

Recent studies on semiconducting material for photoelectrochemical hydrogen evolution under visible light irradiation

Md Nazmodduha Rafat and Won-Chun Oh*

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan-si, Chungnam, Korea

Abstract: Water splitting technology directly stores solar energy into the chemical bonds of diatomic hydrogen to be used as a clean fuel without producing any unwanted side reactions, byproducts or environmentally polluting compounds. Semiconductor materials are needed for a photo-electron chemical (PEC) device to catalytically convert photons from sunlight into chemical energy. Materials implemented in a device for sustainable hydrogen production are required to be inexpensive, highly photo-active, chemically stable, environmentally sustainable, and have a high solar-to-hydrogen conversion efficiency. Although many semiconductor composites and nanostructures have been examined, thus far, no material satisfies all criteria of an implementable photocatalyst and many materials do not show necessary energy conversion efficiency. Materials that depicted a high efficiency often rely on the ultraviolet portion of the solar spectrum, which does not contain enough energy for the industrial utilization of PEC water splitting technologies. Focusing on the use of the visible spectrum is promising for hydrogen production. Herein, recent advancements in the activity of visible light semiconductors are presented, including both platinum and non-platinum group materials. This review touches on the latest developments in various synthesis schemes capable of achieving suitable water splitting compositions and architectures while highlighting the challenges being faced when designing visible light-active water splitting photocatalysts. Interesting advancements in the use of nanostructures for designing the next generation of catalysts will be discussed. Also, for the proper comparison of catalytic efficiencies, it is important to establish terminology that can compare data across a magnitude of experimental conditions. A notable challenge associated with the catalysis is its stability or photo corrosion, which lacks established protocols. Promising future directions for designing next generation materials are discussed.

Keyword: Water splitting, photocatalyst, Semiconductor, hydrogen, visible light

Introduction

The energy crisis in the mid-1970s triggered a worldwide research enthusiasm for the expansion of renewable energy resources to replace conventional fossil fuels. Recently, increasing CO₂ levels and atmospheric pollution have led to the development of several clean energy resources, including solar, wind, geothermal, tidal, etc. With an increase

* Corresponding author: wc_oh@hanseo.ac.kr

in the population and industrialization, the global energy demand increases with each passing day, further leading to the depletion of fossil fuels. Simultaneously the concentration of greenhouse gases in the atmosphere is increasing daily resulting from the burning of fossil fuels to meet ever-growing energy demands. Greenhouse-gas emissions from the energy sector represent roughly two-thirds of all anthropogenic greenhouse-gas emissions, which have steadily risen over the past century. Solar energy via sunlight is one of the most promising alternative energy resources that can replace fossil fuels and fulfill the rising global energy demand. For example, the total energy consumption of the world projected for the entire year of 2020 is approximated to be 663.6 joules, Equivalent to all of the energy from sunlight striking the Earth for just 90 min (given that the average energy rate of sunlight striking the surface of the Earth is ca. 1,200,000 TW) [1]. Hydrogen production from sunlight and water is being considered as a promising solution to supply sustainable energy; it is environmentally clean and can act as a suitable buffer between energy supply and demand. Based on the solar harvesting technology utilized, solar hydrogen production methods can be generally categorized (Fig. 1) as: (a) solar photocatalytic water splitting: utilizes photo-active electrodes, particles, or photovoltaic cells made of semiconductors or semiconductor composites to split water with and without an external bias, (b) electrolysis of water: utilizes electricity to split water with a high energy-conversion efficiency, (c) thermochemical water splitting: utilizes concentrated solar energy to split water at very high temperatures, and (d) photo-biological hydrogen production: utilizes solar hydrogen-producing enzymes (still in an initial laboratory-scale phase) [3]. Presently, electrochemical solar cells that convert solar energy into hydrogen have high fabrication costs, insufficient light absorption, and/or inefficient catalytic charge transfer [4–6]. For the focus of this work, solar photocatalytic water splitting can be divided into three subcategories (Fig. 1): photovoltaic (PV) electrolysis, photocatalysis, and photoelectrochemical (PEC) water splitting; these three subcategories are often interchanged. PV electrolyzes have the photo-absorber isolated from the electrochemical cell where non-photo-active electrodes facilitate water splitting. Photocatalyst systems are typically photo-active particle suspensions or immobilized monoliths where each particle facilitates both the redox and oxidation reactions. PEC water splitting is where one or more photo-active electrodes perform reactions in an electrochemical cell. Though these technologies each may vary, many of the material science properties of the semiconductors and electrodes/particles are similar. In general, PEC water splitting is promising, however the reported solar-to-hydrogen (STH) conversion efficiencies are still considered low for practical use [7, 8]. To address these challenges, intense efforts to design more active photocatalysts and intricate systems are underway [9–11]. A cohesive review of recent advancements is provided herein, including photo-active composites. In addition, recent improvements and advancements are also examined for promising semiconductor compositions. Finally, efficiency calculation methods and meanings found in other work are provided, so that a universal rational for material stability and performance can be achieved for comparison of emerging water splitting catalysts.

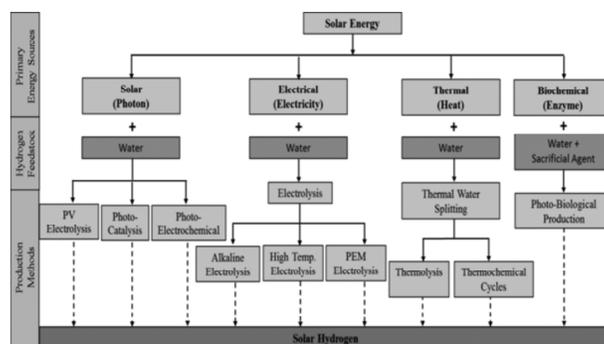


Fig. 1. Classification of solar hydrogen production methods

Photocatalytic water splitting was first demonstrated by Fujishima and Honda in 1972 utilizing TiO_2 electrodes under ultraviolet (UV) irradiation [14]. Later, in 1975, Yoneyama et al. [15] experimentally established that a p-GaP/n-TiO₂ tandem combination could generate H₂ and O₂ without an external bias. Bard [16] used this concept for the design of a photocatalytic water splitting system with suspended semiconductor particles. In the last four decades there has been an upsurge of interest in solar hydrogen production [3, 6, 17–19]. In 1998, Khaselev and Turner [20] developed a PEC water splitting system that combined the harvesting of solar energy and the electrolysis of water into a single device with a solar-to-hydrogen conversion efficiency of 12.4%. Despite a large amount of research activity over the last few decades, water splitting is still a main focus in modern research to this day due to technical complexities involved in the overall process to reach sufficient ST efficiencies and stability goals set by the Department of Energy (USA).

Pt/SrTiO ₃ :Rh, WO ₃	0.1g	2 mM FeCl ₃	300 W Xe with filter $\lambda > 420 \text{ nm}$	7.8	4.0	[60]
K ₄ Nb ₆ O ₁₇	1g	H ₂ O	450 W Hg lamp	8	1	[64]
NiO/K ₄ Nb ₆ O ₁₇	1g	H ₂ O	450 W Hg lamp	77	37	[64]
Pt/SrTiO ₃ :Rh, WO ₃	0.3g	2 mM FeCl ₂ /FeCl ₃	500 W halogen lamp	1.6	0.8	[69]
$\Gamma\text{u}/\text{SrTiO}_3\text{:Rh}$, BiVO ₄	0.4g	5 mM FeCl ₂ /FeCl ₃	300 W Xe lamp	0.8	0.4	[70]

Table 1. Various semiconductor photocatalysts used in water splitting for hydrogen production.

