Malaysian Catalysis-An International Journal

Malay. Catal. Int. J Vol 1 (2021) 26-35

OVERVIEW

Photoelectrochemical water splitting process using titanium dioxide photocatalyst: A brief overview

Chin Wei Lai*[a] Jenny Hui Foong Chau [a]

a. Nanotechnology and Catalysis Research Centre (NANOCAT), Level 3, Block A, Institute for Advanced Studies (IAS), University of Malaya (UM), 50603 Kuala Lumpur, Malaysia

Received 28th June 2021,
Accepted 27th Sept 2021

DOI: 10.22452/mcij.vol1no1.3

Corresponding author:
cwlai@um.edu.my

Abstract

Hydrogen (H_2) has proved itself as a viable future energy carrier and alternative for fossil fuel in terms of ensuring a clean and sustainable energy supply. However, H_2 must be made available at a lower cost so that everyone can benefit from it and prevent causing a worldwide ecological imbalance. The usage of photoelectrochemical water splitting (PEC) technology by using TiO_2 photocatalyst can produce H_2 using renewable solar energy. The essential milestones, as well as the mechanism in PEC H_2 generation, are discussed in this article.

Keywords: Photoelectrochemical cell, Solar illumination, Water splitting

1. Introduction

Nowadays, a variety of environmental problems affect our world. The increased growth in human population and industrial development has resulted in the generation of various waste products and high consumption of energy. As a result, developing a continuous, renewable, and clean energy supply to protect the environment by reducing pollution emissions is the most pressing concern for human civilization. H2 is now widely regarded as an ideal future energy carrier [1], [2]. The energy yield of H2 is approximate 122 kJ/g which this provided energy is larger than the energy provided by conventional hydrocarbon fossil fuels combustion [3]. Besides, the process to provide energy through H_2 combustion is environmental friendly due to the harmless end product of H_2O [4]. H_2 can be generated through various methods using different raw materials, including fossil fuels and biomass [3], [5]. However, these methods contribute to problems such as energy depletion, environmental pollution, production of unwanted CO_2, the need for huge electrical consumption, and low efficiency of H_2 production [3], [5], [6]. Therefore, a suitable method must be invented to resolve all the disadvantages.

Solar energy is the largest, clean, renewable, and free energy source accessible throughout the world providing up to 1.2 x 10^{14} kJ of energy per second [7-8]. The amount of solar energy reaching our planet is approximately 100000 TW of which 36000 TW reaches land surface each year [9]. PEC water splitting is one of the most widely used techniques that use sunlight energy to separate water molecules into H_2 and oxygen (O_2) molecules ($2H_2O \rightarrow 2H_2 + O_2$) and thus reduce electrical energy consumption [8-10]. This technique is effective and environment friendly to make it the most promising method for H_2 production so far. In this method, H_2 and O_2 are going to be generated at two separated photoelectrodes, anode and cathode, respectively. Large varieties of semiconductor (metal oxide) materials are used as photocatalysts in the PEC water splitting process. Photocatalysts activated by solar irradiation produce photogenerated electrons and holes, and they will react with water to generate H_2 and O_2 effectively [1], [9].

In this article, some of the early studies in heterogeneous photocatalysis start from solar photovoltaic to the solar H_2 in PEC water splitting cell will be reviewed. The development of a TiO_2 semiconductor photocatalyst capable of producing H_2 efficiently through both the PEC cell and light activation will be reviewed.

2. Historical overview of PEC application

As the demand for alternative energy sources grows worldwide, there is an increasing interest in cost-effective, conveniently produced energy sources with excellent performance. Alexandre Edmond Becquerel's early experiment based on photocatalysis was published in 1839 [11]. He discovered that an electrode made of silver chloride (AgCl) coupled to a counter electrode immersed in an aqueous electrolyte creates an electrical current and voltage during solar light irradiation. The discovery of capturing solar energy and turning it to electrical power sparked a slew of new ideas for scientists and academics looking for alternate energy sources. The photoelectric effect was then applied to a device for the first time in 1883 by Charles Fritts, who created a gold and selenium n-p junction device with a 1 percent efficiency [12]. There was a scarcity of information about heterogeneous photocatalysis in the early twentieth century.

