Recent Progress in Enhancing Solar-to-Hydrogen Efficiency

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Abstract: Solar water splitting is a promising and ideal route for renewable production of hydrogen by using the most abundant resources of solar light and water. Focusing on the working principal of solar water splitting, including photon absorption and exciton generation in semiconductor, exciton separation and transfer to the surface of semiconductor, and respective electron and hole reactions with absorbed surface species to generate hydrogen and oxygen, this review covers the comprehensive efforts and findings made in recent years on the improvement for the solar-to-hydrogen efficiency (STH) determined by a combination of light absorption process, charge separation and migration, and catalytic reduction and oxidation reactions. Critical evaluation is attempted on the strategies for improving solar light harvesting efficiency, enhancing charge separation and migration, and improving surface reactions. Towards the end, new and emerging technologies for boosting the STH efficiency are discussed on multiple exciton generation, up-conversion, multi-strategy modifications and the potentials of organo-metal hybrid perovskite materials.

Key words: water splitting, solar-to-hydrogen, doping, sensitizing, light absorption, exciton

1. Introduction

Growing economy and increasing population are demanding an increased energy supply. A recent BP report of the 2030 Energy Outlook predicts that an additional 1.3 billion people will become new energy consumers by 2030. [1] Fossil fuels are the popular energy sources because of relative low-cost and high energy density. But the limited fossil fuel deposits cannot afford the predicted energy demands. On the other hand, the global warming caused by the greenhouse gas emission from the refineries and combustion of fossil fuels is becoming one of the most serious environmental issues.

Solar energy is a decentralized and inexhaustible natural resource. The magnitude of the available solar power striking the earth's surface at any instant is equivalent to the power supply by 130 million of 500-MW power plants. Harvesting energy directly from sunlight offers an ideal approach to fulfilling with minimal environmental impact the need for clean and renewable energy. [2] It is therefore desirable to efficiently convert the energy from the sun into chemical fuels that can be stored, transported and used upon demand.

Hydrogen has been identified as a clean chemical fuel or a potential energy carrier in many low greenhouse gas energy scenarios because of the relative abundance of its source of generation (water), high gravimetric energy density, small environmental footprint thanks to its zero post-combustion pollutants and carbon dioxide emissions. Advantages of hydrogen fuel also include the ease of conversion to electricity or other forms of fuel with relatively high efficiencies and the convenience of storage and transmission compared with electrons. Since the discovery of hydrogen production through water splitting over a single crystal titania (TiO_2) photoanode

under the illumination of ultraviolet (UV) light by Fujishima and Honda in 1972, [3] the technology of semiconductor-based photocatalytic water splitting to produce hydrogen using solar energy has been considered as one of the most important approaches to solving the world energy crisis. Indeed, photoelectrolysis of water using semiconductors as both light absorber and energy converter to store solar energy in the simplest chemical bond, H_2 , is seen as the “Holy Grail” of solar energy conversion and storage, [2,4] and tremendous amount of research has been conducted [5].

For a practical water splitting system, at least 10% of solar-to-hydrogen efficiency is necessary. [6] However, at present, less than desired solar-to-hydrogen efficiency, high cost and/or short lifetime of the photocatalysts are still the bottlenecks for realizing the industrial application of semiconductor-based photocatalytic hydrogen generation.

There were a series of articles addressing water splitting issues, including those in solar water splitting cells, [2] photoelectrochemical tandem cells, [7] and Z-scheme water splitting devices employing two different semiconductors. [8] Some individual enhancement strategies were also discussed such as those involving nanostructures, [9-11] plasmon enhancements, [12-14] and co-catalysts. [15] In this review, we focus on a comprehensive evaluation of fundamentally important strategies, parameters, and factors that affect the efficiency of the photocatalytic water splitting processes to reflect most recent developments in this specific research area.

Photocatalytic water splitting reaction on a semiconductor photocatalyst occurs in three steps as shown in Fig.1:

- 1) Photocatalyst absorbs photon energy greater than the bandgap energy of the material and generates photo-excited electron-hole pairs (excitons or carriers) in the bulk;
- 2) Photo-excited carriers separate and migrate to the surface without recombination; and
- 3) Adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H₂ and O₂ respectively. [16]

The first two steps relate to the photon absorption and charge carrier transfer in the semiconductor, which are analogous to the photovoltaic process, and the last step is about electrochemistry and photochemistry. In order to achieve high solar-to-hydrogen efficiency, the efficiency-determining steps or all of the three steps, i.e. light absorption efficiency, charge separation and transport efficiency, and surface chemical reaction efficiency, have to be adequately addressed and optimized. Photocatalytic water splitting requires a semiconductor material that has robust capability for efficient harvesting of a large portion of the solar spectrum, supports charge separation and rapid transfer to the semiconductor/aqueous interface, and exhibits long-term stability.

2. Efficiency of Light Absorption Process

Thermodynamically, the overall water splitting reaction is an uphill reaction with a free energy change (Gibbs free energy) of 237.2 kJ mol⁻¹ corresponding to $\Delta E^0 = 1.23$ V per electron transferred. [17] Fig. 2 shows a schematic illustration of the basic principle of overall water splitting on a photocatalyst.

For high efficient and long-term overall water splitting, the semiconductor photocatalyst must have a bandgap narrower than 3 eV to harvest visible light. In addition, the band edge potentials have to be suitable for overall water splitting and the semiconductor photocatalyst needs to be stable in the photocatalytic reactions. Because semiconductors with a bandgap wider than 3 eV can only absorb ultraviolet light which only constitutes 4-5% of the whole solar spectrum, it is necessary to find and utilize photocatalytic semiconductors with smaller bandgap suitable for absorbing visible light (42% of the whole solar spectrum) and even the near-IR light (40% of the solar spectrum).

Metal oxides are generally stable in aqueous solutions and are less expensive than non-oxide semiconductors, yet unfortunately, the valence band edges of most oxide semiconductors are determined by O2p orbitals and the O2p orbitals locate at ca. +3.0 eV or higher vs. the normal hydrogen electrode (NHE). [17] In order to reduce water to produce hydrogen, the conduction band edge of the semiconductor must be more negative than the water reduction potential, that is 0 eV vs. NHE. As a result, the bandgap of the metal oxide semiconductor will inevitably become larger than 3.0 eV (equivalent to a wavelength 413.57 nm), rendering the material inactive in the visible light region. Fig. 3(a) & (b) show the band levels of various semiconductor materials [18] and theoretical solar-to-hydrogen efficiency as a function of band-gap of the semiconductor taking into account of thermodynamic loss and kinetic loss due to the overpotentials for oxygen or hydrogen production [19,20].

Some metal chalcogenides have suitable narrow band gaps, but they are prone to photocorrosion. Oxides such as hematite (Fe_2O_3) and WO_3 have band gap values

less than 3.0 eV, but their conduction band edge is more positive than H^+/H_2 energy potential and thus, cannot drive the water reduction reaction to produce hydrogen.

In order to improve the efficiency of the first step (i.e., the solar photon absorption), it is necessary to develop narrow bandgap semiconductor materials to absorb broader spectrum of solar energy. Efforts on improving stable wide bandgap semiconductor photocatalysts have been focused on extending the absorption region to visible light. [21-24] For narrower bandgap metal chalcogenides, attentions are mostly paid to improve their stability in the aqueous environment. On the other hand, doping or combined with other semiconductor(s) to form tandem structure has been studied to realize hydrogen evolution on semiconductor hematite and WO_3 . Overall, four strategies are considered to improve the solar light harvesting efficiency as follows:

- 1) Modification of the semiconductor with metal and/or nonmetal ion doping for narrower bandgap;
- 2) Semiconductor sensitization with dye, quantum dots or plasmon enhancement;
- 3) Development of solid solutions for desired bandgap structure;
- 4) Fabrication of novel single-phase visible-light-active photocatalytic materials through bandgap engineering.

Below we evaluate each of these strategies.

2.1. Doping

2.1.1. Doping with metal ions

One of the most effective ways to develop visible-light-active photocatalysts is to create impurity levels in the bandgap through metal ion doping. Fig. 4 illustrates the scheme of the donor and acceptor level in the forbidden band and visible light

response of wide bandgap semiconductor doped by metal ions. Transitional metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing TiO₂ photocatalytic activities. [17, 23, 24] Doping ions can narrow the bandgap of TiO₂ via electronic coupling effect between doping ions and TiO₂, introducing impurity energy level just above the valence band or just below the conduction band of TiO₂ to extend the visible absorption. In addition, dopants can play a role as trapping center for photogenerated electrons to effectively separate the photogenerated electron-hole pairs and the impurity energy level can serve to prolong the lifetime of photogenerated electron-hole pairs, leading to high photocatalytic activity.

Bae et al. reported the effect of H₂ and N₂ annealing on significant increase of the photocurrent of annealed Nb-doped TiO₂. [25] Hall-effect measurements, Photoluminescence (PL), and ultraviolet-visible (UV-Vis) spectrometry confirmed that the annealing process improved the photocurrent by decreasing the carrier concentration to achieve wider depletion region, the recombination level, and the bandgap energy. Khan et al. doped TiO₂ with Fe³⁺, leading to a significant red shift of optical response towards visible light owing to the reduced bandgap energy. [26]

Although metal doping extends the photoabsorption to visible region, the created donor or acceptor levels are discrete, and they usually also serve as recombination centers that kill the photo-excited electron-hole pairs. Therefore, metal doping is not a perfect method and there is a trade-off between photon absorption enhancement and increased recombination.

2.1.2. Doping with nonmetal ions

Nonmetal ion doping is another approach narrowing the bandgap to achieve visible-light-active photocatalysts and has been widely studied to modify TiO₂ or ZnO

UV-light-active photocatalysts. Nonmetal ion doping usually shifts the valence band edge upward as shown in Fig. 5, instead of forming donor levels in the forbidden band.

Kurian [27] reported the surface structure modification and bandgap tuning of TiO₂ nanotube arrays (TNTA) by a short-term quick annealing in air. The effective bandgap is found to be 1.7 eV and the absorption of this TNTA extends to entire visible range with an increase by 350%. The detailed studies show that there is a surface layer composed of substitutional and interstitial carbon along with oxygen vacancies and surface states, which has a low bandgap as carbon doping introduces multiple localized occupied states in the bandgap. The short-term quick annealing causes a band tailing from bulk to surface and reducing the effective bandgap to 1.7 eV at the surface.

Hoang et al. modified single crystalline TiO₂ nanowire arrays via nitridation in NH₃ flow [28] and H₂, NH₃ co-treatment [29]. The N-modified TiO₂ photoanode is visible light active (extending to 520nm) and has an optical bandgap of 2.4 eV. The H, N synergistic effects of hydrogenation and nitridation further extend the active spectrum of TiO₂ NW arrays to ~570nm. The hydrogenation process increases the bulk Ti³⁺ concentration in TiO₂, which introduces Ti³⁺ 3d states below the conduction band edge. The substitutional N introduces N 2p states above the valence band edge, and the interaction between N and Ti³⁺ is the key to the extension of active spectrum and the superior visible light water photo-oxidation activity.