Semiconductor materials are suited for solar water splitting due to their ability to absorb incident photons and convert them into free electrons (i.e., electrochemical energy). A material will absorb a photon with an energy greater than or equal to its band gap, exciting an electron from the valence band (VB) to the conduction band (CB) forming an excited electron-hole (e⁻ and h⁺, respectively) pair. The photo-generated e⁻ and h⁺ reduce protons (H⁺) to H₂ and oxidize H₂O to O₂. In general, the difference between the two redox potentials of the VB and CB of the semiconductor must be equal to the

minimum photon energy thermodynamically required for the overall water splitting reaction. Therefore, for a material to facilitate water splitting, its band gap must exceed 1.23 eV and the corresponding band edges must straddle the redox potentials of 0 and 1.23 eV [21]. In particular, the hydrogen evolution reaction (HER) potential must be more negative than 0 VRHE (or NHE at pH 0, determined by the redox potential of a platinum electrode for the hydrogen half reaction) and the oxygen evolution reaction (OER) potential must be more positive than 1.23 VRHE (Fig. 2A) [22,23]. The photon energy of 1.23 V or greater is equivalent to the wavelength of 1008 nm or less (from the Planck-Einstein relation), indicating that a large portion of photons in the solar spectrum (Fig. 2B) have sufficient energy needed to split water. However, owing to the transparent nature of water in the UV-visible range (ca. 390–800 nm), auto photolysis of water can only be accomplished with wavelengths shorter than 190 nm. A semiconductor that utilizes wavelengths less than 390 nm (UV light) can only achieve a maximum solar conversion efficiency (SCE) of 2%, whereas the SCE is raised to 16% when a semiconductor utilizes wavelengths ≤ 600 nm [22]. For this reason, solar water splitting under visible light irradiation has been of great interest since the discovery of the Honda-Fujishima effect [14]. In practice, the redox potential for water splitting is commonly greater than 1.6 V, arising from the additional energy needed to overcome the kinetic barriers of each half reaction, mainly associated with activating the OER. The additional potential needed for water splitting compared to the theoretical value of 1.23 V is referred to as an “over potential.” Every element, material and phase has a specific over-potential [24]. Morphology also plays a predominant role in light adsorption, the accessibility of electrons/holes on the surface and diffusion of electrons/holes to the surface.

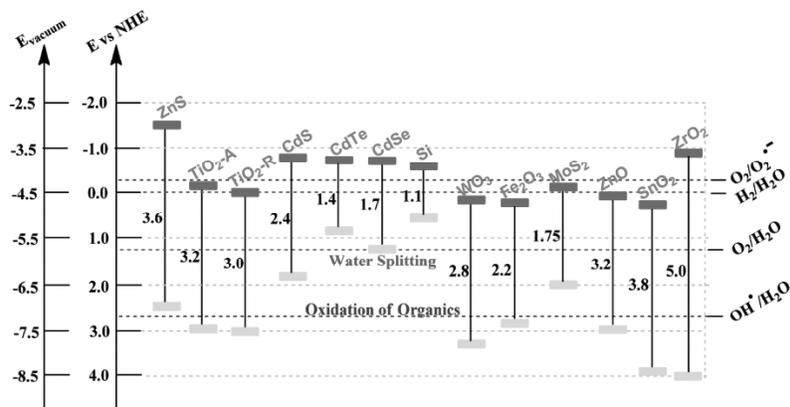


Fig. 2. The band gaps and band edges of semiconductor materials with respect to the vacuum level and NHE.

Experimental description

Many semiconductor materials, such as TiO_2 , WO_3 , CdS , Ta_2O_5 , BiVO_4 , etc., have been extensively studied due to their suitable band gap, stability and effective response for H_2

production under solar irradiation. TiO₂ is the most widely explored photocatalyst due to its global availability, low toxicity, stability and near-visible light photocatalytic activity [26]. The redox potential criterion eliminates semiconductor materials from consideration whose band gap structure does not match the water splitting redox potentials, unless modified. Fig. 2 shows a number of recently examined semiconductor material band gaps and band edge positions compared to the water splitting half reaction redox potentials.

Photocatalytic hydrogen production studies were implemented in a Lab Solar-III system with a top-irradiation reaction vessel in a closed gas-circulation system. The visible light source was provided by a 300 W Xe -lamp (CEL-HXF300) with 420 nm cutoff filter, and the light intensity was measured as 100 m W/cm². The photocatalysts (30 mg) were added to a mixture solution with water (90 mL) and methanol (10 mL), among them, methanol as a sacrificial agent [158]. Prior to their radiation experiments, the reactant solution was evacuated for several times to remove air. During the irradiation process, the reaction temperature was maintained at 15 °C. Gas chromatography (GC3420A) equipped with a TCD detector and 5 Å molecular sieve column was used to analyze the evolved gas. The cycling test of photocatalytic H₂-evolution followed the above-mentioned method except that after 4 h reaction, the system was degassed and then performed the H₂generation reaction again. The photocurrent measurements were carried out on a CHI660E electrochemical system. The working electrode was prepared as following: (1) dispersing 2 mg photocatalyst in 200 μ L Nafion solution (5%) to form the coating suspension; (2) coating ITO glass with 100 μ L suspension and drying at room temperature. A standard three-electrode system with the as-prepared electrode as working electrode, Pt sheet as counter electrode and saturated calomel electrode (SCE) as reference electrode. In the photocurrent testing process, a 300 W Xe lamp (CEL-HXF300) with a 420 nm filter was used as light source to irradiate from the opposite side of the working electrode. 0.1 mol/L Na₂SO₄ aqueous solution was used as the electrolyte. To overcome cost and material supply constraints, PGM free catalysts are highly desirable and many research groups are working on the development of non-platinum group metal (NPGM) catalysts using elements such as Ti, Ni, Mo, Cu, Co, Zn, Ga, In, Bi, Ge, Sn, Si, N, C and B [130]. The core limitation of NPGM catalysts is that their activity is considerably lower than that of PGM, for which various approaches including innovative preparation methods, co-doping, Z schemes, precise morphology control and surface treatments are being utilized. The four most promising NPGM metals (Ti, Ni, Cu and Zn) based on the recent volume of literature and the ascribed photoactivity are presented herein. Since photocatalysis is a surface phenomenon; therefore, the properties of TiO₂ nanoparticles including crystal size, morphology, crystalline phase, specific surface area, pore size and pore volume influence its photocatalytic performance. TiO₂ has become most widely used photocatalyst due to its high photocatalytic efficiency, enhanced biological and chemical stability, environmental friendliness, non-toxicity, economical and corrosion resistance. Many semiconductor materials, such as TiO₂, WO₃, CdS, Ta₂O₅, BiVO₄, etc., have been extensively studied due to their suitable band gap,

stability and effective response for H₂ production under solar irradiation, as shown in Table 1 [25]. In particular, the hydrogen evolution reaction (HER) potential must be more negative than 0 VRHE (or NHE at pH 0, determined by the redox potential of a platinum electrode for the hydrogen half reaction) and the oxygen evolution reaction (OER) potential must be more positive than 1.23 VRHE (Fig. 3 A,B) [22,23].

The properties of a material significantly depend on the experimental conditions and their method of synthesis. TiO₂ is wide band gap transitional metal oxide. TiO₂ crystallizes in a large number of polymorphs. Besides these, TiO₂ exists in three well-known crystalline polymorphs in order of abundance as Rutile, Anatase and Brookite with band gaps (E_g) of 3.02, 3.2, and 2.96 eV, respectively. However, only anatase and rutile can be synthesized at low temperature in pure form. Many significant re-searches have been done on the synthesis and photocatalytic application of both anatase and rutile phases whereas, very few studies have been reported regarding the synthesis of brookite phase. It has been examined that it is very difficult to prepare brookite phase with high purity and large surface area leading to its limited application as compared to the anatase and rutile phases. The structure of brookite form of TiO₂ was found by Pauling and Sturdivant in 1928 having the highest oxidation potential (Š0.46 V) as compared to anatase (Š0.45 V) and rutile (Š0.37 V) phases. Rutile is considered as the most stable phase of TiO₂, whereas anatase and brookite are metastable and can be transformed to rutile phase by providing proper heat treatment. The sol-gel derived TiO₂ typically remains in the anatase phase, but brookite is often observed at low temperature in an acidic medium as a by-product. Heat treatment in terms of calcination time and temperature have a major contribution in the synthesis of photocatalysts by significantly influencing their surface area, morphology, crystallinity, porosity, surface hydroxyl groups and phase transformations. Literature review reveals that the nanomaterials give better H₂ production compared to micro materials. However, all the nano sized photocatalysts are not suitable for effective hydrogen generation due to their insufficient redox potential required for the same.