Bell Laboratories published and reported the first p-n junction solar cell design in 1954, with a 6 percent efficiency [13]. Bell Labs' breakthrough resulted in the first commercially practical solar cell and revolutionized the photovoltaic industry. Improvements have been made to make photovoltaic more accessible in the global market. Solid-state junction devices built of silicon have

dominated the conversion of solar energy to electrical power. The most significant disadvantage of photovoltaics is that it does not work when the sun is not strong or in bad weather. As a result, energy storage is critical, which can be accomplished by creating H_2 and storing the energy as chemical energy in H_2. The stored energy is then can be released as electrical energy when needed. PEC cells have typically relied on nanocrystal structure materials. The nanostructure material is having many advantages such as high current generation efficiency, low cost, and chemical stability [14].

In 1972, Fujishima and Honda discovered the PEC H_2 production using TiO_2 electrodes [15-17]. Because crude oil prices had abruptly risen and a future shortage of crude oil was a real issue, this event heralded the start of a new era in heterogeneous photocatalysis. As a result, scientific interests in semiconductor photocatalysis based on TiO_2 photocatalyst have grown significantly. To have a better understanding of the fundamental mechanisms and to improve the photocatalytic effectiveness of TiO_2, research works have been published. TiO_2 has emerged as the top candidate for PEC cells due to characteristics such as non-toxicity, low cost, excellent stability against photo-corrosion, potent photocatalytic activity, and self-cleaning ability [16-18].

In the early 1980s, TiO_2 in different forms such as solution suspension and solid photoelectrode was used to generate H_2 through the PEC cell. However, this system has several flaws such as the appearance of trapping sites, long travel distances, and disordered contact areas between two particles or spheres. Therefore, the electron transporting time in the TiO_2 bulk phase is relatively long, resulting in the scattering of free electrons with lower mobility. These drawbacks reduce the performance of PEC cells. Other than that, an appropriate substrate is needed to support the particles or spheres in the PEC system and a filtration process might be needed after using them [17], [19].

In the early 1990s, TiO_2 thin film photocatalyst was created in the PEC application because it provides a more resilient and cost-effective solution by removing the issues mentioned above and being reusable in the PEC application. However, thin-film photocatalysts do not have a significantly large surface area [20]. To achieve optimum overall efficiency without increasing the geometric area, it is critical to maximizing the active sites of TiO_2 thin films. Advanced geometries of TiO_2 thin films have recently garnered much attention, especially nanostructured TiO_2, which has a large surface area (active sites) for photon absorption in PEC application [17].

Zwiling and co-researchers reported the first generation of self-organized porous TiO_2 by anodizing Ti foil in chromic acid electrolytes containing hydrofluoric acid (HF) in 1999 [16]. Gong and his research team later constructed self-organized TiO_2 nanotubes arrays with excellent uniformity by anodizing Ti in an aqueous dilute HF electrolyte in 2001. The maximum nanotube lengths were approximately 500 nm. One-dimensional (1D) nanostructured TiO_2 film can be simply removed and replaced after the photocatalytic process. Therefore, 1D nanostructured TiO_2 film is used in photoreactors for cost-effective purposes. Various methodologies such as hydrothermal, sol-gel, and anodization can be used to create 1D TiO_2 nanostructures [16], [21–23].

TiO_2 nanotubes have recently been identified as a possible building element for a new generation of nanoscale devices. Self-organized TiO_2 nanotube arrays bring much attention, not only because of their variable band gap due to the quantum confinement effect but also because of their larger surface area which allows for more photon absorption [15], [17]. However, a suitable method to produce nanotubes arrays must be researched and different effects such as wall thickness, length, pore width, and intertube spacing must be optimized to obtain preferred dimensions and morphologies. Many researchers have found that highly ordered TiO_2 nanotubes are superior and highly efficient in PEC responses due to their higher surface area allows for better light scattering and thus more electron generation [17]. The improvement of charge transport favors PEC features that improve photocurrent resulting in more efficient H_2 generation. As a result, TiO_2 nanotubes have been proved to be a stable photocatalyst or semiconductor for efficient light absorption in water photo-electrolysis reactions.