Contribution of nitrogen to the valence band modification of ZnO plays a major role of extending the absorption of ZnO to the visible region. Yang [30] reported N-doping enhanced visible absorption and photocurrent generation. Zong [31] reported another N-doped ZnO photocatalyst showing high photocatalytic activity for visible-light-induced water oxidation. Qiu [32] reported the photocurrent

enhancement due to a combination of increased roughness factor for boosting light harvesting from ZnO nanotetrapod branching and increased visible light absorption due to the N-doping induced bandgap narrowing of ZnO.

2.1.3. Co-doping

Monodoping TiO₂ with metal ions has gained some success in extending the absorption spectrum to the visible region by introducing a donor level under the conduction band. However, the formation of strongly localized d states within the bandgap and the existence of carrier recombination centers significantly decrease the carrier mobility and then reduce the photocurrent. [25]

Co-incorporation of both metal cations and nonmetal anions can neutralize positive and negative charges in the semiconductor lattice, thus reduce the charge recombination centers and enhance the photocatalytic activity. [33-45]

Density-functional theory calculations suggest that co-doping TiO₂ with donor-acceptor pairs is more effective than monodoping for improving photoelectrochemical water splitting performance because co-doping can reduce charge recombination, improve material quality, enhance light absorption, and increase solubility limits of dopants. [33] Cho et al. co-doped TiO₂ with W and C and the co-doped TiO₂:(W, C) nanowires exhibit improved saturation photocurrent density than monodoped TiO₂:W and TiO₂:C and 2.4 times higher saturation photocurrent density than the undoped TiO₂ NWs. The enhancement is attributed to mainly charge transport efficiency improvement and minor charge transfer efficiency improvement. Wu et al. [34] co-doped TiO₂ with Nd and C (Nd-C-TiO₂) by calcination assisted solvothermal reaction method. Co-doped Nd and C introduced C electron states above the valence band and Nd electron states below the conduction band of TiO₂ simultaneously, which extend the absorption of TiO₂ into the whole

range of solar light from 200 to 900 nm. Hoang et al. [35] reported the co-incorporation of N and Ta into TiO₂ nanowires by nitridation Ta-incorporated TiO₂ nanowires arrays in NH₃ flow at 500 °C. The active spectrum of (N,Ta):TiO₂ extends to ~520nm as compared to ~550 nm for N:TiO₂ and ~420 nm for pristine TiO₂ and Ta:TiO₂. Co-incorporation of Ta and N can reduce charge recombination centers via charge compensation effects and improve hole extraction to electrolyte and PEC performance via suppressing the formation of the amorphous layer during the nitridation process.

WO₃ has a bandgap of ~2.8 eV making it suitable for the absorption of visible solar light. The position of the valence band maximum (VBM) is good for O₂ evolution in water splitting, but its conduction band (CB) is too low for H₂ reduction. In addition, the bandgap should be reduced to improve activity with visible light. Wang et al. [45] studied the electronic properties of doped tungsten oxide (WO₃) using DFT calculations. Results show that replacing W in the lattice by isovalent Mo or Cr ions narrows the bandgap but shifts the CB edge further down. Substitution of O with S can narrow the bandgap due to introducing localized occupied states above the VB and shifting the CB minimum upward. Replacing of W by low-valence Ti, Zr, or Hf ions widens the bandgap and shifts the CB edge to higher energies. But the simultaneous presence of substitutional Hf and O vacancy results in a shift of both VB and CB to higher energies and a reduction of the bandgap, which provides potential benefits for photocatalytic hydrogen production.

2.1.4 Hydrogenation

Regardless how the dopants are introduced for specific enhancements, they generally also act as charge carrier recombination centers that may cause a major issue on the photocatalytic efficiency. Recently, some appealing approaches based on

dopant-free, pure TiO_2 phase were proposed in order to overcome this limitation. Ariga et al. observed visible light photochemical reaction on $\text{TiO}_2(001)$ surface. [36] Tao et al. prepared a two-dimensional phase of TiO_2 with a bandgap of ~ 2.1 eV by oxidation of bulk titanium interstitials. [37] Zuo et al. synthesized partially reduced TiO_2 with the presence of Ti^{3+} in the bulk. Ti^{3+} extends the photoresponse of TiO_2 from the UV to the visible light region. [38] The photoelectrochemical performance was significantly enhanced by the visible-light harvesting ability of the electronic interband state induced from Ti^{3+} self-doping of TiO_2 photonic crystals coupled with the trapping of visible light by a periodical morphological structure. [39] Chen et al. [40] reported the enhancement of solar absorption by introducing disorder in the surface layers of nanophase TiO_2 through hydrogenation. The onset of optical absorption of black hydrogenated TiO_2 nanocrystals is lowered to about 1.0 eV (~ 1200 nm). Naldoni et al. synthesized crystalline core/disordered shell black TiO_2 NPs with oxygen vacancies in the bulk crystalline phase and nearly stoichiometric disordered surface. The bandgap narrowing is dictated by the synergistic presence of oxygen vacancies and surface disorder. [41]

Formation of oxygen vacancies leads to the increase of donor density for the improvement of charge transport, [42] facilitates the charge transfer efficiency by providing additional active sites for water adsorption, [43] and enables efficient charge separation and effective suppression of electron-hole recombination at -0.6V vs. Ag/AgCl . [44]

2.2 Sensitizing

2.2.1 Dye Sensitization

Dye sensitization is another powerful strategy to extend the absorption spectrum range of wide bandgap semiconductors. Dye sensitized solar cell has been widely studied since the seminal work by O'Regen and Gratzel in 1991. [46] The same concept can also be applied to solar water splitting. Recent advances in dye sensitized solar water splitting have been discussed in a few review and perspective articles. [17,21,47,48] For the interest of solar water splitting applications, the stability of the dye in aqueous electrolyte becomes a critical issue. Abe et al. reported [49] the stabilization of coumarin and carbazole dyes through the insertion of an oligothiophene moiety between the donor and acceptor components of these dyes. Compared with the activities in dye sensitized solar cell research, [46,50,51] dye sensitization for solar water splitting appears to be an area with challenging yet potentially transformational opportunities.

2.2.2 Quantum dot (QD) sensitization

Tunable bandgaps upon sizes, high extinction coefficients, and large intrinsic dipole moment make quantum dots a promising sensitizer for wide bandgap semiconductors (Fig. 6). Holmes et al. [52] demonstrated a quantitative relationship between the degree of quantum size confinement in suspended nanocrystal dots and their photocatalytic water splitting activity. Their results emphasized the dependency of the charge transfer kinetics on the thermodynamic driving force of the reaction, and the possibility of fine-tuning photocatalytic activity through particle sizing.

Cadmium chalcogenides usually have narrow bandgaps and absorb visible light. They are widely used in sensitizing wide bandgap semiconductors to enable visible light activity. $\text{TiO}_2/(\text{CdS}, \text{CdSe}, \text{CdSeS})$ nanorod heterostructures extend the absorption spectral to visible range effectively. [53-60] A maximum conversion efficiency of 8.5% is obtained. [61] Chi et al. [60] reported CdS sensitized

mesoporous TiO₂ film showing a photoconversion efficiency of 3.67% under visible light illumination of 100 mW cm⁻². Photocurrent density of CdTe QD-sensitized TiO₂ nanotube array is improved to 6 mA cm⁻² compared to 0.17 mA cm⁻² (for pristine TiO₂). [63] The visible light response decreases while the electron injection driving force increases as the decrease of the particle size. [64,65] PbS/CdS co-sensitized mesoporous TiO₂ further extends the absorption spectral range to infrared photons [66]. TiO₂/PbS/CdS heterostructures exhibit a photocurrent density of 6 mA cm⁻².

Chen et al. [67] combined TiO₂ inverse opal photonic crystal with CdS QD sensitization for solar-light-driven hydrogen production. CdS QDs acting as “light antennas” can greatly improve the visible-light harvesting and the CdS/TiO₂ heterojunction promotes interfacial charge transfer and separation. The highly ordered and percolated 3D pore structures provide efficient and fast electron-transport pathways. Moreover, the periodical 3D inverse opal provides an additional photonic bandgap effect to enhance the light-matter interactions by controlling the propagation of light via back reflections, slow photons, and surface resonant modes. The photonic bandgap feature facilitates photon-QD interaction, leading to further enhancement of light absorption. Sang et al. [68] investigated the effect of quantum dot deposition on the interfacial flat-band potential, depletion layer in TiO₂ nanotube electrodes, and the resulting H₂ generation rates. Results show that CdS QD-modified TiO₂ nanotube arrays exhibit a more negative flat-band potential and a lower energy barrier for interfacial electron transfer (i.e., electron injection from QD into titania). The modified samples have a wider depletion layer resulting in longer lifetime of the charger carriers. Modification with CdS enlarges both of the depletion layer capacitance and double-layer capacitance and reduces the charge-transfer resistance and electrochemical impedance.

CuInS₂/CdS co-sensitized TiO₂ nanocrystalline films have shown a saturated photocurrent of 16 mA cm⁻² in a polysulfide solution under AM 1.5 solar illumination at 100 mW cm⁻². [69,70] Liu utilized CdSe QD-sensitized Au/TiO₂ hybrid mesoporous films to demonstrate QD-enhanced photoelectrochemical performance. [71]

CdS QD-coupled graphitic carbon nitride (g-C₃N₄) photocatalyst has a red shift and a strong absorption in the visible light region. [72] It also shows efficient separation of photogenerated charge carriers and activity enhancement for visible light photocatalytic H₂ evolution.