Results and discussion

Platinum (Pt) is the most widely reported co-catalyst for H₂ evolution photocathodes due to its fast electron trapping from the semiconductor CB which improves visible light photo-activity [147]. For example, platinized TiO₂ has been used as a photocatalyst for a variety of reactions including HER [150]. A Pt doped TiO₂ photocatalyst produced 11.7 μmol h⁻¹ g⁻¹ hydrogen in the presence of iodate/iodide (IO₃⁻/I⁻) under visible light (> 420 nm) [151]. A Pt loading of 1 wt% on rutile TiO₂ nanoparticles (< 10 nm) gave hydrogen production of 932 μmol h⁻¹ g⁻¹ under visible light illumination and 1954 μmol h⁻¹ g⁻¹ under the full solar spectrum [152]. This high activity is attributed to the effective transfer of photoelectrons from TiO₂ to Pt clusters where chemically dissociated H⁺ ions are adsorbed to generate hydrogen. In another work, the addition of Pt on g-C₃N₄ significantly enhanced the hydrogen evolution rate without using a sacrificial agent [153]. Pt deposited C-HS-TiO₂ hollow sphere exhibited a superior activity and produced

a higher yield of hydrogen ($2857 \mu\text{mol h}^{-1}$) with excellent long-term stability under visible light irradiation (22 days) [154]. Kahn et al. [155] investigated that Pt- and Ir-ionized titanium nanotubes synthesized via an ion-exchange process are effective photocatalysts in the production of stoichiometric H_2 , where Pt and Ir ionization reduced the band gap energy correlating to a visible photo response. According to Bamwenda et al. [156], Pt provides a better trapping site for photoelectrons than Au and showed a better activity towards H_2 generation. In another study, Hara and coworker [157] doped Ru, Rh, and Ir on SrTiO_3 loaded with Pt co-catalysts and observed a visible light response due to the formation of an electron donor level from the Rh ions adding to the conduction band composed of Ti 3d orbitals. Furthermore, Moriya et al. [158] reported that the layered deposition of modified Pt on a CuGaSe_2 semiconductor material exhibited a remarkable PEC performance and stability compared to pristine CuGaSe_2 . A parallel study conducted by Manikandan et al. [48], confirmed the influence of Pt co-catalyst on the catalytic performance of Sn_3O_4 , where the modified catalyst produced $5 \mu\text{mol h}^{-1}$ hydrogen under visible light illumination with more than 96 h stability. Further details on Pt co-catalyst semiconductor materials and their hydrogen production rates are reported in Table 1.

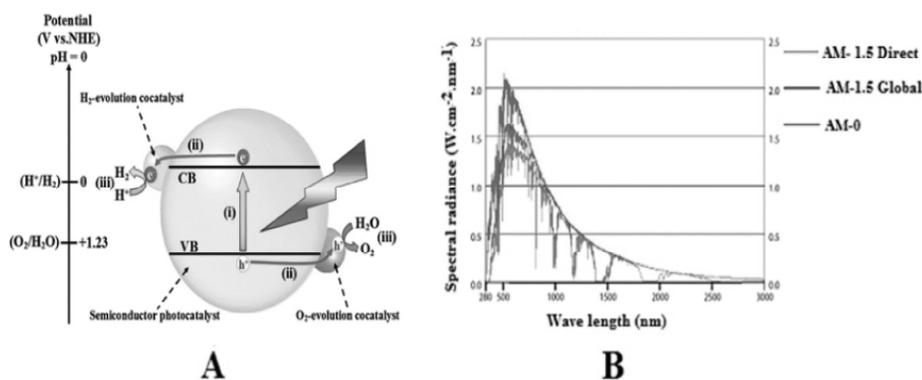


Fig. 3. (A) Schematic of a semiconductor band diagram, and (B) the solar spectrum at different 'Air Mass (AM)' ratios. [23]

TiO_2 is the most studied photocatalyst since the first articles published on PEC water splitting in 1972 [14]. TiO_2 , an n-type semiconductor, is undoubtedly one of the most important photocatalysts due to its high photostability, low cost, and non-toxicity. Due to its excellent photo-chemical stability, in both acidic and basic media, TiO_2 has also been utilized as a protection or passivation layer for photo electrodes [26]. Particle size, the degree of aggregation and the surface area determine the substrate adsorption ability of TiO_2 . Due to a high surface area, fast charge transport and crystallite alignment, mesoporous TiO_2 films and arrays with ordered structures greatly enhanced photocatalytic activity for PEC water splitting. Kavan et al. reported the first anodic deposition condition for TiO_2 from acidic TiCl_3 solutions at pH 1.5–3.1. Recently, Xu et al. [178] reported that Au-modified branched TiO_2 nanorod arrays, synthesized via hydrothermal and followed by a photo-reduction treatment, exhibited an enhanced

photocurrent density of 2.5 mA/cm² at 1.23 VRHE, due to the synergistic effect of a branched TiO₂ structure and a surface plasmon resonance (Fig. 4). Modifying TiO₂ with a lower band gap semiconductor to form a heterojunction is another promising route to enhance photocatalytic activity, in which the second semiconductor works as a photosensitizer, forming an internal electric field across the interface. For instance, Li et al. developed a polycrystalline and uniformly distributed ZnO/ TiO₂ films on conductive FTO substrates for PEC water splitting. The authors claimed that, at the optimum conditions, the current density of the ZnO photo anode under self-biased voltages are 10 times higher than the value without a self-biased voltage. In another case, ZnO was grafted on the TiO₂ nanotube arrays (ZnO/TiO₂NTs) by chemical bath deposition followed by pyrolysis [102], where a higher photo-activity was observed due to a high specific surface area and direct conduction path through the aligned nanotubes. Recent experiments on similarly shaped TiO₂/BiVO₄/Co-Pi nanorod arrays fabricated by hydrothermal treatment on a FTO substrate yielded a photocurrent of ca. 1.86 mA/cm² at 1.0 VRHE and produced ca. 7.31 μmol cm⁻² h⁻¹ hydrogen at 450 nm [113]. Woo and Sung [83] conducted a detailed study on TiO₂ and nitrogen doped TiO₂ (N-TiO₂) films for different composition of rutile and anatase phases prepared by a micro-arc oxidation method. The nitrogen-doped 81% anatase-19% rutile sample showed a photocurrent density of 0.594 mA/cm² at 0 VRHE and a photo conversion efficiency of 0.66% at 419 nm, which is much higher than that for pure anatase TiO₂. The synthesized N-TiO₂ film narrows the band gap due to the formation of an energy level above the valance band structure. Furthermore, Shin et al. [99] reported that sulfur doping on TiO₂ nanotube arrays, owing to the rough tube shape and atomic-level defects in the edge region, yielded an IPCE of 2.4% at 500 nm and a photocurrent density of 2.92 mA/cm² at 1.0 VRHE. Shang et al. [96] developed unique SrTiO₃_x/TiO₂_x hetero structured arrays via a hydrothermal reaction of TiO₂ nanotube arrays followed by a facile aluminum reduction (Fig. 5), which significantly enhanced the charge transfer and reduced the recombination of charge carriers for a prolonged time. The presence of Ti³⁺ enhanced the photocurrent density to 1.38 mA/cm² at 0.84 VNHE and hydrogen evolution rate to 21.01 μmol h⁻¹ under visible light. In another study, Tan et al. [97] proposed a new Ce/Ce₂O₃/CeO₂/TNTs photocatalyst that can produce H₂ without any external bias or sacrificial agents, and showed an improved IPCE of 6.1% and a photocurrent density ca. 11.2 mA/cm² under visible light attributed to an increase in electron hole pair separation and a decrease in electron-hole recombination.

In recent years, TiO₂ nanocomposites with carbon-based material have been examined. Song and co-worker [84] reported H₂ evolution on TiO₂/Sb₂S₃ nanoparticles and reduced graphene oxide (r-GO) nanocomposites synthesized by a chemical bath deposition. An improved photocurrent density of 0.96 mA/cm² at 0.82 VRHE was obtained for the TiO₂/r-GO/Sb₂S₃ electrode in visible light. Following this work, an electro phoretical deposition method was introduced to construct well dispersed photo-active Au/graphene oxide/hydrogenated TiO₂ nanotube composites (Au/RGO/H-TNTs) [92], here r-GO acts as a superb mediator for transferring electrons from Au to H-

TNTs, which enhanced the current density and hydrogen evolution rate. Another important study carried out by Jumeri et al. [180] examined the influence of a r-GO thin layer on a TiO_2 (TiO_2 -rGO) surface, synthesized by dip coating, and reported that the graphene layer provided electron transfer channels that reduced the recombination of e^-/h^+ , enhancing hydrogen production.