3. Principle and mechanism of PEC water splitting

The main components of PEC water splitting device are made up of semiconductor photoelectrodes which can absorb light, electrolyte, and separation membrane. There are three main processes involved in a complete PEC water splitting process. The first process is light absorption by semiconductor photoelectrode. Different semiconductors are having different band gap energies. Band gap reading is the difference between the valence band (highest occupied molecular orbital) and conduction band (lowest unoccupied molecular orbital) of the semiconductor [9]. A pair of charge carriers is generated when the semiconductor material received photons (from sunlight irradiation) with energies larger than its band gap energy. Excited

electrons located in the valence band will tend to move to the conduction band and leaving holes in the valence band. In the water splitting process, the valence band potential of the semiconductor must be positive than the O_2/H_2O redox potential of 1.23 V vs. NHE (pH = 0) and the conduction band potential must be more negative than the H^+/H_2 redox potential of 0 V vs. NHE to carry out water oxidation and reduction reactions respectively [9], [10], [16].

The second process is the separation and transportation of photoexcited charge carriers. The third process is the redox reactions of water splitting. Fig. 1 demonstrates the set-up of a simple PEC device (type I) based on n-type semiconductor as the photoanode where (I) to (III) represent first to third processes. In this type, I PEC device, a single semiconductor can be used either as a photoanode or photocathode to carry out water oxidation or reduction process.

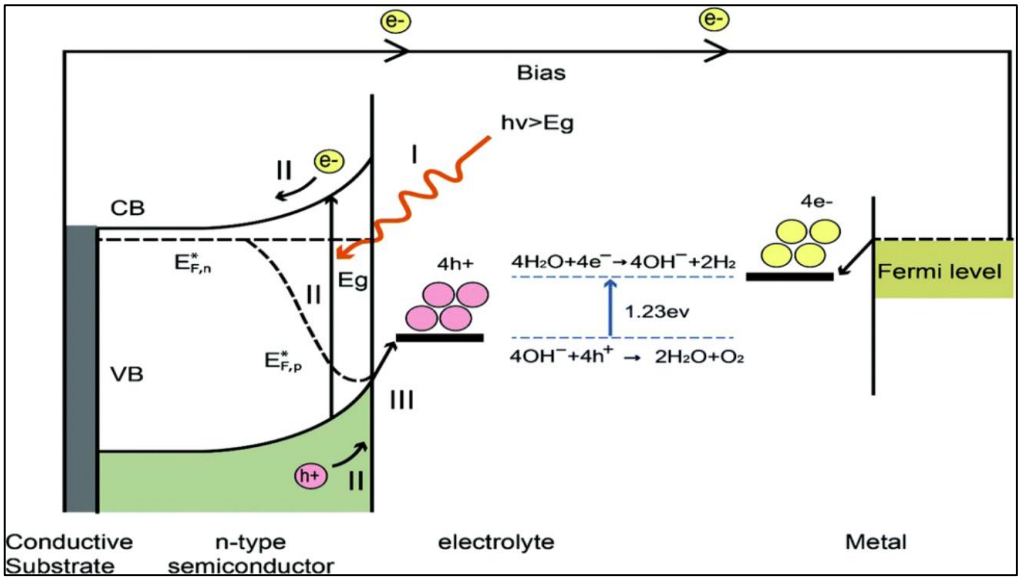

Fig. 1 Type I PEC cell with n-type semiconductor as photoanode and metal as the counter electrode. Reproduced from [9] with permission from the Royal Society of Chemistry.

Metal oxide has gotten much attention in PEC water splitting process due to benefits including chemical and physical stability, low cost, easy accessibility, wide varieties, etc. [10]. Despite all the advantages, the problems of weak electrical characteristics, large band gap reading, fast photogenerated electron, and holes recombination need to be solved to enhance the H_2 production in the water splitting process [18], [24]. Fig. 2 demonstrates different semiconductors together with their valence and conduction band edge readings. Band positions of the semiconductor depend on the pH of the electrolyte. It is important to research a low cost, efficient, high stability,

non-toxic, and easy to access material for PEC water splitting process. The suitable semiconductor used in the PEC systems must have four essential characteristics as shown below [9], [16-18]:

i. Photochemical stability:

   The material must be stable in an aqueous solution to avoid photo-corrosion during the photo-electrolysis reaction. Photo-corrosion occurs when the photoexcited charge carrier does not carry out water oxidation or reduction but instead decomposes the photocatalyst itself. Semiconductors such as zinc oxide, molybdenum disulfide, and bismuth vanadate are undergoing photo-corrosion easily.

ii. Band gap:

   Sunlight is made up of approximately 5% of UV light (wavelength of 300 to 400 nm), 43% of visible light (wavelength of 400 to 700 nm), and infrared radiation (wavelength of 700 to 2500 nm). Thus, the light absorption of the semiconductor must be within the visible region to enhance the efficiency of water splitting. The theoretical minimum band gap energy for PEC water splitting process is 1.23 eV (light absorption around the wavelength of 1100 nm) due to the O_2/H_2O redox potential as mentioned before. Besides, the possibility of both the thermodynamic energy losses during charge carrier transportation and overpotential requirement for surface reaction kinetics must be considered to evaluate suitable band gap energy reading. Thus, the semiconductor candidate must display a band gap energy of more than 1.8 eV (light absorption around 700 nm). The band gap reading should not be more than 3.2 eV due to the possibility of low sunlight intensity for wavelength under 390 nm considering the possibility of overpotential losses and the initial energy required to begin the water splitting reaction.

iii. Charge carrier separation and transportation

   The fast recombination rate of the charge carrier affects the water splitting efficiency. A study carried out by researchers shows that approximately 60-90% of photoexcited electrons recombine with holes within 10 ns.

iv. Energy level:

   The reduction and oxidation potential of the photocatalyst must lie between the conduction and valence band edges for the immediate water splitting reaction.

TiO_2, as mentioned in the previous section is widely used in this application due to its distinctive characteristics [18]. Fig. 3 displays the layout of a simple PEC water splitting set-up using TiO_2

photoanode and platinum photocathode. In Fig. 3, when TiO_2 is irradiated with light energy larger than its band gap energy, charge carriers are formed. The exciting form of electrons produced by TiO_2 will travel through the circuit towards the platinum electrode and undergoes a reduction process to synthesize H_2 while holes carry out an oxidation process to form O_2 [2], [16], [18]. The overall process is shown in Eq 1 to 3 as follow:

$$TiO_2 + 2\,h\nu \rightarrow TiO_2 + 2e^- + 2h^+ \quad (1)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

However, TiO_2 can only absorb UV light due to its large band gap reading (approximate 3.2 eV for anatase and 3.0 eV for rutile phase). Besides, the fast recombination rate of photoexcited electron-hole pairs also affects their water splitting efficiency [15], [18]. Today, methods including doping with other metal or non-metal materials [25]–[29] and formation of binary [30], ternary [31], quaternary composite heterostructures [32] have been reported in numerous publications to promote more efficient charge separation, longer charge carrier lifetimes, and improved interfacial charge transfer in TiO_2. Furthermore, the recombination rate of electron-hole pairs can be enhanced by constructing a TiO_2 heterojunction photoanode [31]. Furthermore, the formation of this structure also improves the efficiencies of both the surface reaction kinetics and photo-redox process [31].

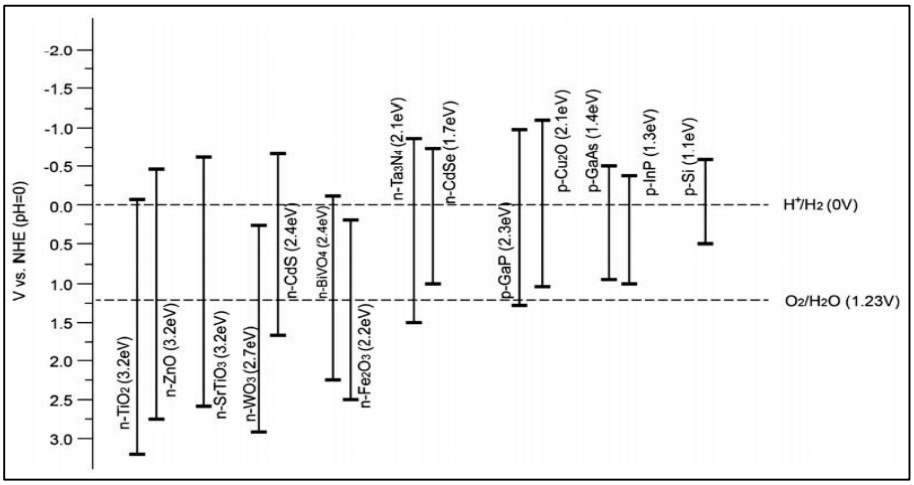

Fig. 2 Band positions of different semiconductors corresponding to the redox potential of water splitting at pH = 0. Reproduced from [9] with permission from the Royal Society of Chemistry.