Emin [73] reported the PEC performance of Cadmium Chalcogenide sensitized porous ZnO plate electrodes. CdSe-sensitized ZnO electrode shows ~3.1 mA cm⁻² at 1.2 V vs RHE due to enhanced absorption in the visible range. Choulhan et al. [74] reported CdSe-sensitized ZnO nanorods exhibiting a photocurrent density of 2.48 mA cm⁻² at 0 V bias under AM 1.5G illumination. CdS/CdSe co-sensitized ZnO nanowires show a photocurrent density 13.9 mA cm⁻² at 0.6V vs RHE. [75] CdSe/CdS co-sensitized NW photoanodes show a photocurrent density 9.15 mA cm⁻² at 0 V bias vs SCE. [76] CdS sensitized ZnO nanorod array shows a photocurrent densities of 23.7 and 15.8 mA cm⁻² at a 0 V bias under the illumination of simulated sunlight and visible light, respectively. [77] CdSe sensitized ZnO nanotube shows ~5 mA cm⁻² at 0.35V vs SCE. [78] Wang et al. [79] reported double-sided CdS and CdSe quantum dot co-sensitized ZnO nanowire arrays yielding a photocurrent of ~12 mA cm⁻² at 0.4 V vs. Ag/AgCl. Kim et al. [80] reported hierarchically shelled ZnO nanostructure consisting of a two-dimensional ZnO nanosheet shell and a ZnO nanowire core coupled with CdS and CdSe QDs as visible sensitizers for a PEC hydrogen generation system which generated a photocurrent density of 17.5 mA cm⁻²

under the 1 sun illumination condition at 0V vs SCE bias condition. CdSe/CdS co-sensitized ZnO/WO_x hierarchical heterostructure consisting of ZnO nanowire branches grown on WO_x nanowhisker stems produces a photocurrent density of 11 mA cm⁻² at -0.5V (vs SCE) under 1.5 AM irradiation for hydrogen generation. [81] Chen et al. [82] reported CdTe QDs sensitized ZnO nanowires with a maximum photoconversion efficiency of 1.83%, which is more than 200% higher than that of pristine ZnO nanowires. The high efficiency is attributed to extended light absorption spectrum and enhanced charge carrier separation on CdTe/ZnO interface. Wang et al. [83] reported the effect of energy level alignment on enhanced photoelectrochemical performance of CdS/CdSe core/shell nanorod arrays. Low bandgap CdSe extended the absorption edges of the array. CdS/CdSe Fermi level alignment enhanced the separation of photogenerated charges. Table 1 summarizes the reported photocurrent density of cadmium chalcogenide QDs sensitized ZnO.

Mi et al. [84] reported a double-band InGaN/GaN core/shell nanowire, in which GaN has a bandgap of 3.4 eV and InGaN 2.38 eV, extends the light absorption to 522 nm. The same research group also reported one-step overall water splitting under visible light using multiband InGaN/GaN nanowire heterostructures (Fig. 7). [85] Ten self-organized ~3 nm high InGaN/GaN quantum dots and a ~30 nm high InGaN segment, which is separated from the InGaN quantum dots by ~15 nm GaN layer, are subsequently incorporated along the axial dimension of GaN nanowires. Such InGaN/GaN well-dot-in-a-wire nanoscale heterostructures enable the harness of sunlight in the green spectral range.

Cuprous Oxide (Cu₂O) has a bandgap of 2.2 eV and can also be used as quantum dots to sensitize TiO₂ [86-88]. Tsui et al. [86] reported a significant improvement of the photoelectrochemical performance of TiO₂ nanotubes by

extending absorption into visible spectrum via modification with electrodeposition of cuprous oxide. Li et al. prepared $\text{Cu}_2\text{O}/\text{Cu}/\text{TiO}_2$ nanotube heterojunction arrays by assembling $\text{Cu}@\text{Cu}_2\text{O}$ core-shell nanoparticles on TiO_2 nanotube arrays (NTAs). [89] $\text{Cu}@\text{Cu}_2\text{O}$ core/shell nanoparticles extend the light absorption to 700 nm resulting from the narrow bandgap of Cu_2O and plasmonic effect of Cu core.

InP is another effective sensitizer [90] and Chen et al. [91] investigated multi-bandgap-sensitized ZnO nanorod photoelectrode arrays for water splitting. They concluded that the high photocurrent resulted from the extended light absorption of InP quantum dots of varied sizes in visible region rather than the driving force of charge injection.

2.2.3 Plasmonic Enhancement

An alternative to QDs and dye sensitizers is the use of plasmonic metal nanostructures combined with the metal oxide semiconductors to form plasmonic photocatalysts. The plasmonic nanostructures serve as the sensitizer for semiconductor catalyst. Here, localized plasmon resonances refer to the collective electron oscillations in noble metal nanocrystals induced by their interaction with light. Many metals have plasmon resonances that overlap with the solar spectrum. The material composition, shape, size and dielectric environment of metallic nanostructure affect the surface plasmon resonance (SPR). [13,14,92] The unique capability of plasmonic nanostructures to concentrate electromagnetic fields, scatter electromagnetic radiation, and convert the energy of photons into heat makes them suitable for various applications. Additionally, the solar flux is a fairly diffuse energy source with ~ 100 mW (or $\sim 10^{17}$ solar photons) impinging on the surface area of 1 cm^2 each second. Photo-excited plasmonic nanostructures are characterized by the strong electric field of orders of magnitude higher than the field of photons used to photo-

excite the nanostructure. [12] For solar-to-hydrogen energy conversion applications, studies have been limited to silver and gold. Plasmonic enhancement extends the light absorption wavelength to visible and even near-infrared region. [93] An illustration of a plasmonic solar water splitting system is shown in Fig. 8.

Au/TiO₂ significantly increases the hydrogen production compared to pristine TiO₂ because Au nanoparticles not only act as electron traps and active sites but also play an important role in SPR enhancement extending light absorption to visible region. [94] Liu et al. [95] believed that the photocatalytic activity in visible range is caused by increased electron hole pair generation rate at the surface of TiO₂ due to the local electric field enhancement near the TiO₂ surface, rather than by the direct transfer of charges between the two materials. Thomann et al. [96] reported that plasmonic resonances in metallic nanostructures could be engineered to strongly concentrate sunlight close to the electrode/liquid interface, precisely where the relevant reactions take place. Shi et al. [97] investigated Au/TiO₂ interfacial structure and its effects on photocurrent generation efficiency in visible wavelength region. The photocurrent generation efficiency of Au/TiO₂ photoelectrode is highly dependent on the annealing temperature of Au nano-islands, which is due to the different hot electron injection ability caused by different interfacial structure between Au-Ni and TiO₂.

Zhang et al. [98] designed and synthesized a visible light responsive TiO₂ nanotube photoelectrode with plasmonic Au nanocrystals coupled seamlessly with photonic crystal. The SPR wavelength of Au matches the photonic bandgap of the photonic crystal and thus the SPR of Au receives remarkable assistance from the photonic crystal substrate, which significantly increases the Au SPR intensity and consequently boosts the hot electron injection from Au nanocrystals into the

conduction band of TiO₂, leading to enhanced water splitting performance of the material under visible light. Au(566)/TiO₂ NTPC (nanotube with photonic crystal on top) shows a photocurrent density of $\sim 150 \mu\text{A cm}^{-2}$, which is 50 times that of the TiO₂ NTPC and is much higher than the photocurrent density of $\sim 60 \mu\text{A cm}^{-2}$ on the Au/TiO₂ NT without a PC (photonic crystal) layer.

Pu et al. [99] reported that TiO₂ decorated with a mixture of Au nanoparticles and nanorods showed enhanced photoelectrochemical water oxidation in the entire UV-visible region from 300 to 800nm. Results show that enhanced photoactivity of Au decorated TiO₂ NWs in UV region is due to effective surface passivation as well as electric-field amplification effect, while the photoactivity enhancement in visible region is mainly caused by the electrical field amplification effect and hot electron generation upon SPR excitation.

Zhan et al. [100] found that TiO₂/Au electrode structure affected the plasmon-enhanced photocatalytic water splitting performance. The Au-in-TiO₂ electrode greatly outperformed the Au-on-TiO₂ electrode, and 3D Au-embedded TiO₂ electrode could further improve the photocatalytic performance due to the enhanced light absorption. Under visible light irradiation (wavelength $>420 \text{ nm}$), Au-on-TiO₂ shows a photocurrent density of $0.35 \mu\text{A cm}^{-2}$, while it increases 3 times in Au-in-TiO₂ ($1.1 \mu\text{A/cm}^2$) and 5 times in 3D Au-embedded TiO₂ ($1.8 \mu\text{A cm}^{-2}$).

Au/Pt co-decoration in the TiO₂ nanofibers leads to remarkably enhanced photocatalytic activity and the enhancement is attributed to a synergistic effect from the electron-sink function of Pt and the SPR of Au nanoparticles, which significantly improves charge separation of photo-excited TiO₂. [101]

Pany et al. [102] synthesized nano Au deposited mesoporous S,N-TiO₂ (SNT) nanocomposite and obtained an energy conversion efficiency of 17.6%. It

synergistically combines surface plasmon resonance from 3.5 nm Au, narrower bandgap energy from N doping and effective charge transfer from the interaction between Au and sulfate.

Mubeen et al. [103] reported an autonomous photosynthetic nano-device in which all charge carriers were derived from the hot electrons resulting from the excitation of surface plasmons of an Au nanorod array which served as light-harvesting antennae and was capped with a crystalline TiO_2 layer forming a metal-semiconductor Schottky junction. Photogenerated electrons are injected from Au into CB of TiO_2 and further transfer to the surface of Pt nanoparticles on the TiO_2 to reduce H^+ to H_2 while holes are transfer to the surface of cobalt-based oxygen evolution catalyst oxidize H_2O to O_2 . Lee et al. [104] reported similar plasmonic water splitting cell except that the hydrogen reduction reaction was taken place at a Pt counter electrode, rather than on the surface of Pt nanoparticles attached to the TiO_2 surface.

Au- BiVO_4 heterogeneous nanostructure exhibits enhanced visible-light-driven photocatalytic activities compared to pure BiVO_4 . [105] The improved photocatalytic efficiency is due to the SPR absorption of Au nanoparticles and the improved charge separation on BiVO_4 surface because the conjugated Au nanoparticles on BiVO_4 surface act as electron sinks to retard the recombination of photogenerated electrons and holes in BiVO_4 so as to improve the charge separation on its surface.

Chen et al. [106] studied the localized plasmon-induced effects and charge separation in photoelectrochemical processes using X-ray absorption spectroscopy. Hot electrons generated by Au nanostructure plasmon are injected into the CB of ZnO , while the plasmon-induced electromagnetic field creates vacancies in the CB of the surface of ZnO , promoting the separation of photogenerated electrons and holes.

Hematite has a desirable bandgap of 2.2 eV to absorb visible light and it is earth-abundant, cost-effective, and photoelectrochemically stable, making hematite an excellent candidate for photoanodes in water splitting. However, hematite suffers a lot from its low absorption coefficient and low charge carrier mobility. SPR can readily boost light absorption and generate electron-hole pairs in the surface layer, thus reduce the length that the charge carrier needs to travel before reach the active sites at semiconductor/liquid interface where the water redox reaction happens. Gao et al. [107] reported plasmon-enhanced photocatalytic activity of iron oxide on Au nanopillars. A net enhancement as high as 50% was observed over solar spectrum and the enhancement could be attributed to increased optical absorption originated from both surface plasmon resonances and photonic-mode light trapping in the nanostructured topography. Wang et al. reported Au nanorod-enhanced light absorption and photochemical performance of hematite thin-film electrode for solar water splitting. [108] Li et al. [109] incorporated a hematite nanorod array into a plasmonic Au nanohole array pattern, which significantly improved the photoelectrochemical water splitting performance. The photocurrent was significantly enhanced for 150 nm long hematite nanorods grown on the gold nanohole array pattern when compared with hematite grown on bare FTO, with an enhancement factor of 10 (0.9 mA cm^{-2}) at bias of 0.23 V vs Ag/AgCl under the simulated solar full spectrum. The IPCE at 425 nm was 1.37% and 17.4% for hematite nanorods on the bare FTO and on a long-range ordered Au nanohole array.