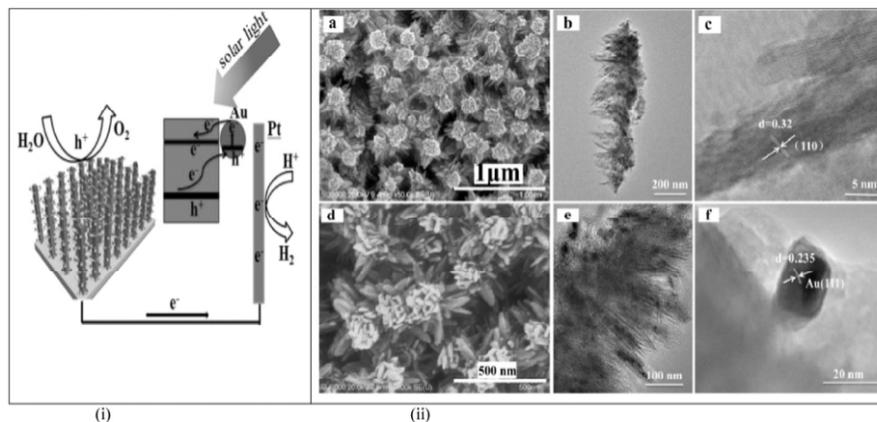


Fig. 4. (i) Schematic diagram of PEC water splitting on Au/B- TiO_2 array photoanode, and (ii) FESEM images (a), TEM image (b), HRTEM (c), of B- TiO_2 ; FESEM image (d), TEM image (e), and HRTEM (f) of Au/B- TiO_2 .

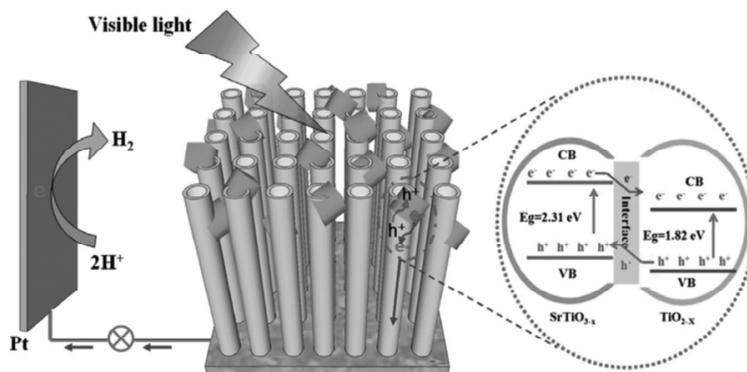


Fig. 5. Charge migration and separation in $\text{SrTiO}_3^x/\text{TiO}_2^x$ heterostructured nanotube array [96].

Conclusion and future outlook

Photoelectrochemical water splitting using semiconductor photocatalysts is a potentially promising technology for the production of renewable hydrogen energy via utilizing abundant solar light. Over the last decade or so, a number of studies were conducted to develop semiconductor photocatalysts that can efficiently use visible light for hydrogen production. Several recent achievements demonstrated that the impact of factors such

as preparation routes, PEC conditions and the light intensity play a vital role on the water splitting process. Although numerous recent innovations, including elemental doping and alloying, Z-scheme compositions, optical modifications, and surface modifications, have enhanced hydrogen production under visible light irradiation, the overall efficiency remains low. For this reason, we need to emphasize on visible range photo-absorbers to increase STH conversion efficiencies. The STH conversion efficiencies have ranged from < 1% to 14% for visible light irradiation, with only a few studies reporting > 7%. Without consideration of visible range photo-absorbers, STH efficiencies are low, mainly because the UV-active photocatalysts exhibit a low light harvesting capability.

References

- [1] International Energy Outlook. (IEO2016), U.S. Energy Information Administration, Release date: May 11, 2016. [https://www.eia.gov/outlooks/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf); 2016.
- [2] Xie WT, Dai YJ, Wang RZ, Sumathy K. Concentrated solar energy applications using Fresnel lenses: a review. *Renew Sustain Energy Rev* 2011; 15:2588–606.
- [3] Guo L, Zhao L, Jing D, Lu Y, Yang H, Bai B, et al. Reprint of: solar hydrogen production and its development in China. *Energy* 2010; 35:4421–38.
- [4] Huang Q, Ye Z, Xiao X. Recent progress in photocathodes for hydrogen evolution. *J Mater Chem A* 2015; 3:15824–37.
- [5] Kibria M, Mi Z. Artificial photosynthesis using metal/nonmetal-nitride semiconductors: current status, prospects, and challenges. *J Mater Chem A* 2016; 4:2801–20.
- [6] Chen X, Shen S, Guo L, Mao SS. Semiconductor-based photocatalytic hydrogen generation. *Chem Rev* 2010; 110:6503–70.
- [7] Ager JW, Shaner MR, Walczak KA, Sharp ID, Ardo S. Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. *Energ Environ Sci* 2015; 8:2811–24.
- [8] Hisatomi T, Kubota J, Domen K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem Soc Rev* 2014; 43:7520–35.
- [9] Jafari T, Moharreri E, Amin AS, Miao R, Song W, Suib SL. Photocatalytic water splitting – the untamed dream: a review of recent advances. *Molecules* 2016 21:900.
- [10] Callejas JF, Read CG, Roske CW, Lewis NS, Schaak RE. Synthesis, characterization, and properties of metal phosphide catalysts for the hydrogen-evolution reaction. *Chem Mater* 2016; 28:6017–44.
- [11] Horiuchi Y, Toyao T, Takeuchi M, Matsuoka M, Anpo M. Recent advances in visible-light-responsive photocatalysts for hydrogen production and solar energy conversion—from semiconducting TiO₂ to MOF/PCP photocatalysts. *Phys Chem Phys* 2013; 15:13243–53.
- [12] Gerischer H. Electrochemical behavior of semiconductors under illumination. *J Electrochem Soc* 1966; 113:1174–82.
- [13] Boddy P. Oxygen evolution on semiconducting TiO₂. *J Electrochem Soc* 1968; 115:199–203.
- [14] Fujishima A. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972; 238:37–8.
- [15] Yoneyama H, Sakamoto H, Tamura H. A photo-electro chemical cell with production of hydrogen and oxygen by a cell reaction. *Electrochim Acta* 1975; 20:341–5.
- [16] Bard AJ. Photoelectrochemistry. *Science* 1980; 207:139–44.
- [17] Bolton JR, Strickler SJ, Connolly JS. Limiting and realizable efficiencies of solar photolysis of water. *Nature* 1985; 316:495.