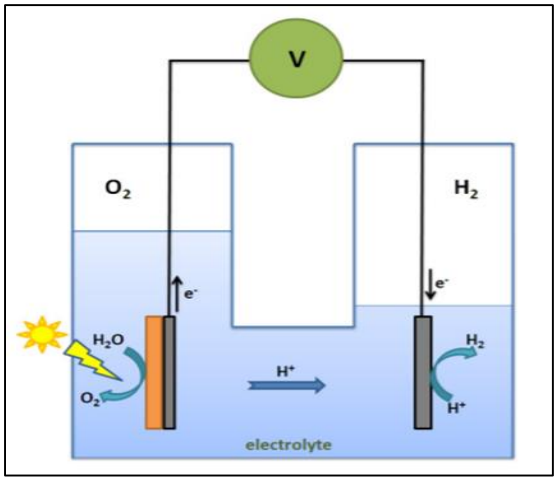

Fig. 3 PEC water splitting using TiO_2 photoanode and platinum photocathode. Reproduced with permission from [33].

4. Conclusion

All in all, this review sought to provide an overview of the metal oxide semiconductor in the PEC H_2 production application so that the reader may gain a better understanding of the historical context, basic fundamental investigations, and mechanism in PEC H_2 generation. TiO_2 photocatalyst can be used as the photoanode material in PEC cells to generate H_2 because of their distinctive characteristics such as low costs, chemically stability, long lifetime of charge carriers, powerful photocatalytic ability, high resistance towards photo-corrosion, and large surface area.

Acknowledgement

This research work was financially supported by Fundamental Research Grant Scheme FRGS/1/2020/TK0/UM/02/8 (No. FP023-2020), and Global Collaborative Programme – SATU Joint Research Scheme (No. ST004-2021).

References

1. Y. Zhang, Y. Bu, L. Wang, and J.-P. Ao, Regulation of the photogenerated carrier transfer process during photoelectrochemical water splitting: A review, Green Energy Environ. 2020, pp. 479-495

2. R. Singh and S. Dutta, A review on H_2 production through photocatalytic reactions using TiO_2/ TiO_2-assisted catalysts, Fuel, 2018, 220, pp. 607–620.

3. S. E. Hosseini and M. A. Wahid, Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development, Renew. Sustain. Energy Rev., 2016, 57, pp. 850–866.

4. C. Acar and I. Dincer, Review and evaluation of hydrogen production options for better environment, J. Clean. Prod., 2019, 218, pp. 835–849.

5. P. Nikolaidis and A. Poullikkas, A comparative overview of hydrogen production processes, Renew. Sustain. Energy Rev., 2017,67, pp. 597–611.

6. V. TD, M. TS, dos S. DDRM, and C. AD, Hydrogen: Trends, production and characterization of the main process worldwide, Int. J. Hydrogen Energy, 2017, 42(4), pp. 2018–2033.

7. I. Roger, M. A. Shipman, and M. D. Symes, Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting, Nat. Rev. Chem., 2017, 1(1), pp. 3.

8. R. Li *et al.*, Achieving overall water splitting using titanium dioxide-based photocatalysts of different phases, Energy Environ. Sci., 2015 8,(8), pp. 2377–2382.

9. C. R. Jiang, S. J. A. Moniz, A. Wang, T. Zhang, and J. Tang, Photoelectrochemical devices for solar water splitting – materials and challenges, Chem. Soc. Rev., 2017, 46(15), pp. 4645–4660.

10. N. Han et al., Perovskite and related oxide based electrodes for water splitting, J. Clean. Prod., 2021, 318, pp. 128544.

11. R. Michal, S. Sfaelou, and P. Lianos, Photocatalysis for renewable energy production using Photo Fuel Cells, Molecules, 2014, 19(12), pp. 19732–19750.

12. E. Kim, J. H. Park, and G. Han, Design of TiO2 nanotube array-based water-splitting reactor for hydrogen generation, J. Power Sources, 2008,184, pp. 284–287.

13. K. Yu and J. Chen, Enhancing Solar Cell Efficiencies through 1-D Nanostructures, Nanoscale Res. Lett., 2008, 4(1), pp. 1.

14. N. Baig, I. Kammakakam, and W. Falath, Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges, Mater. Adv., 2021,.2(6), pp. 1821–1871.

