Recent Progress and Strategies for Enhancing Photocatalytic Water Splitting

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Abstract

Solar-light-driven water splitting provides a promising way to store and utilize abundant solar energy in the form of gaseous hydrogen which is the cleanest chemical fuel for mankind; therefore this field has been attracting increasing attention over the past decades. The fundamental steps for efficient photocatalyst for water splitting include uptake of photons of targeted energy range by appropriate electronic band structure, excited electrons and holes (excitons) migration and recombination and selective conversion excited electrons for H^+ reduction to H_2 and holes and OH^- to O_2 on catalyst surface. Each step if not efficient taken place could hamper the overall photocatalytic activity. Numerous semiconductors with appropriate band gaps have mainly been developed as candidates for effective solar energy capture, whereas at present, their low quantum efficiency still remains as the major obstacle in further applications. In this mini-review, we will disentangle the progress to develop photocatalysts with good photon uptake from photocatalytic water splitting performance. According to thermodynamic and kinetic considerations of the photocatalytic water splitting reaction, different strategies for improving the fundamental processes have been briefly reviewed. Some recent advances in facilitating charge carriers separation have also been presented. Photocatalytic water splitting at elevated temperatures is emphasised as a novel approach to suppress photo-excitons recombination on catalyst surface due to adsorption of enhanced concentration of ionic species including H^+ and OH^- to create their local polarization to the excitons. Stronger polarization to hinder the excitons recombination can also be obtained by using polar-faceted support materials to the active phase of semiconductor. It is clearly demonstrated in this mini-review that such high temperature-promoted photocatalytic water splitting systems could open up a new direction and provide a new innovation to this field.

Keywords: photocatalysis; water splitting; hydrogen evolution; solar light conversion; clean energy

1. Introduction

Energy and environmental issues have been of increasingly importance in recent decades, due to the subtle global climate change arising from the use of fossil fuels. Thus, renewable and carbon-emission-free energy sources are in great demand [1-3]. Solar energy is attracting considerably interest as a sustainable and clean energy source, but for practical application, the solar energy is required to be converted to other forms of energy such as chemical fuels, so that it can be stored and transported more efficiently [4-6]. Hydrogen (H_2) is considered as an ideal chemical fuel because of its highest energy-capacity of 143 MJ kg^{-1} for all matters in the universe and its emission-free advantage with the only by-product water from combustion energy [7-9]. Therefore, solar-light-driven photocatalytic water splitting has become a promising method to convert solar energy into hydrogen. Since the first photoelectrochemical water splitting system was demonstrated by Fujishima and Honda in 1972 [10], photocatalytic water splitting have been persistently studied and significant progresses have been achieved since then. Visible-light-driven oxygen and hydrogen evolutions from water has been extensively explored separately, with the help of various sacrificial reagents [11-15]. For example, Han and Hu have recently reported an enhanced hydrogen production using input of methanol as hole-scavenger at elevated temperatures [15]. Apparently, the methanol molecules contribute to the overall hydrogen production via their decomposition. The additional capital cost for the methanol input and the unwanted hydrocarbon/alcohols by-products would largely hinder any practical application. Before further discussion, it should be clarified in this review that water splitting reaction is mainly focused upon. This refers to the overall splitting of water, where water molecule is only the required reactant and with the help of photocatalyst and sunlight, stoichiometric hydrogen and oxygen are produced. Therefore sacrificial oxygen and hydrogen evolutions are not hereby considered as water splitting.

Semiconductors like TiO_2, $SrTiO_3$, GaN, CdS, MoS_2 and some conjugated semiconductors have been extensively studied as photocatalysts [3-5,14-22]. In general, photocatalytic water splitting reaction over semiconductors mainly involves the following fundamental processes (as shown in Fig. 1a) [23,24]: (1) formation of electron-hole pairs (excitons) by photon absorption; (2) charge separation and migration to trapping sites on catalyst surface; (3) construction of surface chemical reactions for H_2 and O_2 evolutions. In the process (3), protons in water are reduced by the excited electrons in the conduction band (CB) to produce H_2, and simultaneously, oxygen evolution happens from the water oxidation by the excited holes in valance band (VB). Therefore, to achieve the stoichiometric H_2 and O_2 evolution, the valence band maximum (VBM) should be more positive than $E^0_{O2/H2O}$= 1.23 V (vs. NHE) and conduction band minimum (CBM) is more negative than $E^0_{H+/H2}$= 0.00 V (vs. NHE) to make oxygen and hydrogen evolutions to happen at the same time to sustain the catalysis (Fig. 1b). Obviously, the minimum bandgap of the semiconductor photocatalyst is 1.23 eV, corresponding to a wavelength of around 1000 nm. Despite the wide range of solar emission spectrum, the most intense solar radiation lies in the regime of visible light, which contributes nearly 43% of the solar energy [23]. Thus, an ideal photocatalyst for water splitting reaction should possess a corresponding bandgap to best utilize the visible light, bearing in mind that the bandgap should be at least 1.23 eV to drive the water splitting reaction.