Torimoto et al. prepared $\text{CdS@SiO}_2/\text{Au@SiO}_2$ nanocomposite photocatalyst, in which SiO_2 layer acts as an insulator to prevent direct electron transfer from photo-excited CdS to Au particles. Both SiO_2 shell thickness and Au core size affect the plasmonic effect in $\text{CdS@SiO}_2/\text{Au@SiO}_2$. [110] H_2 evolution rate of

CdS@SiO₂//Au@SiO₂ with 17 nm SiO₂ layer on Au core is larger than that of CdS@SiO₂, while H₂ evolution rate of CdS@SiO₂//Au@SiO₂ with 2 nm SiO₂ layer on Au core is smaller than that of CdS@SiO₂. H₂ evolution was enhanced in CdS@SiO₂//Au@SiO₂ with 19 nm or 73 nm Au cores.

Besides Au, Ag also can be used in plasmonic enhancement. [111, 112] Ag@Cu₂O core-shell nanoparticles exhibit photocatalytic activity over an extended wavelength range due to the localized SPR (LSPR) in Ag core. [111] The plasmonic energy is transferred from Ag to Cu₂O via plasmon-induced resonant energy transfer and direct electron transfer simultaneously. The light absorption of Ag@Cu₂O extends to longer wavelengths as the Cu₂O shell thickness increases.

2.3 Solid Solutions

In addition to doping and sensitization, forming solid solution between wide and narrow bandgap semiconductors is another method for controlling photocatalyst band structure.

GaN and ZnO are both well-known wide bandgap semiconductors and are most stable in Wurtzite form with similar lattice parameters. [17] They can be combined to form a solid solution with a general formula of (GaN)_{1-x}(ZnO)_x. This new material is capable of splitting water into hydrogen and oxygen under visible light with good reproducibility. [113-115] The bandgap of this system can be tuned by changing the composition of the solid solution. Reinert obtained a direct bandgap of 2.53 eV at the composition of x~0.55. [116]

Wu et al. [117] proposed a new Ta₃N₅:Ti₃O₃N₂ solid solution as a promising water splitting photocatalyst. First principle computation results show that the solid solution has a bandgap lower than both its end members and the minimal bandgap

may be around 2.0 eV. In addition, the CB and VB of the solid solution are predicted to be bracketing the water redox levels.

2.4 New single phase visible-light-active materials

An ideal semiconductor material for the photoelectrode should have a bandgap large enough (>1.6 eV) to split water and, at the same time, small enough (<2.2 eV) to absorb a wide range of the solar spectrum. [118] Meanwhile, the conduction band and valence band of the semiconductor should straddle the water redox potentials in order to split water without external bias. Finally, the semiconductor materials must be stable in aqueous solutions, from which most non-oxide semiconductors suffer in solar water splitting due to strong oxidation of photogenerated hole.

Many novel single-phase visible-light-responsive photocatalysts have been developed. Many oxides consist of metal cations with d0 and d10 configurations have been discussed in a few previous reviews and perspectives. [17,18,119,120] Table 2 lists a photocatalyst library offered by Kudo's Laboratory at Tokyo University of Science in which photocatalysts are grouped based on their functions. Such a library would be more useful if additional details from systematic research could be added to the table.

Metal (oxy)sulfide and metal (oxy)nitride are new types of visible light-driven photocatalysts. [118,121-125] The valence bands of these photocatalysts consist of N 2p and S 3p orbitals, in addition to O 2p, resulting in the formation of narrow bandgaps. Ta_3N_5 with a bandgap of 2.1 eV and suitable band positions is one of the few semiconductor materials that satisfy all the three requirements simultaneously. [118] Vertically aligned 1D Ta_3N_5 nanostructure has shown enhanced photocurrent density by a factor of 3.2 compared to that of a thin film photoelectrode. At an applied

potential of 1.23 V vs. RHE, the photocurrent density reached 3.8 mA cm^{-2} under AM 1.5 G simulated sunlight at 100 mW cm^{-2} . But the photocurrent decayed rapidly upon illumination for the bare Ta_3N_5 nanorod photoelectrode due to the photo-oxidation of the Ta_3N_5 . Modification with proper co-catalyst may suppress the degradation of the photoanode and improve the stability.

3. Efficiency of charge separation and migration

The electron-hole pairs can separate and migrate to photocatalyst/electrolyte interface or undesirably recombine. In order to improve the solar-to-hydrogen efficiency, it is essential to promote the charge separation and transport to the surface (i.e. the interface between semiconductor and water) to drive the H^+ reduction and H_2O oxidation reactions.

During the transport of the excitons to the surface, they may run into the following 5 scenarios: [126]

- 1) Reside in the conduction band and valence band respectively and subsequently recombine;
- 2) Diffuse away from each other, leading to charge separation, simultaneously the electrons and holes relax to the corresponding edges of the bulk CB and VB;
- 3) Captured by trap states during diffusion and separation due to the bulk or surface defects and vacancies;
- 4) Trapped electrons and holes recombine with the VB holes and CB electrons, or trapped electrons recombine with the trapped holes;
- 5) Surviving electrons and holes arrive at the surface reaction sites to promote reduction and oxidation reaction respectively.

Charge separation efficiency is related to the exciton binding energy and the driving force. The exciton binding energy is proportional to $1/\epsilon^2$ and the semiconductors with low dielectric constants generate excitons with high binding energy. The driving force can be thermal energy or built-in electromagnetic field. Thermal energy (kT , k = Boltzmann constant and T = temperature) at room temperatures is approximately 25 meV [127], which cannot separate the tightly bound electron-hole pairs. For separation, the exciton must diffuse to the junction without recombination. The charge separation efficiency is therefore associated with the exciton diffusion length and the exciton dissociation driving force. For example, excitons in ZnO have a binding energy of about 60 meV [127], bigger than the thermal energy at room temperature (i.e., 25 meV), and need a higher driving force to dissociate. In another case, the binding energy of excitons in TiO_2 is only about 6 meV. Illumination of TiO_2 generates free carriers in the bulk which segregate to the electrodes due to the built-in potential of p-n junction.

In general, semiconductors suffer greatly from the charge carriers' bulk and surface recombination. It is therefore critical to develop and exploit effective approaches to reducing electron-hole recombination including nanostructuring the photoactive materials, decreasing the distance of the charge carriers to travel before reaching surface reactive sites, utilizing interfacial space regions to enable localization of single charge carrier at the materials interface, applying co-catalysts to accelerate interfacial oxidation-reduction kinetics, constructing heterojunction structures to achieve spatial separation of electrons and holes, and employing composite materials, such as graphene or carbon nanotubes to serve as electron or hole sinks.

3.1 Co-catalyst loading

As shown in Fig. 10, loading co-catalysts can promote charge separation, reduce the charge recombination and accelerate the surface chemical reactions.

The co-catalysts can act as trapping sites for the photogenerated charges and promotes the charge separation to enhance the quantum efficiency. They also improve the photostability of the photocatalysts by timely consumption of the photogenerated charges, particularly the holes. [15]

Pan et al. [128] integrated oxygen vacancies formation and noble-metal deposition to achieve efficient visible light absorption and photogenerated electron-hole separation. The results show that the oxygen vacancy creation noticeably enhances the visible-light absorption of semiconductor TiO_2 and the noble-metal deposition effectively improves charge separation efficiency of $\text{TiO}_2\text{-O}_v$ under visible-light irradiation. Palladium quantum dots-sensitized TiO_2 nanotube arrays show promoted photocatalytic hydrogen production rate due to synergistic effects between the nanotubular structure of TiO_2 and uniformly dispersed Pd and QDs on TiO_2 , [129] which facilitates the charge transfer of photoinduced electrons from TiO_2 nanotubes to Pd QDs as well as the activity of Pd QDs catalytic center.

Huang et al. [130] reported effective photoluminescence quench by loading dual co-catalysts, indicating efficient charge separation and suppression of electron-hole pair recombination.

Modification with cobalt phosphate (Co-Pi) can improve the photoinduced charge separation in nc- TiO_2 through effectively capturing of holes by cobalt (II) cations to produce high-valence cobalt cations with strong oxidation ability. [131] Zhong et al. [132] reported that loading Co-Pi co-catalyst on the surface of W:BiVO_4 could almost completely suppress the surface recombination of electron-hole pairs.

Barroso et al. [133] observed that the addition of cobalt-based electrocatalysts could increase the lifetime of the photogenerated holes in the photoelectrode by more than 3 orders of magnitude without the application of electrical bias. Formation of a Schottky-type heterojunction between Co-Pi and α -Fe₂O₃ enhances the charge separation and reduces recombination losses, leading to enhanced photoelectrochemical activity.

3.2 Semiconductor combinations

3.2.1 Heterojunction structure

The use of heterojunction structures is an important strategy because it utilizes a combination of properties from each component and the mini-device, leading to an improved overall efficiency. [134,135] The heterojunction can extend the spectral range of light absorption, [136,137] promote photogenerated electron-hole separation, [136] minimize electron-hole recombination, [138,137] and thus significantly enhance energy conversion efficiency. [123,140]

Fang et al. [136] constructed ternary Au@TiO₂-CdS nanostructures by decorating CdS nanoparticles onto Au@TiO₂ core-shell structures. CdS nanoparticles extend the absorption into visible light range and the ternary design builds up a transfer path for the photo-excited electrons of CdS to the core Au particles via the TiO₂ nanocrystal bridge and thus effectively suppresses the electron-hole recombination.

CdTe layer deposited on FTO shows p-type behavior and generates a cathodic photocurrent, but TiO₂/CdTe electrodes generate an anodic photocurrent, indicating that when the TiO₂/CdTe/electrolyte junction is formed, the injection of photogenerated electrons from CdTe to TiO₂ is more favored than that from CdTe to

the electrolyte. [141]

Wang et al. [138] synthesized crystalline core/amorphous shell W doped TiO_2 NW using a simultaneous etching and doping method, showing improved photocurrent density attributable to the enhancement of charge transfer and increase of charge carrier density resulting from combined effects of etching and W-doping.

MoS_2 has an indirect absorbance edge at ~ 1040 nm, which seems ideal for solar light harvesting, but MoS_2 alone has negligible photocatalytic activity. When combined with photocatalyst, MoS_2 then exhibits photoelectrochemical activity. [137,139] In the combination of MoS_2 and CdS, [137] MoS_2 not only extends the light absorption region but also inhibits the photocorrosion of CdS. In addition, the heterojunction between MoS_2 and CdS promotes the electron injection from MoS_2 to CdS and hole injection from CdS to MoS_2 , which leads to an efficient charge separation.