15. F. X. Xiao and B. Liu, Plasmon-dictated photo-electrochemical water splitting for solar-to-chemical energy conversion: Current status and future perspectives, Adv. Mater. Interfaces, 2018, 5, pp. 1701098.

16. Y. Zhao, N. Hoivik, and K. Wang, Recent advance on engineering titanium dioxide nanotubes for photochemical and photoelectrochemical water splitting, Nano Energy, 2016, 30, pp. 728–744,

17. Y. Lan, Y. Lu, and Z. Ren, Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications, Nano Energy, 2013, 2(5), pp. 1031–1045.

18. A. Gellé and A. Moores, Water splitting catalyzed by titanium dioxide decorated with plasmonic nanoparticles, Pure Appl. Chem., 2017, 89 (12), pp. 1817-1827.

19. M. Jefferson, Sustainable energy development: Performance and prospects, Renew. Energy,

2006, 31, pp. 571–582.

20. L. C. Escaliante, K. O. Rocha, and J. H. D. Silva, Stability of the photocatalytic activity of TiO2 deposited by reactive Sputtering, Mater. Res., 24(1).

21. J. Cabrera, H. Alarcón, A. López, R. Candal, D. Acosta, and J. Rodríguez, Synthesis, characterization and photocatalytic activity of 1D TiO_2 nanostructures, Water Sci. Technol., 2014, 70, pp. 972–979.

22. M. Ge et al., A review of one-dimensional TiO2 nanostructured materials for environmental and energy applications, J. Mater. Chem. A, 2016, 4(18), pp. 6772–6801.

23. Q. Zhang et al., Anodic Oxidation Synthesis of One-Dimensional TiO_2 Nanostructures for Photocatalytic and Field Emission Properties, J. Nanomater., 2014, pp. 831752.

24. H. Sudrajat et al., Origin of the overall water splitting activity over Rh/Cr_2O_3@ anatase TiO_2 following UV-pretreatment, Int. J. Hydrogen Energy, 2021, pp. 31228-31238.

25. J. Cai, M. Zhou, X. Xu, and X. Du, Stable boron and cobalt co-doped TiO2 nanotubes anode for efficient degradation of organic pollutants, J. Hazard. Mater., 2020, 396.

26. X. Hou et al., Enhanced photoelectrocatalytic degradation of organic pollutants using TiO2 nanotubes implanted with nitrogen ions, J. Mater. Sci., 2020, 55(14), pp. 5843–5860.

27. A. Zada et al., Improved visible-light activities for degrading pollutants on TiO2/g-C3N4 nanocomposites by decorating SPR Au nanoparticles and 2,4-dichlorophenol decomposition path, J. Hazard. Mater., 2018, 342, pp. 715–723.

28. M. Coto et al., Tuning the properties of a black TiO2-Ag visible light photocatalyst produced by a rapid one-pot chemical reduction, Mater. Today Chem., 2017, 4, pp. 142–149.

29. S. A. Ansari, M. M. Khan, M. O. Ansari, and M. H. Cho, Silver nanoparticles and defect-induced visible light photocatalytic and photoelectrochemical performance of Ag@m-TiO2 nanocomposite, Sol. Energy Mater. Sol. Cells, 2015, 141, pp. 162–170.

30. Z. N. Kayani, A. Kamran, Z. Saddiqe, S. Riaz, and S. Naseem, Probe of ZrTiO2 thin films with TiO2-ZrO2 binary oxides deposited by dip coating technique, J. Photochem. Photobiol. B Biol., 2018, 183, pp. 357–366.

31. X. Shi et al., Facile construction TiO2/ZnIn2S4/Zn0.4Ca0.6In2S4 ternary hetero-structure photo-anode with enhanced photoelectrochemical water-splitting performance, Surfaces and Interfaces, 2021, 26, pp. 101323.

32. S. S. M. Bhat et al., Substantially enhanced photoelectrochemical performance of TiO2 nanorods/CdS nanocrystals heterojunction photoanode decorated with MoS2 nanosheets, Appl. Catal. B Environ., 2019, pp. 118102.

33. C. H. Liao, C. W. Huang, and J. C. S. Wu, Hydrogen production from semiconductor-based photocatalysis via water splitting, Catalysts, 2012, 2(4), pp. 490–516.