- [18] O'regan B, Grifitzi M. A low-cost, high-efficiency solar cell based on dye-sensitized. *Nature* 1991; 353:737-40.
- [19] Hilgendorff M, Spanhel L, Rothenhäusler C, Müller G. From ZnO colloids to monocrystalline highly conductive films. *J Electrochem Soc* 1998; 145:3632-7.
- [20] Khaselev O, Turner JA. A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. *Science* 1998; 280:425-7.
- [21] Smith WA, Sharp ID, Strandwitz NC, Bisquert J. Interfacial band-edge energetics for solar fuels production. *Energ Environ Sci* 2015; 8:2851-62.
- [22] Grimes CA, Varghese OK, and Ranjan S. *Hydrogen generation by water splitting*. Springer; 2008.
- [23] Ran J, Zhang J, Yu J, Jaroniec M, Qiao SZ. Earth-abundant co catalysts for semiconductor- based photocatalytic water splitting. *Chem Soc Rev* 2014; 43:7787-812.
- [24] Walter MG, Warren EL, Mc Kone JR, Boettcher SW, Mi Q, Santori EA, et al. Solar water splitting cells. *Chem Rev* 2010; 110:6446-73.
- [25] Lu Q, Yu Y, Ma Q, Chen B, Zhang H. 2D Transition metal dichalcogenide nanosheet based composites for photocatalytic and electrocatalytic hydrogen evolution reactions. *Adv Mater* 2016; 28:1917-33.
- [26] Ma Y, Wang X, Jia Y, Chen X, Han H, Li C. Titanium dioxide-based nanomaterials for photocatalytic fuel generations. *Chem Rev* 2014; 114:9987-10043.
- [27] Khan MA, Yang O-B. Photocatalytic water splitting for hydrogen production under visible light on Ir and Co ionized Titania nanotube. *Catal Today* 2009; 146:177-82.
- [28] Dholam R, Patel N, Adami M, Miotello A. Hydrogen production by photocatalytic water-splitting using Cr-or Fe-doped TiO₂ composite thin films photocatalyst. *Int J Hydrog Energy* 2009; 34:5337-46.
- [29] Khan MA, Woo SI, Yang O-B. Hydrothermally stabilized Fe (III) doped Titania active under visible light for water splitting reaction. *Int J Hydrog Energy* 2008; 33:5345-51.
- [30] Wu Y, Lu G, Li S. The long-term photocatalytic stability of Co 2⁺-modified P25-TiO₂ powders for the H₂ production from aqueous ethanol solution. *J Photo hem Photobiol A: Chem* 2006; 181:263-7.
- [31] Wang J, Sun H, Huang J, Li Q, Yang J. Band structure tuning of TiO₂ for enhanced photoelectrochemical water splitting. *J Phys Chem C* 2014; 118:7451-7.
- [32] Niu M, Cheng D, Cao D. Enhanced photoelectrochemical performance of anatase TiO₂ by metal-assisted S-O coupling for water splitting. *Int J Hydrog Energy* 2013; 38:1251-7.
- [33] Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 2001; 293:269-71.
- [34] Chen X, Liu L, Peter YY, Mao SS. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* 2011; 331:746-50.
- [35] Wang Y, Zeng Y, Li B, Li A, Yang P, Yang L, et al. In-situ hydrothermal synthesized α -Al₂O₃/OgC₃N₄ heterojunctions with enhanced visible-light photocatalytic activity in water splitting for hydrogen. *J Energy Chem* 2016; 25:594-600.
- [36] Suzuki TM, Saeki S, Sekizawa K, Kitazumi K, Takahashi N, Morikawa T. Photoelectrochemical hydrogen production by water splitting over dual-functionally modified oxide: p-type N-doped Ta₂O₅ photocathode active under visible light irradiation. *Appl Catal B: Environ* 2017; 202:597-604.
- [37] Sun Z, Lv B, Li J, Xiao M, Wang X, Du P. Core-shell amorphous cobalt phosphide/ cadmium sulfide semiconductor nanorods for exceptional photocatalytic hydrogen production under visible light. *J Mater Chem A* 2016; 4:1598-602.
- [38] Pan C, Takata T, Domen K. Overall water splitting on the transition metal oxynitride photocatalyst LaMg_{1/3}Ta_{2/3}O₂N over a large portion of the visible light spectrum. *Chem Eur J* 2016; 22:1854-62.
- [39] Ma G, Chen S, Kuang Y, Akiyama S, Hisatomi T, Nakabayashi M, et al. Visible lightdriven Z-scheme water splitting using oxysulfide H₂ evolution photocatalysts. *J Phys Chem Lett* 2016; 7:3892-6.

- [40] Iwashina K, Iwase A, Nozawa S, Adachi Si, Kudo A. Visible-light-responsive $\text{CuLi}_{1/3}\text{Ti}_{2/3}\text{O}_2$ powders prepared by a molten CuCl treatment of Li_2TiO_3 for photocatalytic H_2 evolution and Z-schematic water splitting. *Chem Mater* 2016; 28:4677-85.
- [41] Wang F, Zheng M, Zhu C, Zhang B, Chen W, Ma L, et al. Visible light photocatalytic H_2 -production activity of wide band gap ZnS nanoparticles based on the photosensitization of graphene. *Nanotechnology* 2015; 26:345402.
- [42] Patra KK, Gopinath CS. Bimetallic and plasmonic Ag-Au on TiO_2 for solar water splitting: an active nanocomposite for entire visible light region absorption. *Chem Cat Chem* 2016; 8:3294-311.
- [43] Lee G-J, Anandan S, Masten SJ, Wu JJ. Photocatalytic hydrogen evolution from water splitting using Cu doped ZnS microspheres under visible light irradiation. *Renew Energ* 2016; 89:18-26.
- [44] Ozel F, Aslan E, Istanbulu B, Akay O, Patir IH. Photocatalytic hydrogen evolution based on $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{NiSnS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ nanocrystals. *Appl Catal B: Environ* 2016; 198:67-73.
- [45] Zhang N, Shan C-X, Tan H-Q, Zhao Q, Wang S-P, Sun Z-C, et al. Black-colored ZnO nanowires with enhanced photocatalytic hydrogen evolution. *Nanotechnology* 2016; 27:22LT01.
- [46] Yin X-L, Li L-L, Jiang W-J, Zhang Y, Zhang X, Wan L-J, et al. MoS_2/CdS nanosheet- on-nanorod heterostructure for highly efficient photocatalytic H_2 generation under visible light irradiation. *ACS Appl Mater Interfaces* 2016; 8:15258-66.
- [47] Liu T, Chen W, Huang T, Duan G, Yang X, Liu X. Titania-on-gold nan architectures for visible-light-driven hydrogen evolution from water splitting. *J Mater Sci* 2016; 51:6987-97.
- [48] Manikandan M, Tanabe T, Li P, Ueda S, Ramesh GV, Kodiyath R, et al. Photocatalytic water splitting under visible light by mixed-valence Sn_3O_4 . *ACS Appl Mater Interfaces* 2014; 6:3790-3.
- [49] Maeda K, Domen K. Preparation of $\text{BaZrO}_3\text{-BaTaO}_2\text{N}$ solid solutions and the photocatalytic activities for water reduction and oxidation under visible light. *J Catal* 2014; 310:67-74.
- [50] Kong HJ, Won DH, Kim J, Woo SI. Sulfur-doped $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ composite photocatalyst for water oxidation under visible light. *Chem Mater* 2016; 28:1318-24.
- [51] Li Z, Kong C, Lu G. Visible photocatalytic water splitting and photocatalytic two electron oxygen formation over Cu -and Fe -doped $\text{g-C}_3\text{N}_4$. *J Phys Chem C* 2015; 120:56-63.
- [52] Zhang J, Liu Z, Liu Z. Novel $\text{WO}_3/\text{Sb}_2\text{S}_3$ heterojunction photocatalyst based on WO_3 of different morphologies for enhanced efficiency in photoelectrochemical water splitting. *Acs Appl Mater Inter* 2016; 8:9684-91.
- [53] Borno P, Abdi FF, Tilley SD, Dam B, Van De Krol R, Graetzel M, et al. A bismuth vanadate-cuprous oxide tandem cell for overall solar water splitting. *J Phys Chem C* 2014; 118:16959-66.
- [54] Du H, Liang K, Yuan C-Z, Guo H-L, Zhou X, Jiang Y-F, et al. Bare $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ZB/ WZ heterophase Nanojunctions for visible light photocatalytic hydrogen production with high efficiency. *ACS Appl Mater Interfaces* 2016; 8:24550-8.
- [55] Xie L, Ai Z, Zhang M, Sun R, Zhao W. Enhanced hydrogen evolution in the presence of plasmonic Au -photo-sensitized gC_3N_4 with an extended absorption spectrum from 460 to 640 nm. *PLoS One* 2016; 11:e0161397.
- [56] Shang L, Tong B, Yu H, Waterhouse GI, Zhou C, Zhao Y, et al. CdS nanoparticle decorated Cd nanosheets for efficient visible light driven photocatalytic hydrogen evolution. *Adv Energy Mater* 2016:6.
- [57] Yamato K, Iwase A, Kudo A. Photocatalysis using a wide range of the visible light spectrum: hydrogen evolution from doped AgGaS_2 . *Chem Sus Chem* 2015; 8:2902-6.
- [58] Peters AW, Li Z, Farha OK, Hupp JT. Toward inexpensive photocatalytic hydrogen evolution: a nickel sulfide catalyst supported on a high-stability metal-organic framework. *ACS Appl Mater Interfaces* 2016; 8:20675-81.
- [59] Peerakiatkhajohn P, Butburee T, Yun J-H, Chen H, Richards RM, Wang L. A hybrid photo electrode