Meng [139] reported a p- MoS_2 /n-rGO heterostructure with significant photocatalytic activity towards hydrogen evolution reaction (HER). Here the rGO refers to reduced graphene oxide. The photoelectrochemical measurement shows that the heterojunction greatly enhances charge generation and suppresses charge recombination.

Impedance spectroscopy analysis indicates that $\text{CaFe}_2\text{O}_4/\text{TaON}$ heterojunction enhances electron-hole separation by reducing the resistance to the transport of charge carriers. [123] Lin [140] reported nanonet $\text{TiSi}_2/\alpha\text{-Fe}_2\text{O}_3$ hetero-nanostructures (Fig. 11) with high external quantum efficiency of hematite in water splitting. TiSi_2 nanonets are highly conductive and have high surface area to serve as structural scaffold and efficient charge collector so as to enhance charge transport.

3.2.2 Graphene

Graphene has excellent charge carrier mobility as electron mediators for shuttling electrons and effectively promoting the separation of photogenerated carriers. [135,142,143]

Hou et al. [135] reported a novel heterojunction array of α -Fe₂O₃/graphene/BiV_{1-x}Mo_xO₄ core/shell nanorod with α -Fe₂O₃ nanorod cores, graphene interlayer, and BiV_{1-x}Mo_xO₄ shells. Mo-doped BiVO₄ enhances the light absorption, and graphene serves as fast transfer pathway of charge carriers to promote electron separation and transfer so as to achieve enhanced photoelectrochemical (PEC) water splitting performance.

Meng et al. [144] reported the enhancement photocatalytic water oxidation activity of hematite (α -Fe₂O₃) by coupling with reduced graphite oxide (rGO). Transient absorption spectroscopy and time-domain terahertz spectroscopy show the direct evidence that the photogenerated electrons have transferred from α -Fe₂O₃ to rGO, which enhances the charge separation and suppresses the charge recombination.

TiO₂-graphene hybrids possessed enhanced light absorption ability and charge separation efficiency. [145] The property of interface between TiO₂ and graphene was seen to greatly affect the rates of H₂ production and photocurrent generation. [146] A direct contact interface between reduced nanosized graphene oxide (r-NGO) and TiO₂ in reduced nanosized graphene oxide-coated TiO₂ nanoparticles (r-NGOT) is much larger than that in reduced large graphene oxide coated with TiO₂ nanoparticles (r-LGOT) (TiO₂ nanoparticles loaded on a larger graphene sheet), indicating the r-NGO facilitates the interfacial electron transfer and retard the charge recombination. Xiang et al. [147] reported an enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles due to synergetic effect of MoS₂ and graphene to efficiently suppress

charge recombination, improve interfacial charge transfer and provide a greater number of active absorption sites and photocatalytic reaction centers.

CdS/graphene shows about 4.87 times higher H₂-production rate than pure CdS nanoparticles. [148,149] The high photocatalytic H₂-production activity is attributed to the presence of graphene serving as an electron collector and transporter to efficiently lengthen the lifetime of the photogenerated charge carriers. Ng et al. [150] reported significant H₂ and O₂ evolution in BiVO₄/rGO PEC water splitting cell while negligible gas evolution was observed in pure BiVO₄ cell. The enhancement is again due to a longer electron lifetime of excited BiVO₄ as the electrons are injected to rGO instantly at the site of generation resulting in a minimized charge recombination.

3.3 Modification of crystal structure and morphology

In general, the separation and transportation of photogenerated charges are strongly affected by the material crystallinity, defects and crystal structure distortion. In addition, surface properties such as particle size, surface area, surface structure and active reaction sites, which are mainly related to the size and morphology of the materials, are also important. [17]

3.3.1 Modification of crystal structure

The collection efficiency of photogenerated charge carriers is determined by the overall lifetime of the charge carriers, distance that the charge carriers have to travel, and the bulk recombination rate. The bulk recombination rate is determined by the electronic structure of the semiconductor. Modifications of the crystal structure leading to increased crystallinity, reduced defects, and improved charge carrier density will result in improved conductivity and enhanced charge carrier transport.

The as-grown ZnO NWs are defect-rich, attributable to intrinsic defect states, including V_O and V_{Zn} acceptor states. Air annealing can improve the crystal structure and reduce the defects and hydrogen treatment can reduce defect-related recombination by passivating V_{Zn} trap states. A combination of air annealing and hydrogen treatments can create films with no detectable donor-acceptor pair recombination. [151]

Ng et al. [152,153] reported a self-photochargeability phenomenon that extends the functionality of the WO_3 photoelectrodes without continuous irradiation, allowing photo-excited charges to be stored and utilized for H_2 generation in the absence of light. For the self-photochargeability phenomenon, the charge storage capability increases as calcination temperature decreases with films exhibiting short-range order displayed the highest storage capability. [154] For the charge separation and transportation, the conductivity of WO_3 increases with increasing calcination temperature. But high calcination temperature decreases the effective surface area of the films and worsens the contact between WO_3 and charge collecting electrode. Therefore, film annealed at 400 °C shows the best performance in PEC water splitting application.

Wang et al. [155] reported computational and photoelectrochemical study of hydrogenated $BiVO_4$. $BiVO_4$ is reduced by hydrogen gas during the hydrogenation process to form oxygen vacancies and hydrogen impurities. DFT calculation results show that both oxygen vacancies and hydrogen impurities are shallow donors for $BiVO_4$ with low formation energy, which can increase the donor density of $BiVO_4$ without introducing deep trap states. Hydrogen-treated $BiVO_4$ photoanode shows a maximum photocurrent density of 3.5 $mA\ cm^{-2}$ at 1.0 V vs. Ag/AgCl, which is 1 order of magnitude higher than the value of 0.3 $mA\ cm^{-2}$ obtained for air-annealed

BiVO₄ at the same potential. Abdi et al. [156] reported gradient W-doped BiVO₄ photoanode with a stable short circuit water splitting photocurrent of ~4 mA cm⁻² (corresponding to a solar-to-hydrogen efficiency of 4.9%). Gradient dopant concentration in the BiVO₄ film creates a distribution of n⁺-n homojunction through which carrier-separation efficiencies of up to ~80% are achieved.

Kim et al. [157] reported Pt-doped hematite coupled with Co-Pi co-catalyst exhibiting a stable, record-breaking performance of 4.32 mA cm⁻² PEC water oxidation current at 1.23 V vs. RHE under simulated 1-sun irradiation. Pt-doping effectively improves the electrical conducting property of hematite by increasing its donor density.

Wang et al. [158] reported nanostructured hematite photoanodes with lattice defects showing water splitting photocurrent density of 1.2 mA cm⁻² at 1.6 V vs. RHE, 1.5 folds compared with the value achieved with a defect free sample. Lattice defects introduced in hematite nanostructure decrease the flatband potential from 0.63 to 0.58 V vs. RHE, increase the carrier density from 1.83×10²⁰ cm⁻³ to 5.44×10²⁰ cm⁻³, reduce the oxygen evolving potential from 0.9 to 0.8 V vs. RHE, hence enhance the light harvest for more efficient hydrogen production via PEC.

Ling et al. [159] reported Sn-doped hematite nanowire and nanocorals showing photocurrent densities of 1.24 and 1.86 mA cm⁻² at 1.23 V vs. RHE respectively. The enhanced photoactivity of Sn-doped hematite nanostructures results from improved electrical conductivity and increased surface area [160] rather than the suppressing of electron-hole recombination since ultrafast spectroscopy studies show that Sn-doping has no major effects on the ultrafast dynamics of the charge carriers on the picosecond time scale. Frites et al. [161] reported that carbon modified (CM)-n-Fe₂O₃ showed a photocurrent density of 3.14 mA cm⁻² at 0.0 V/SCE, doubling that of

n-Fe₂O₃ in the same condition due to the incorporation of carbon in iron oxide during flame oxidation which leads to the increase of conductivity in CM-n-Fe₂O₃.

Reducing the concentration of carrier trapping states of ultrathin film by improving crystallinity of hematite via controlled nucleation and growth process leads to a photocurrent of 0.63 mA cm⁻² at 1.5 V vs. RHE under standard illumination conditions. [162-165]

Controlled doping of Sn into TiO₂ NWs can enhance the PEC conversion efficiency through the improvement of photocurrent arising from the increased charge carrier densities. [166]

3.3.2 Modification of size and morphology

A crucial obstacle that limits the efficiency of almost every oxide semiconductor photocatalyst is the high charge-carrier recombination fundamentally related to the discrepancy between the relatively large penetration depth of photon and the short diffusion length of charge carriers. One of the approaches to addressing this problem is to control the photocatalyst structure to maximize photon absorption and minimize the distance charge carriers travel before reaching the surface. Typical photoelectrode designs include mesoporous nanostructures [167], one-dimensional (1D) nanostructures (nanowire [168,169], nanotube [170], nanorod [171]), thin films [172], as well as 3D hierarchical nanostructures. [173-177]

Introducing nano-ATO (nano-antimony-doped tin oxide) conductive underlayer between hematite and FTO substrate largely increases light absorption, effectively reduces electron-charge recombination, and thus enhances the photocurrent density to 0.83 mA cm⁻², 3-fold higher than that of the pristine photoanode without nano-ATO conductive underlayer. [167]

One-dimensional (1D) nanostructures such as nanowire and nanotube arrays can decouple the directions of light absorption and charge carrier collection. [9,47] Hwang studied the photoelectrochemical properties of TiO_2 nanowires. [168] Results show that photon absorption increases with the length of nanowire. Atomic layer deposition of epitaxial rutile TiO_2 shell on nanowire enhances the charge separation and further increases the photocurrent density. Decorating TiO_2 nanotube with quantum-sized anatase nanowires induces great enhancement of interfacial area of the tubular structure. In addition, the band alignment of anatase and rutile TiO_2 promotes the charge carrier separation and transfer. [170]

BiVO_4 has a bandgap of 2.4 eV and is a promising photocatalytic material candidate. However, EIS (electrochemical impedance spectrum) study shows poor charge transport characteristics of BiVO_4 which leads to low photoactivity of bare BiVO_4 film. [172] On the other hand, when coupled with WO_3 to form heterojunction, the photogenerated electrons in BiVO_4 are transferred to WO_3 layers with good charge transport characteristics resulting in high photoactivity. [172] $\text{WO}_3/\text{BiVO}_4$ heterojunction nanorod-array shows significantly improved photoelectrochemical properties due to high surface area and improved separation of photogenerated charge at $\text{WO}_3/\text{BiVO}_4$ interface. [171] $\text{WO}_3/\text{BiVO}_4$ core/shell nanowire with BiVO_4 as primary light absorber and WO_3 as electron conductor achieves the highest light absorption and charge separation efficiencies among BiVO_4 -based photoanodes to date. [169]

Yang et al. [173] constructed a 3D hierarchical TiO_2 nanostructured array with rutile TiO_2 nanodendrite (ND) array as core and anatase TiO_2 nanoparticles (NPs) in the shell. TiO_2 ND array provides a fast electron transport pathway due to its quasi-single-crystalline structure. The 3D configuration with NPs in the shell provides a

large surface area for efficient photocharge separation and the rutile-anatase TiO_2 heterojunction further enhances charge separation and suppresses charge recombination at the interfacial region.

