060.
- [12]. Sharma, Shailja (2016) <http://hdl.handle.net/10603/230164>, Department of Chemistry, Dayalbagh Educational Institute