- with plasmonic Au@TiO₂ nanoparticles for enhanced photoelectrochemical water splitting. *J Mater Chem A* 2015; 3:20127–33.
- [60] Morales-Guio CG, Tilley SD, Vrubel H, Grätzel M, Hu X. Hydrogen evolution from a copper (I) oxide photocathode coated with an amorphous molybdenum sulphide catalyst. *Nat Commun* 2014;5.
- [61] Peng R, Wu C-M, Baltrusaitis J, Dimitrijevic NM, Rajh T, Koodali RT. Ultra-stable CdS incorporated Ti-MCM-48 mesoporous materials for efficient photocatalytic decomposition of water under visible light illumination. *Chem Commun* 2013; 49:3221–3.
- [62] Sun J, Chen G, Pei J, Jin R, Wang Q, Guang X. A simple approach to strontium sodium tantalite mesocrystals with ultra-high photocatalytic properties for water splitting. *J Mater Chem* 2012; 22:5609–14.
- [63] Zhang F, Yamakata A, Maeda K, Moriya Y, Takata T, Kubota J, et al. Cobalt modified porous single-crystalline LaTiO₂N for highly efficient water oxidation under visible light. *J Am Chem Soc* 2012; 134:8348–51.
- [64] Horiuchi Y, Toyao T, Saito M, Mochizuki K, Iwata M, Higashimura H, et al. Visible light-promoted photocatalytic hydrogen production by using an amino-functionalized Ti (IV) metal-organic framework. *J Phys Chem C* 2012; 116:20848–53.
- [65] Hong J, Xia X, Wang Y, Xu R. Mesoporous carbon nitride with in situ sulfur doping for enhanced photocatalytic hydrogen evolution from water under visible light. *J Mater Chem* 2012; 22:15006–12.
- [66] Tay Q, Kanhere P, Ng CF, Chen S, Chakraborty S, Huan ACH, et al. Defect engineered g-C₃N₄ for efficient visible light photocatalytic hydrogen production. *Chem Mater* 2015; 27:4930–3.
- [67] Manwar NR, Chilkalwar AA, Nanda KK, Chaudhary YS, Subrt J, Rayalu SS, et al. Ceria supported Pt/PtO-nanostructures: efficient photocatalyst for sacrificial donor assisted hydrogen generation under Visible-NIR light irradiation. *ACS Sustain Chem Eng* 2016; 4:2323–32.
- [68] Zhang J, Chen A, Wang L, Li Xa, Huang W. Striving toward visible light photocatalytic water splitting based on natural silicate clay mineral: the interface modification of attapulgite at the atomic-molecular level. *ACS Sustain Chem Eng* 2016; 4:4601–7.
- [69] Kato T, Hakari Y, Ikeda S, Jia Q, Iwase A, Kudo A. Utilization of metal sulfide material of (CuGa)_{1-x}Zn_{2x}S₂ solid solution with visible light response in photocatalytic and photoelectrochemical solar water splitting systems. *J Phys Chem Lett* 2015; 6:1042–7.
- [70] Tao J, Luttrell T, Batzill M. A two-dimensional phase of TiO₂ with a reduced bandgap. *Nat Chem* 2011; 3:296–300.
- [71] Su F, Lu J, Tian Y, Ma X, Gong J. Branched TiO₂ nano arrays sensitized with CdS quantum dots for highly efficient photoelectrochemical water splitting. *Phys Chem Phys* 2013; 15:12026–32.
- [72] Yang J-S, Liao W-P, Wu J-J. Morphology and interfacial energetics controls for hierarchical anatase/rutile TiO₂ nanostructured array for efficient photoelectrochemical water splitting. *ACS Appl Mater Interfaces* 2013; 5:7425–31.
- [73] Li H, Zhao G, Chen Z, Song B, Han G. TiO₂-Ag nanocomposites by low-temperature sol-gel processing. *J Am Ceram Soc* 2010; 93:445–9.
- [74] Kong M, Li Y, Chen X, Tian T, Fang P, Zheng F, et al. Tuning the relative concentration ratio of bulk defects to surface defects in TiO₂ nanocrystals leads to high photocatalytic efficiency. *J Am Chem Soc* 2011; 133:16414–7.
- [75] Kato H, Asakura K, Kudo A. Highly efficient water splitting into H₂ and O₂ over lanthanum-doped NaTaO₃ photocatalysts with high crystallinity and surface nanostructure. *J Am Chem Soc* 2003; 125:3082–9.
- [76] Tan HL, Amal R, Ng YH. Exploring the different roles of particle size in photoelectrochemical and photocatalytic water oxidation on BiVO₄. *ACS Appl Mater Interfaces* 2016; 8:28607–14.
- [77] Yan H, Yang J, Ma G, Wu G, Zong X, Lei Z, et al. Visible-light-driven hydrogen production with

- extremely high quantum efficiency on Pt-PdS/CdS photocatalyst. *J Catal* 2009; 266:165-8.
- [78] Wu C-C, Cho H-F, Chang W-S, Lee T-C. A simple and environmentally friendly method of preparing sulfide photocatalyst. *Chem Eng Sci* 2010; 65:141-7.
- [79] Bao N, Shen L, Takata T, Domen K. Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. *Chem Mater* 2007; 20:110-7.
- [80] Zhang W, Wang B, Hao C, Liang Y, Shi H, Ao L, et al. Au/Cu₂O Schottky contact heterostructure with enhanced photocatalytic activity in dye decomposition and photoelectrochemical water splitting under visible light irradiation. *J Alloy Compd* 2016; 684:445-52.
- [81] Kurnia F, Ng YH, Amal R, Valanoor N, Hart JN. Defect engineering of ZnS thin films for photoelectrochemical water-splitting under visible light. *Sol Energ Mater Sol C* 2016; 153:179-85.
- [82] Ain N-u, Shaheen W, Bashir B, Abdelsalam NM, Warsi MF, Khan MA, et al. Electrical, magnetic and photoelectrochemical activity of r-GO/MgFe₂O₄ nanocomposites under visible light irradiation. *Ceram Int* 2016; 42:12401-8.
- [83] Woo S-R, Sung Y-M. Enhanced photoelectrochemical water splitting of micro-Arc oxidized TiO₂ via anatase/rutile phase control and nitrogen doping. *J Electrochem Soc* 2016; 163:H278-85.
- [84] Song Y-T, Lin L-Y, Hong J-Y. Enhanced Visible-light response and conductivity of the TiO₂/reduced graphene oxide/Sb₂S₃ heterojunction for photoelectrochemical water oxidation. *Electrochim Acta* 2016; 211:576-85.
- [85] Upadhyay AP, Behara DK, Sharma GP, Gyanprakash M, Pala RGS, Sivakumar S. Fabricating appropriate band-edge-staggered heterosemiconductors with optically activated Au nanoparticles via click chemistry for photoelectrochemical water splitting. *ACS Sustain Chem Eng* 2016; 4:4511-20.
- [86] Kamimura S, Higashi M, Abe R, Ohno T. Fabrication of a porous ZnRh₂O₄ photocathode for photoelectrochemical water splitting under visible light irradiation and a significant effect of surface modification by ZnO necking treatment. *J Mater Chem A* 2016; 4:6116-23.
- [87] Wang D, Chang G, Zhang Y, Chao J, Yang J, Su S, et al. Hierarchical three-dimensional branched hematite nanorod arrays with enhanced mid-visible light absorption for high-efficiency photoelectrochemical water splitting. *Nanoscale* 2016; 8:12697-701.
- [88] Song Y-T, Lin L-Y, Chen Y-S, Chen H-Q, Ni Z-D, Tu C-C, et al. Novel TiO₂/Sb₂S₃ heterojunction with whole visible-light response for photoelectrochemical water splitting reactions. *RSC Adv* 2016; 6:49130-7.
- [89] Shi J, Guo P, Liu Y, Su J, Guo L. PbO-sensitized ZnO nanorod arrays for enhanced visible-light-driven photoelectrochemical performance. *J Mater Res* 2016; 31:1622-30.
- [90] Cheng K-W, Hinano K, Antony MP. Photoelectrochemical water splitting using Cu (In, Al) Se₂ photo electrodes developed via selenization of sputtered Cu-In-Al metal precursors. *Sol Energ Mater Sol Cells* 2016; 151:120-30.
- [91] Yang W, Xiong Y, Zou L, Zou Z, Li D, Mi Q, et al. Plasmonic Pd nanoparticle-and plasmonic Pd nanorod-decorated BiVO₄ electrodes with enhanced photoelectrochemical water splitting efficiency across visible-NIR region. *Nanoscale Res Lett* 2016; 11:1-8.
- [92] Luo J, Li D, Yang Y, Liu H, Chen J, Wang H. Preparation of Au/reduced graphene oxide/hydrogenated TiO₂ nanotube arrays ternary composites for visible-lightdriven photoelectrochemical water splitting. *J Alloy Compd* 2016; 661:380-8.
- [93] Gómez-Solís C, Ballesteros J, Torres-Martínez LM, Juárez-Ramírez I. RuO₂-NaTaO₃ heterostructure for its application in photoelectrochemical water splitting under simulated sunlight illumination. *Fuel* 2016; 166:36-41.
- [94] Zheng XL, Song JP, Ling T, Hu ZP, Yin PF, Davey K, et al. Strongly coupled nafion molecules and ordered porous CdS networks for enhanced visible light photoelectrochemical hydrogen evolution. *Adv Mater* 2016; 28:4935-42.
- [95] Sarkar A, Karmakar K, Singh AK, Mandal K, Khan GG. Surface functionalized H₂Ti₃O₇ nanowires