Kong et al. [174] investigated highly porous 3D hierarchical nanostructures with ZnO nanorods grown on polyacrylonitrile (PAN)/indium tin oxide (ITO) nanofibers. The double light-trapping effects brought by increased light-ZnO interaction and the suspended PAN/ITO nanofibers lead to effective light absorption with almost zero transmission. This effective light absorption coupled with large contact area of ZnO nanorods with electrolyte and the conduction paths formed by the ITO particles contributes to high photoelectrochemical properties.

Surface plasmon resonance induced formation of charge carriers near the semiconductor surface also contribute to minimizing the travel distance of charge carriers before reaching the surface. [178]

Peng et al. [179] made use of solution-processed ATO nanoparticle films on FTO glass as core conductive scaffold to enhance the charge separation and transfer from TiO_2 semiconductor shell so as to inhibit the electron-hole charge recombination. The scaffold enables efficient charge separation and transportation and addresses the dilemma of large optical penetration depth and short diffusion length of minority carriers.

Kargar et al. reported three-dimensional (3D) ZnO/CuO [175], n-ZnO/p-Si [177] and ZnO/p-Si [176] heterojunction branched nanowires. Lightly doped p-type Si and CuO NW core show broadband absorption from UV to near IR region, 3D branched nanowires reduce the photogenerated charge carrier diffusion length, Zn/CuO and ZnO/p-Si heterojunction promotes the electron-hole separation. Liu reported similar hierarchical CuO/ZnO “corn-like” architecture in 2011. [180]

Liu et al. [181] synthesized a nanotree heterostructure in which the Si nanowire served as the trunk and the TiO₂ nanowires as the branches. Sun et al. [182] fabricated 3D branched nanowire heterojunction photoelectrodes with Si nanowire as backbone and ZnO nanowire branch. Bandgap combination and energy level alignment enhance the light absorption and charge separation simultaneously. Other than TiO₂ or ZnO, InGaN was also used to construct core/shell hierarchical nanowire arrays in which single phase InGaN nanowires grew vertically on the sidewalls of Si wires and acted as a high surface area photoanode for solar water splitting. [183]

Yin et al. [184] reported the tree-like heterostructures ZnO/TiO₂/CuO, that is, 1D vertical ZnO NWs (tree trunk) coated with two-dimensional (2D) TiO₂ nanosheets (tree bark) on which 1D CuO nanoneedles (tree branches) were anchored. 1D ZnO NWs give high electron mobility, TiO₂ NS exhibits high photocatalytic activity and excellent sustainability and CuO NN extends the light absorption to near-infrared region.

Nanostructured photoelectrodes and photocatalysts offer large surface area, shorten carrier diffusion pathways, improve light distribution, and promote charge transfer so that enhanced light absorption, charge carrier transportation and redox reaction efficiency become achievable. But large surface area and nanostructure can also lead to increased surface recombination and reduced space charge layer thickness, which is detrimental to charge separation and transportation.

3.4 Surface passivation

Surface recombination at trapping states is an important factor that affects water reduction and oxidation overpotential. Using conformal overlayers or surface-

modification to passivize trapping states can decrease the overpotential effectively and hence increase photoelectrochemical performance. [185-188]

Gholami et al. [185] reported Ag₂S nanoparticle incorporated TiO₂ nanotube array for visible water splitting. Results show that Ag₂S nanoparticles can passivize the charge recombination centers and enhance electron-hole separation. Ultra-thin coating of Al₂O₃ reduces the overpotential 100 mV and increases the photocurrent by a factor of 3.5 at 1.0 V vs. RHE. [186]

There are high densities of surface states in hematite, which causes Fermi level pinning at the energy corresponding to such states and consequent decrease in the space charge layer. Passivation of these states by treatment of hematite surface with CoO_x and Ga₂O₃ enhances electron depletion within the film for a given bias. [187] The origin of the cathodic shift of the photocurrent onset of CoO_x or Ga₂O₃ treated hematite is attributed to the reduced electron-hole recombination and increased yield of long-lived holes at the electrode surface rather than the removal of surface recombination centers or enhanced kinetics of water photo-oxidation. Sun et al. [188] reported the surface-modification of nanosized α -Fe₂O₃ with phosphate. Partial substitution of –Fe-OH with –Fe-O-P-OH surface ends greatly improves the amount of O₂ adsorbed on the surfaces of Fe₂O₃, which is responsible for the enhanced charge separation and the visible photocatalytic activity.

3.5 Improving the exciton diffusion length

Minority charge carrier diffusion length is another important parameter that affects the charge carrier transfer efficiency. Most of the widely studied photocatalysts suffer from the short minority carrier diffusion length. For example, TiO₂ has a hole diffusion length of 10-100 nm while the hole diffusion length in

Fe₂O₃ is only 2~4 nm. Short diffusion length is associated with high recombination rate, hence decreases the charge separation and transportation efficiency. Meanwhile, short diffusion length also restricts the thickness of absorption layer leading to low absorption efficiency. Both of them are detrimental to the water splitting efficiency.

Organo-metal hybrid Perovskite materials show promises to work with mesoporous titania and alumina due to its large carrier diffusion length. [189-191] Lam et al. [192] reported a solar cell power conversion efficiency (PCE) of 5.2% under simulated AM 1.5G irradiation (100 mW cm⁻²) and an internal quantum efficiency of close to 100% suggesting nearly all of the absorbed photons are converted to electrons efficiently collected at the electrodes. This implies that the exciton diffusion, charge transfer and charge collection are all highly efficient. The high exciton diffusion efficiency is enabled by the long diffusion length of CH₃NH₃PbI₃ relative to its thickness.

The efficiency of the solar cell based on the mentioned perovskite material has been improved from 3.8% [193] to 15.4% [194] in the past four years (2009-2013). The high efficiency comes from its appropriate bandgap as well as extraordinary charge carrier diffusion length exceeding 1 micrometer. [194] Large charge carrier diffusion length leads to low electron-hole recombination rate and high electron/hole transfer rate. These attributes are equally critical to the solar water splitting efficiency.

4. Efficiency of Catalytic Reduction and Oxidation Reactions

As stated before, the overall water splitting reaction is a thermodynamically uphill reaction involving multiple electron transfer processes. Even if the photogenerated electrons and holes have thermodynamically sufficient potentials for water splitting reaction, they may recombine if there are no suitable active/reaction

sites available on the surface of the light harvesting semiconductor. Therefore, in the third step illustrated in Fig. 1, the surface character (active sites) and quantity (surface area) play a key role.

Amirav and Alivisatos studied luminescence of individual quantum dot photocatalysts. [195] The results imply that manipulating photoinduced charge-transfer rates and prolonging the lifetime of charge-separated state, in the 10^{-7} s time regime, might suffice for significant improvement of the catalytic efficiency. This information can benefit the design of effective artificial photocatalytic systems for renewable direct solar-to-fuel energy conversion.

4.1 Loading of cocatalyst

Proper loading of oxidation and/or reduction cocatalysts on semiconductors can facilitate oxidation and reduction reactions by providing the active sites/reaction sites and suppressing the charge recombination and reverse reactions. [15] Most importantly, the cocatalysts catalyze the reactions by lowering the activation energy.

4.1.1 Cocatalyst for water oxidation half reaction: $4h^+ + 2H_2O \rightarrow O_2 + 4H^+$

Due to the reaction dynamics, it usually needs large overpotential to drive the water reduction or oxidation reaction. Loading with cocatalyst can increase the kinetics of the hydrogen or oxygen evolution reaction. Water oxidation with simultaneous oxygen evolution is a four-proton-coupled electron transfer process with an approximately 3 orders of magnitude lower rate than the hydrogen evolution reaction in water electrolysis. [196] The activation energy of the water oxidation dominates the activation energy of the overall water splitting. Water oxidation reaction is considered to be the greatest challenge in the photocatalytic water splitting,

and more efficient water oxidation cocatalysts remain to be a research frontier to be explored. [15]

McCrory et al. [197] evaluated the activity of a series of electrocatalysts (CoO_x , CoPi , CoFeO_x , NiO_x , NiCeO_x , NiCoO_x , NiCuO_x , NiFeO_x and NiLaO_x) for water oxidation ($4\text{h}^+ + 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+$) by measuring the overpotential required to achieve a photocurrent density of 10 mA cm^{-2} per geometric area (approximately the current density expected for a 10% efficient solar-to-fuel conversion device). The results show that, in alkaline solution, every non-noble metal system can achieve 10 mA cm^{-2} at similar operating overpotentials between 0.35 and 0.43 V and every system but IrO_x is unstable under oxidative conditions in acidic solutions. Grimaud et al. [198] reported a new double perovskites $(\text{Ln}_{0.5}\text{Ba}_{0.5})\text{CoO}_{3-\delta}$ ($\text{Ln}=\text{Pr}$, Sm , Gd and Ho) as a family of highly active catalysts for the oxygen evolution reaction upon water oxidation in alkaline solution. The high activity and stability of these double perovskites can be attributed to having the O p-band center neither too close nor too far from the Fermi level computed from ab initio studies.

Kanan and Nocera [199] deposited CoPi on an inert indium tin oxide electrode from phosphate-buffered water containing cobalt (II) ions which catalyzed the oxygen production from water without excessive overpotential. The CoPi catalysts exhibited a Tafel slope of $2.3 \times RT/F$ for the production of oxygen from water in neutral solutions, together with an inverse first order dependence on proton activity and zeroth order dependence on phosphate for $[\text{Pi}] > 0.03\text{M}$ [200]. Pijpers et al. [201] prepared CoPi on ITO-passivated silicon electrodes, which enabled the water-splitting reaction to happen under lower overpotential at neutral pH. CoPi catalyst formed from cobalt metal film on ITO-passivated silicon photoanode shows a catalytic onset at 0.85 V under illumination, which is lower than that of solution-deposited CoPi catalyst

(catalytic activity onset at 1.05 V) and ITO only contact (catalytic activity onset at 1.6 V). [202]

CoPi catalysts prepared from sputter-deposited cobalt metal film [203] exhibit similar composition and function with the catalysts deposited from aqueous solutions containing phosphate and Co^{2+} . Costi et al. [204] prepared CoPi OER catalyst by transformation of Co metal film on CdSe photoanodes. The formed CoPi serves as OER catalyst enhancing water splitting and protects the CdSe from oxidation and degradation.

Esswein et al. [205] deposited cobalt-based oxygen evolving catalysts (Co-OEC) from pH 7 phosphate Pi, pH 8.5 methylphosphonae, MePi, and pH 9.2 borate electrolyte, Bi. Co-OEC can achieve appreciable current density in near neutral pH buffered natural water, which makes this catalyst a viable oxygen evolution reaction catalyst.

Nickel-borate oxygen evolution reaction catalyst can be electrodeposited from dilute Ni^{2+} solutions in borate electrolyte at pH 9.2 (Bi). [206] Anodic activation can change the structure and oxidation state of NiBi and subsequently achieve dramatic increase in its catalytic rate. [207] Anodic activated NiBi exhibits low Tafel slope of $2.3 \times RT/2F$ (30 mV/decade at 25 °C), which, together with an inverse third order rate dependence on H^+ activity, makes NiBi an ideal co-catalyst for oxygen evolution reaction in water splitting. [208]

Manganese oxide catalyst (MnO_x) was electrodeposited from Mn^{2+} solutions in a weakly basic electrolyte and could be operated in acid by exploiting a self-healing process [209,210].

The research in Nocera group included the preparation [202,203,211], structure [212-214], and catalytic performance and mechanism [200,215-218] of

several kinds of oxygen evolution reaction catalysts, such as CoPi [199,201,219], CoBi [205,220], NiBi [206-208] and MnO_x. [209,210] These materials can be loaded on photoanodes as cocatalysts for the oxygen evolution reaction.

Liu et al. [221] reported *in situ* loading transition metal oxide clusters (MnO_x, FeO_x, CoO_x, NiO_x and CuO_x) on TiO₂ nanosheets as co-catalysts for exceptional high photoactivity. The heterojunctions formed between TiO₂ nanosheets and metal oxide clusters enhance the charge separation and transfer across the interface. These transition metal oxides clusters serve as co-catalysts to trap photogenerated holes and participate in photocatalysis. Co-Pi modified TiO₂ shows high photocatalyst activity for PEC water oxidation. [131] The phosphate groups can make cobalt ions connect to the surfaces of TiO₂ and transport charge. The linked Co²⁺ can effectively capture photogenerated holes to form high valence Co ions so as to promote charge separation, and the produced high-valence Co ions easily induce the water oxidation reactions to evolve O₂ and simultaneously change to Co²⁺.

The photocurrent density of Co₃O₄/Fe₂O₃ nanorods is improved from 0.72 for pristine Fe₂O₃ nanorods to 1.20 mA cm⁻² at 1.23 V vs. RHE (i.e., a 67% improvement), and the onset potential is shifted by ~40 mV. [132] The photocurrent of submonolayer Co(OH)₂/Co₃O₄ catalyst coated nanostructured inverse opal scaffold hematite reaches 0.81 and 2.1 mA cm⁻² at 1.23 and 1.53 V vs. RHE respectively. [223] EIS study shows that loading of just 1 ALD cycle cocatalyst can accelerate the charge transfer kinetics from the surface of the photoanode to the electrolyte due to the reduction of steady-state concentration of oxidized surface states, along with the reduction of charge transfer resistance from those surface states. Thermal decomposition deposition CoO modified hematite shows a photocurrent density of 0.7 mA cm⁻² at 2.13 V vs RHE [224] (180% improvement comparing with pure hematite).

BiVO_4 has suitable bandgap and bandgap edge for water oxidation, but pristine BiVO_4 produces low and unsustainable photocurrent due to poor catalytic ability of the BiVO_4 surface. [225] Loading catalytic FeOOH layer on the BiVO_4 surface leads to significantly improved photocurrent (reaching 1.0 mA cm^{-2} at ca 0.5 V vs RHE) and stability for photo-oxidation of water. Wang [226] reported the use of electrocatalyst as oxidation cocatalyst in photocatalytic water oxidation on BiVO_4 . Results show that the O_2 evolution rate of photocatalytic water splitting under visible light irradiation can be significantly enhanced by deposition of electrocatalyst Co-Pi on BiVO_4 .

Klahr et al. [227] found that Co-Pi catalyst could efficiently collect and store photogenerated holes from hematite electrode under illumination. This charge separation reduces surface state recombination leading to increased water oxidation efficiency. Zhong et al. [228,229] reported that deposition of Co-Pi on Fe_2O_3 exhibits a 5-fold enhancement in the photocurrent density and O_2 evolution rate at 1.0 V vs RHE. Tilley et al. [230] achieved a water splitting photocurrent of over 3 mA cm^{-2} at 1.23 V vs RHE under AM 1.5G 100 mW cm^{-2} simulated sunlight condition via nanostructure and IrO cocatalyst loading.

4.1.2 Cocatalyst for water reduction half reaction: $2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2$

Most semiconductors cannot give high H_2 evolution activities without a co-catalyst even in the presence of sacrificial electron donor due to the facile recombination of electron-hole pairs and the slow kinetics of the surface reaction. [15] Cocatalyst loading can serve as electron sinks and provide effective proton reduction sites, hence provides a redox pathway with low overpotential and catalyzes the reaction by lowering the active energy.

Ikeda et al. [231] reported the activity of size-controlled Rh nanoparticle cocatalyst and results showed that the smaller Rh cores gave higher activity than the larger ones when loaded in the same conditions due to the increase of surface area of Rh core, improvement of charge separation and increase of active sites for H₂ evolution as the size of Rh NPs decreases. Yoshida et al. [232] investigated the enhancement photoactivity of Lanthanide oxide modified Rh metal nanoparticles on (Ga_{1-x}Zn_x)(N_{1-x}O_x) photocatalyst. The formation of redox-inactive lanthanoid oxide layers on the Rh nanoparticles effectively suppresses the backward water formation reaction from H₂ and O₂ on Rh.

The SPR of Au nanoparticles on TiO₂ surface exhibits photo absorption around 550 nm, which leads to visible light induced hydrogen formation. At the same time, metal cocatalyst (M) in Au/TiO₂-M affects the H₂ evolution rate which decreases in the order Pt>Pd>Ru>Rh>Ag>Cu>Ir. [233]

Dasgupta et al. [234] reported atomic layer deposition (ALD) of platinum catalysts on nanowire surface to achieve conformal coating of ultra-high-aspect-ratio structures with precise control of catalyst loading and size to minimize the overall raw material cost.

Yu et al. [235] studied hydrogen reduction by photocatalytic water splitting over Pt/TiO₂ nanosheets with exposed (001) Facets. Results show that photocatalytic hydrogen production rates of TiO₂ nanosheets can be significantly enhanced by loading Pt on the TiO₂ nanosheets, and the TiO₂ nanosheets with a 2 wt% Pt deposition exhibits the highest photocatalytic activity.

The photocatalytic activities of titanate, niobate, and tantalate photocatalysts for water splitting are improved by the loading of fine gold particles. The back-

reaction between H_2 and O_2 to produce water on the Au cocatalyst was found to be negligible in comparison with that on a Pt cocatalyst. [236]

4.2 High surface area

Surface chemical reaction process involves adsorption of reactive molecules, reaction between photogenerated electrons and holes and adsorbed molecules mediated by photocatalyst or cocatalyst, desorption of product molecules. The reaction efficiency is affected by the characteristics and quantity of the reaction sites. Cocatalyst serves as the reaction sites and catalyzes the reactions. Water-accessible surface area greatly affects the quantity of the reaction sites. Mesoporous structure, 1D nanostructure, 3D hierarchical structure can greatly increase the surface area of the photocatalyst and therefore enhance the solar water splitting efficiency.

5. Summary and Outlook

Solar water splitting is a promising route for the renewable production of hydrogen. For commercial applications, solar driven water splitting should meet the requirements of efficiency, cost and longevity. Jaramillo et al. [237] analyzed the technical and economic feasibilities of four types of solar-to-hydrogen devices. The final cost varied from \$1.60 - \$10.40 per kg H_2 with the particle bed system having significantly lower cost. However, the particle-based system has safety concerns due to the cogeneration of H_2 and O_2 in a single bed system and long molecular transport lengths in the dual bed system, leading to greater uncertainty in their operation. Photoelectrode systems are more expensive due to their significant capital costs. Fortunately, sensitivity analysis also reveals that improving efficiency and employing solar concentration can significantly reduce the cost.

Strategies to improve solar-to-hydrogen efficiency include (1) bandgap engineering for the development of narrower bandgap semiconductor materials to absorb broader spectrum of solar energy, (2) materials engineering to tune the physical properties for efficient charge separation and migration, and (3) band level engineering to match the redox potentials of water reduction and oxidation.

Bandgap engineering strategies include metal/nonmetal ion doping, dye/quantum dots sensitization, plasmonic enhancement, and solid solution formation. Materials engineering includes modification of crystal structure, improvement of crystallinity, surface passivation, nanostructure design, and combination of semiconductors to form hetero-junctions. For surface water reduction and oxidation reactions, loading cocatalysts and creating high surface area are the major strategies to enhance the surface reaction efficiency.

Taking into account of the additional voltage (overpotential) to be generated necessarily in the device for driving the electrochemical oxidation and reduction of water, the minimum single junction bandgap needs to be greater than 2.0 eV. [238] This requirement leaves out much of the solar spectrum and limits a maximum practically achievable efficiency with this configuration to be less than 10%. Therefore, new technologies are needed to boost the solar-to-hydrogen efficiency, such as multiple exciton generation (MEG) [239] and hot electron transfer, up-conversion, and multi-strategy modifications.

The MEG is a process whereby multiple electron-hole pairs, or excitons, are produced upon absorption of a single high-energy photon in semiconductor nanocrystals. [240] Utilization of high-energy photons to generate multiple charge carriers or capturing hot electrons before their thermalization can boost the operation

efficiency of quantum dot solar cell (QDSC). [241,242] This concept can be equally used in solar water splitting to improve solar-to-hydrogen efficiency.

For further improvement of solar-to-hydrogen efficiency, it is necessary to use combined strategies. For example, Jeong et al. [243] attempted multi-strategic modification of BiVO₄ for improving photoelectrochemical water oxidation performance. Ternary heterojunction WO₃/Mo-BiVO₄/Co-Pi shows a photocurrent density of ~2.4 mA cm⁻² at 1.23 V_{RHE} (corresponding to the solar-to-hydrogen efficiency of ca. 3%). Mo⁶⁺-doping increases the electron density and hence decreases the charge transfer resistance, resulting in an approximate 2-fold increase in charge separation efficiency to about 25%. WO₃/Mo-BiVO₄ binary heterojunction promotes the charge separation efficiency to ~50%. Loading of oxygen evolution cocatalyst Co-Pi enhances charge injection efficiency from ~50 to ~70% at 1.23 V_{RHE}. Ternary heterojunction (WO₃/Mo-BiVO₄/Co-Pi) further improves the charge separation efficiency to ~60% and charge injection efficiency to ~90%.