- engineered for visible-light photoswitching, electrochemical water splitting, and photocatalysis. *Phys Chem Phys* 2016; 18:26900-12.
- [96] Shang M, Hu H, Lu G, Bi Y. Synergistic effects of SrTiO₃ nanocubes and Ti³⁺ dual-doping for highly improved photoelectrochemical performance of TiO₂ nanotube arrays under visible light. *J Mater Chem A* 2016; 4:5849-53.
- [97] Tan Y, Zhang S, Shi R, Wang W, Liang K. Visible light active Ce/Ce₂O/CeO₂/TiO₂ nanotube arrays for efficient hydrogen production by photoelectrochemical water splitting. *Int J Hydrog Energy* 2016; 41:5437-44.
- [98] Wang L, Xia L, and Wu Y, Tian Y. Zr-doped α -In₂S₃ ultrathin nano flakes as photo anodes: enhanced visible-light-driven photoelectrochemical water splitting. *ACS Sustain Chem Eng* 2016; 4:2606-14.
- [99] Shin SW, Lee JY, Ahn K-S, Kang SH, Kim JH. Visible light absorbing TiO₂ nanotube arrays by sulfur treatment for photoelectrochemical water splitting. *J Phys Chem C* 2015; 119:13375-83.
- [100] Zhuang H, Miao J, Huang H, Long J, Zhang Y, Yang H, et al. Interim anatase coating layer stabilizes rutile@Cr_xO_y photoanode for visible light driven water oxidation. *Chem Phys Chem* 2015; 16:1352-5.
- [101] Cai L, Ren F, Wang M, Cai G, Chen Y, Liu Y, et al. V ions implanted ZnO nanorod arrays for photoelectrochemical water splitting under visible light. *Int J Hydrog Energy* 2015; 40:1394-401.
- [102] Momeni MM, Ghayeb Y. Visible light-driven photoelectrochemical water splitting on ZnO-TiO₂ heterogeneous nanotube photo anodes. *J Appl Electrochem* 2015; 45:557-66.
- [103] Wang G, Xiao X, Li W, Lin Z, Zhao Z, Chen C, et al. Significantly enhanced visible light photoelectrochemical activity in TiO₂ nanowire arrays by nitrogen implantation. *Nano Lett* 2015; 15:4692-8.
- [104] Zhang Y, Zhang J, Nie M, Sun K, Li C, Yu J. Photoelectrochemical water splitting under visible light over anti-photo corrosive In₂O₃-coupling ZnO nanorod arrays n photoanode. *J Nanopart Res* 2015; 17:322.
- [105] Wang M, Ren F, Zhou J, Cai G, Cai L, Hu Y, et al. N doping to ZnO nanorods for photoelectrochemical water splitting under visible light: engineered impurity distribution and terraced band structure. *Sci Rep-Uk* 2015; 5:12925.
- [106] Higashi M, Yamanaka Y, Tomita O, Abe R. Fabrication of cation-doped BaTaO₂N photo anodes for efficient photoelectrochemical water splitting under visible light irradiation. *APL Mater* 2015; 3:104418.
- [107] Han J, Liu Z, Guo K, Zhang X, Hong T, Wang B. AgSbS₂ modified ZnO nanotube arrays for photoelectrochemical water splitting. *Appl Catal B: Environ* 2015; 179:61-8.
- [108] Xiao J, Zhang X, Li Y. A ternary gC₃N₄/Pt/ZnO photoanode for efficient photoelectrochemical water splitting. *Int J Hydrog Energy* 2015; 40:9080-7.
- [109] Ma Y, Jia Y, Wang L, Yang M, Bi Y, Qi Y. Exfoliated thin Bi₂MoO₆ nanosheets supported on WO₃ electrode for enhanced photoelectrochemical water splitting. *Appl Surf Sci* 2016; 390:399-405.
- [110] Zhou L, Zhao C, Giri B, Allen P, Xu X, Joshi H, et al. High light absorption and charge separation efficiency at low applied voltage from Sb-doped SnO₂/BiVO₄n core/shell nanorod-array photoanodes. *Nano Lett* 2016; 16:3463-74.
- [111] Yang M, Zhang L, Jin B, Huang L, Gan Y. Enhanced photoelectrochemical properties and water splitting activity of self-ordered MoO₃-TiO₂ nanotubes. *Appl Surf Sci* 2016; 364:410-5.
- [112] Valenti M, Kontoleta E, Digdaya IA, Jonsson MP, Biskos G, Schmidt Ott A, et al. The role of size and dimerization of decorating plasmonic silver nanoparticles on the photoelectrochemical solar water splitting performance of BiVO₄ photoanodes. *Chem Nano Mat* 2016; 2:739-47.
- [113] Tong R, Wang X, Zhou X, Liu Q, Wang H, Peng X, et al. Cobalt-phosphate modified TiO₂/BiVO₄ nano arrays photoanode for efficient water splitting. *Int J Hydrog Energy* 2016.
- [114] Ding Y, Nagpal P. Standalone anion-and co-doped titanium dioxide nanotubes for photocatalytic and