In another example of integrating multiple strategies in water-splitting system, Wang [244] considered silicon/hematite core/shell nanowire array decorated with gold nanoparticles for unbiased solar water oxidation, exhibiting a calculated efficiency of 6.0% through photocurrent measurement under AM 1.5G illumination. Silicon/hematite core/shell nanowire array configuration integrates the advantages of enhanced light absorption, rapid carrier collection and transport. It captures a wider solar spectrum since lower bandgap semiconductor silicon can absorb the long-wavelength sunlight that is not absorbed by hematite. Core/shell nanowire overcomes the incongruity between short hole diffusion length and long photon penetration depth in hematite. Further, the plasmonic enhancement of Au NPs in hematite enhances light absorption and photocurrent.

In the area of improving the solar light absorption efficiency, the majority of studies focus on enabling the absorption of the visible light, but fewer attentions are paid to near-infrared (IR) light which constitutes about 52% of the solar spectrum. Developing near-IR absorbing materials to simultaneously harvest near-IR or making use of up-conversion nanocrystals to convert near-IR into visible light are promising ways to improve solar-to-hydrogen efficiency. Chen et al. [245] reported the near-infrared-driven photoelectrochemical water splitting using a ZnO nanorod-array decorated with CdTe quantum dots and plasmon-enhanced up-conversion nanoparticles. CdTe quantum dots extends the light absorption to visible region. Up-conversion emission of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped NaYF_4 further extends it to near-infrared region. Plasmon enhances the efficiency of up-conversion emission.

Organo-metal halide perovskite has a bandgap of 1.5 eV and a huge charge carrier diffusion length. [190,191,246] This advanced material has received tremendous interest for photovoltaic (or solar cell) applications and can also be applied for water-splitting to produce hydrogen. Large charge carrier diffusion length renders low electron-hole recombination rate and high electron/hole transfer rate which potentially can significantly improve the solar water splitting efficiency. A current bottleneck for utilizing this type of materials in solar water splitting appears to be the material stability in aqueous electrolyte or humid environment. Nevertheless, it is our opinion that the organo-metal halide perovskites may contribute to a long waited breakthrough in solar water splitting efficiency as soon as the material stability issue is resolved.

Given the minimal ohmic losses (0.4 eV) and kinetic losses (0.4 eV) due to the overpotential for oxygen and hydrogen production, hypothetical ideal photoelectrode materials with a bandgap of 2.03 eV exhibit a maximum STH of 16.8%. [19, 20] This

is the upper limit efficiency of a single absorber. Practically, the maximum achievable efficiency of single absorber is often less than 10%. [238] Apart from the above-mentioned strategies for enhancing solar-to-hydrogen efficiency, further improvements may come from “Z-scheme” water splitting or tandem structure. Sivula et al. predicted a maximum STH of 21.6% using optimum values of $E_{g1}=1.89$ and $E_{g2}=1.34$ eV with a 2.0 eV total loss. [7] Furthermore, with the assumed losses by Lewis and co-workers, the maximum STH efficiency for a tandem cell was up to 29.7% with $E_{g1}=1.60$ and $E_{g2}=0.95$ eV. [247]

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Table content:

Table 1 Photocurrent density of cadmium chalcogenide QDs sensitized ZnO

Sensitizer	Photocurrent density mA cm^{-2}	Applied bias	Light source	Reference
CdSe	3.1	1.2 V vs RHE	Simulated sun light	Emin [73]
CdSe	2.48	0 V vs SCE	Simulated sun light	Chouhan [74]
CdS/CdSe	13.9	0.6 V vs RHE	Simulated sun light	Seol [75]
CdS/CdSe	9.15	0 vs SCE	Simulated sunlight	Seol [76]
CdS	23.7	0 V vs Ag/AgCl	Simulated sun light	Bu [77]
	15.8		Visible light	
CdSe	5	0.35 vs RHE	Simulated sun light	Chouhan [78]
CdS/CdSe	12	0.4 V vs SCE	Simulated sun light	Wang [79]
CdS/CdSe	17.5	0 V vs SCE	Simulated sun light	Kim [80]
CdS/CdSe	11	-0.5 V vs SCE	Simulated sun light	Kim [81]
CdTe	2.0	1 V vs Ag/AgCl	Simulated sun light	Chen [82]

Table 2 Photocatalyst Library offered by Kudo's Laboratory at Tokyo University of Science

<i>UV light Responsive Photocatalysts</i>	<i>Visible Light Responsive Photocatalysts</i>		
<i>Overall Water Splitting</i>	<i>Overall Water Splitting</i>	<i>H₂ Production</i>	<i>O₂ Production</i>

ANb_2O_6 (A: Sr, Ba) $\text{Sr}_2\text{Nb}_2\text{O}_7$ ATa_2O_6 (A: Ca, Sr, Ba) $\text{K}_3\text{Ta}_3\text{Si}_2\text{O}_{13}$ ATaO_3 (A: Li, Na, K) AgTaO_3 NaTaO_3 :La $\text{K}_2\text{LnTa}_5\text{O}_{15}$ NaTaO_3 :A (A: Ca, Sr, Ba) $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ $\text{ALa}_4\text{Ti}_4\text{O}_{15}$ (A: Ca, Sr, Ba) ATa_3O_8 (A: Rb, Cs) $\text{Cs}_6\text{Ta}_{16}\text{O}_{43}$	$\text{Pt/SrTiO}_3\text{:Rh-BiVO}_4$ $\text{Pt/SrTiO}_3\text{:Rh-Bi}_2\text{MoO}_6$ $\text{Pt/SrTiO}_3\text{:Rh-WO}_3$ $\text{Ru/SrTiO}_3\text{:Rh-BiVO}_4$ $\text{Ru/SrTiO}_3\text{:Rh-WO}_3$	ZnS:Cu ZnS:Ni ZnS:Pb,Cl NaInS_2 $\text{SrTiO}_3\text{:Cr,Sb}$ $\text{SrTiO}_3\text{:Cr,Ta}$ AgGaS_2 CuGaS_2 $\text{CuInS}_2\text{-AgInS}_2\text{-ZnS}$ $\text{CuInS}_2\text{-AgInS}_2$ $\text{SrTiO}_3\text{:Rh}$ $\text{Sr}_2\text{TiO}_4\text{:Rh}$ $\text{SrTiO}_3\text{:Ir}$ SnNb_2O_6	BiVO_4 Bi_2MoO_6 AgNbO_3 $\text{TiO}_2\text{:Cr,Sb}$ Ag_3VO_4 $\text{Ag}_{0.5}\text{Pr}_{0.5}\text{TiO}_3$ $\text{TiO}_2\text{:Ni,Nb}$ $\text{TiO}_2\text{:Rh,Sb}$ $\text{PbMoO}_4\text{:Cr}$ $\text{SrTiO}_3\text{:Ir}$ SnNb_2O_6
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Figure captions:

Fig. 1 Processes in photocatalytic overall water splitting on a semiconductor particle. [16] Reprinted with permission from ref 16. Copyright 2007, American Chemical Society.

Fig. 2 Overall water splitting on a photocatalyst superimposed with a bandgap chart. The y axis E vs. NHE refers to the potential, in unit V, as measured against the normal hydrogen electrode.

Fig.3 Band levels of various semiconductor materials and theoretical solar-to-hydrogen efficiency as a function of bandgap of the semiconductor taking into account of thermodynamic loss and kinetic loss due to the overpotentials for oxygen or hydrogen production (a) Relationship between bandgap structures of semiconductors and redox potentials of water splitting. [18] (b) Dependence of theoretical solar-to-hydrogen efficiency and solar photocurrent density of photoelectrodes on their bandgap absorption edges under AM 1.5 G irradiation (100 mW cm^{-2}). [19,20] Fig. 3(a) is reprinted with permission from ref 18. Copyright 2008, Royal Society of Chemistry. Fig. 3(b) is reprinted with permission from ref 19. Copyright 2008, Royal Society of Chemistry.

Fig. 4 Donor level and acceptor level formed by metal ion doping.

Fig. 5 New valence band formation by doping of nonmetal ion doping (a) and surface band level of modified TiO_2 (b). [27] Fig. 5(b) is reprinted with permission from ref 27. Copyright 2013, American Chemical Society.

Fig. 6 Schematic to illustrate the principle of bandgap alignment between a wide bandgap semiconductor and a sensitizer quantum dot. QD improves the photo absorption and allows electron injection from QD into the wide bandgap semiconductor.

Fig. 7 Growth and characterization of InGaN/GaN nanowire heterostructure. (a) Schematic of the InGaN/GaN nanowire heterostructure. (b) Room temperature photoluminescence spectra of InGaN/GaN nanowire arrays. (c) Schematic of InGaN/

GaN triple-band nanowire heterostructure. (d) A 45° tilted SEM image of GaN/InGaN nanowire heterostructures grown on GaN nanowire templates on Si(111) substrate. (e) High angle annular dark field (HAADF) TEM image in pseudocolor display of an as-grown InGaN/GaN nanowire heterostructure, showing the z-contrast between InGaN (red) and GaN (green) layers. The unit of intensity scale is 104 counts. [85] Reprinted with permission from ref 85. Copyright 2013, American Chemical Society.

Fig. 8 An illustration of plasmonic solar water splitting. N-type semiconductor nanostructure sitting on a metallic substrate in contact with water and (A) a metal nanoparticle or (B) a core-shell metal-insulator nanoparticle. [13] Reprinted with permission from ref 13. Copyright 2012, Royal Society of Chemistry.

Fig. 9 Schematic band structures of GaN and $(\text{GaN})_{1-x}(\text{ZnO})_x$ with $x=0.05\sim0.22$. [113] Reprinted with permission from ref 113. Copyright 2005, American Chemical Society.

Fig. 10 Schematics of a semiconductor surface loaded with co-catalysts to mediate oxidation and/or reduction. The reduction co-catalyst could be different from the oxidation co-catalyst. Adapted with permission from ref 14. Copyright 2013, American Chemical Society.

Fig. 11 (a) Schematic illustration of the design principle involving the use of a highly conductive TiSi_2 nanonet as an effective charge collector. The electronic band structure is shown in the enlarged cross-sectional view. Efficient charge collection is achieved when the hematite thickness is smaller than the charge-diffusion distance. (b) Low-magnification transmission electron microscopy (TEM) image showing the structural complexity of a typical heteronanostructure and its TiSi_2 core/hematite shell nature. (c) High-resolution (HR) TEM data. A dashed line has been added at the interface as a guide to the eyes. Insets: (left) lattice-fringe-resolved HRTEM image showing the hematite lattice spacing for (110) (0.250 nm) and (330) (0.145 nm); (right) electron diffraction pattern of hematite. [140] Reprinted with permission from ref 140. Copyright 2011, American Chemical Society.

Fig. 1

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Fig. 11

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