- photoelectrochemical solar-to-fuel conversion. *Nanoscale* 2016; 8:17496–505.
- [115] Li J-M, Cheng H-Y, Chiu Y-H, Hsu Y-J. ZnO-Au-SnO₂ Z-scheme photoanodes for remarkable photoelectrochemical water splitting. *Nanoscale* 2016; 8:15720–9.
- [116] Zheng XL, Dinh CT, de Arquer F, Zhang B, Liu M, Voznyy O, et al. ZnFe₂O₄ leaves grown on TiO₂ trees enhance photoelectrochemical water splitting. *Small* 2016; 12:3181–8.
- [117] Zhang Z, Gao C, Wu Z, Han W, Wang Y, Fu W, et al. Toward efficient photoelectrochemical water-splitting by using screw-like SnO₂ nanostructures as photoanode after being decorated with CdS quantum dots. *Nano Energy* 2016; 19:318–27.
- [118] Xu R, Li H, Zhang W, Yang Z, Liu G, Xu Z, et al. The fabrication of In₂O₃/In₂S₃/Ag nanocubes for efficient photoelectrochemical water splitting. *Phys Chem Phys* 2016; 18:2710–7.
- [119] Carraro G, Maccato C, Gasparotto A, Kaunisto K, Sada C, Barreca D. Plasma assisted fabrication of Fe₂O₃-Co₃O₄ nanomaterials as anodes for photoelectrochemical water splitting. *Plasma Process Polym* 2016; 13:191–200.
- [120] Sohila S, Rajendran R, Yaakob Z, Teridi MAM, Sopian K. Photoelectrochemical water splitting performance of flower like ZnO nanostructures synthesized by a novel chemical method. *J Mater Sci: Mater Electron* 2016; 27:2846–51.
- [121] Hou L, Bu Q, Li S, Wang D, Xie T. Ni₃S₂-decorated TiO₂ nanotube arrays as effective photoanodes for photoelectrochemical water splitting. *RSC Adv* 2016; 6:99081–7.
- [122] Akiyama S, Nakabayashi M, Shibata N, Minegishi T, Asakura Y, Abdulla Al Mamun M, et al. Highly efficient water oxidation photoanode made of surface modified LaTiO₂N particles. *Small* 2016; 12:5468–76.
- [123] Fan X, Gao B, Wang T, Huang X, Gong H, Xue H, et al. Layered double hydroxide modified WO₃ nanorod arrays for enhanced photoelectrochemical water splitting. *Appl Catal A: General* 2016; 528:52–8.
- [124] Li M, Zhao R, Su Y, Hu J, Yang Z, Zhang Y. Hierarchically CuInS₂ nanosheet constructed nanowire arrays for photoelectrochemical water splitting. *Adv Mater Interfaces* 2016:3.
- [125] Feng X, Chen Y, Qin Z, Wang M, Guo L. Facile fabrication of sandwich structured WO₃ nano plate arrays for efficient photoelectrochemical water splitting. *ACS Appl Mater Interfaces* 2016; 8:18089–96.
- [126] Naeem R, Ehsan MA, Yahya R, Sohail M, Khaledi H, Mazhar M. Fabrication of pristine Mn₂O₃ and Ag-Mn₂O₃ composite thin films by AACVD for photo electrochemical water splitting. *Dalton Trans.* 2016; 45:14928–39.
- [127] Sharma S, Singh S, Khare N. Enhanced photosensitization of zinc oxide nanorods using polyaniline for efficient photocatalytic and photoelectrochemical water splitting. *Int J Hydrog Energ* 2016; 41:21088–98.
- [128] Liu C, Li X, Su J, Guo L. Enhanced charge separation in copper incorporated BiVO₄ with gradient doping concentration profile for photoelectrochemical water splitting. *Int J Hydrog Energ* 2016; 41:12842–51.
- [129] Fàbrega C, Murcia-López S, Monllor-Satoca D, Prades J, Hernández-Alonso M, Penelas G, et al. Efficient WO₃ photoanodes fabricated by pulsed laser deposition for photoelectrochemical water splitting with high faradaic efficiency. *Appl Catal B: Environ* 2016; 189:133–40.
- [130] Kang D, Kim TW, Kubota SR, Cardiel AC, Cha HG, Choi K-S. Electrochemical synthesis of photo electrodes and catalysts for use in solar water splitting. *Chem Rev* 2015; 115:12839–87.
- [131] Gholipour MR, Dinh C-T, Bèland F, Do T-O. Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting. *Nanoscale* 2015; 7:8187–208.
- [132] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. *Int J Hydrog Energ* 2013; 38:4901–34.

- [133] Khan SU, Akikusa J. Photoelectrochemical splitting of water at nano crystalline n- Fe₂O₃ thin-film electrodes. *J Phys Chem B* 1999; 103:7184–9.
- [134] Kudo A, Ueda K, Kato H, Mikami I. Photocatalytic O₂ evolution under visible light irradiation on BiVO₄ in aqueous AgNO₃ solution. *Catal Lett* 1998; 53:229–30.
- [135] Yu J, Kudo A. Effects of structural variation on the photocatalytic performance of hydrothermally synthesized BiVO₄. *Adv Funct Mater* 2006; 16:2163–9.
- [136] Tran F, Blaha P. Accurate band gaps of semiconductors and insulators with a semi local exchange-correlation potential. *Phys Rev Lett* 2009; 102:226401.
- [137] Kudo A, Miseki Y. Heterogeneous photocatalyst materials for water splitting. *Chem Soc Rev* 2009; 38:253–78.
- [138] Maeda K, Teramura K, Lu D, Takata T, Saito N, Inoue Y, et al. Photocatalyst releasing hydrogen from water. *Nature* 2006; 440:295.
- [139] Yasuda T, Kato M, Ichimura M, Hatayama T. SiC photo electrodes for a self-driven water-splitting cell. *Appl Phys Lett* 2012; 101:053902.
- [140] Kushwaha A, Aslam M. ZnS shielded ZnO nanowire photoanodes for efficient water splitting. *Electrochim Acta* 2014; 130:222–31.
- [141] Cristino V, Caramori S, Argazzi R, Meda L, Marra GL, Bignozzi CA. Efficient photoelectrochemical water splitting by anodically grown WO₃ electrodes. *Langmuir* 2011; 27:7276–84.
- [142] Wei Y, Ke L, Kong J, Liu H, Jiao Z, Lu X, et al. Enhanced photoelectrochemical water-splitting effect with a bent ZnO nanorod photoanode decorated with Ag nanoparticles. *Nanotechnology* 2012; 23:235401.
- [143] Zhang Z, Wang P. Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy. *J Mater Chem* 2012; 22:2456–64.
- [144] Abe R. Recent progress on photocatalytic and photoelectrochemical water splitting under visible light irradiation. *J Photo chem Photobiol C: Photo chem Rev* 2010; 11:179–209.
- [145] Ismail AA, Robben L, Bahnemann DW. Study of the efficiency of UV and visible light photocatalytic oxidation of methanol on mesoporous RuO₂-TiO₂ nanocomposites. *Chem physchem* 2011; 12:982–91.
- [146] Ismail AA. Single-step synthesis of a highly active photocatalyst for oxidation of trichloroethylene. *Appl Catal B: Environ* 2008; 85:33–9.
- [147] Atabaev TS, Hossain MA, Lee D, Kim H-K, Hwang Y-H. Pt-coated TiO₂ nanorods for photoelectrochemical water splitting applications. *Results Phys* 2016; 6:373–6.
- [148] Ye M, Gong J, Lai Y, Lin C, Lin Z. High-efficiency photo electrocatalytic hydrogen generation enabled by palladium quantum dots-sensitized TiO₂ nanotube arrays. *J Am Chem Soc* 2012; 134:15720–3.
- [149] Kawasaki S, Takahashi R, Yamamoto T, Kobayashi M, Kumigashira H, Yoshinobu J, et al. Photoelectrochemical water splitting enhanced by self-assembled metal nanopillars embedded in an oxide semiconductor photo electrode. *Nat Commun* 2016:7.
- [150] Mohapatra SK, Misra M, Mahajan VK, Raja KS. Design of a highly efficient photo electrolytic cell for hydrogen generation by water splitting: application of TiO₂- x C x nanotubes as a photoanode and Pt/TiO₂ nanotubes as a cathode. *J Phys Chem C* 2007; 111:8677–85.
- [151] Tanigawa S, Irie H. Visible-light-sensitive two-step overall water-splitting based on band structure control of titanium dioxide. *Appl Catal B: Environ* 2016; 180:1–5.
- [152] Li L, Yan J, Wang T, Zhao Z-J, Zhang J, Gong J, et al. Sub-10 nm rutile titanium dioxide nanoparticles for efficient visible-light-driven photocatalytic hydrogen production. *Nat Commun* 2015:6.
- [153] Zhang G, Lan Z-A, Lin L, Lin S, Wang X. Overall water splitting by Pt/gC₃N₄ photocatalysts without using sacrificial agents. *Chem Sci* 2016; 7:3062–6.

- [154] Zhu Z, Chen J-Y, Su K-Y, Wu R-J. Efficient hydrogen production by water-splitting over Pt-deposited C-HS-TiO₂ hollow spheres under visible light. *J Taiwan Inst Chem Eng* 2016; 60:222-8.
- [155] Khan MA, Akhtar MS, Woo SI, Yang O-B. Enhanced photo response under visible light in Pt ionized TiO₂ nanotube for the photocatalytic splitting of water. *Catal Commun* 2008; 10:1-5.
- [156] Bamwenda GR, Tsubota S, Nakamura T, Haruta M. Photo assisted hydrogen production from a water-ethanol solution: a comparison of activities of Au-TiO₂ and Pt-TiO₂. *J Photo chem Photobiol A: Chem* 1995; 89:177-89.
- [157] Hara S, Yoshimizu M, Tanigawa S, Ni L, Ohtani B, Irie H. Hydrogen and oxygen evolution photocatalysts synthesized from strontium titanate by controlled doping and their performance in two-step overall water splitting under visible light. *J Phys Chem C* 2012; 16:17458-63.
- [158] C.L. Tan, H. Zhang, *Nat. Commun.* 6 (2015) 7873-7885.