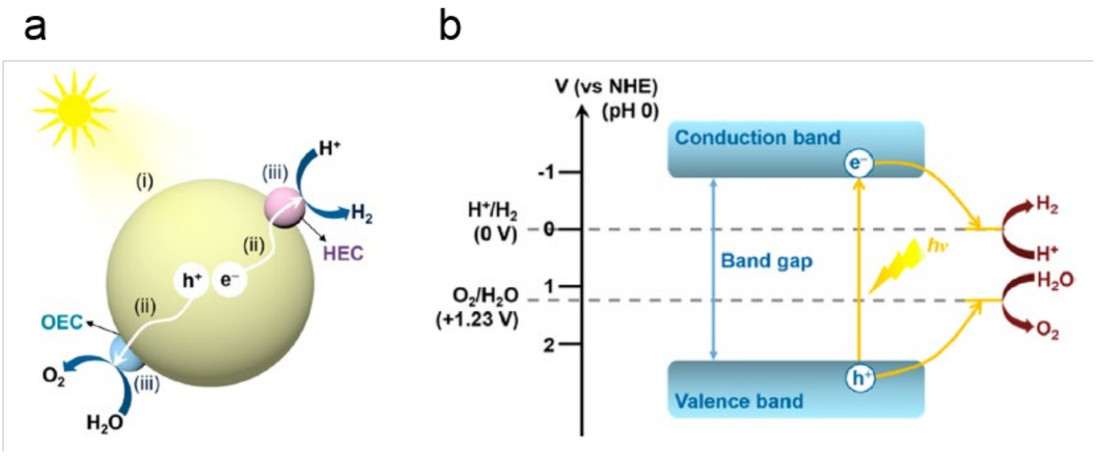

Figure 1. (a) Fundamental steps during photocatalytic water splitting on a semiconductor photocatalyst: (i) photo-excitation, (ii) charge separation and transport, and (iii) surface chemical reactions; (b) Schematic band structure and energy levels for photocatalytic water splitting based on one-step excitation [23].

Apart from capturing photons from solar radiation with corresponding band gap, photocatalytic activity and quantum efficiency (QE) are important aspects to evaluate the performance of a photocatalyst in gauging the effectiveness in conversion of capture energy to chemical products. Typically, TiO_2 based materials have attracted most attention in the recent decades, and various methods have been applied to reduce the wide bandgap of TiO_2 (3.2eV) resulting in modified TiO_2 in different colours (Fig. 2a) [16,25-27]. Although high activity and QE can be easily obtained over coloured TiO_2 under the UV light irradiation, the QE does not sustain but drops dramatically when it switches to visible light irradiation. This means that good degree of visible light absorption by the photocatalyst does not necessarily lead to good photocatalytic performance [12,17,28]. Perovskite also shows promising results in the field of solar energy applications, such as for solar cell and photocatalytic water splitting (Fig. 2b) [29-32]. Doped perovskites show promising quantum efficiency of 56% at 365 nm [31]. Narrow bandgap materials like $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, CdS and C_3N_4 exhibit promising photocatalytic activity under the visible light irradiation [5,33,34]. Besides, it has been reported recently a Z-scheme photocatalytic water splitting system consisting of $BiVO_4$ and $SrTiO_3$ shows a QE of 30% at 419 nm with the help of cocatalysts (Fig. 2c) [35]. Despite the exploration of different materials and efforts made on the enhancement of visible light absorption, low H_2 evolution rate and low QE under visible light and ambient conditions still hinder the current water splitting systems from practical applications. This is due to the rapid recombination of excitons to dissipate the captured solar energy to heat to environment. On the other hand, recent reports show that polarization plays an important role in the separation of these photogenerated electrons and holes from rapid recombination, which prolongs the exciton lifetime, therefore leading to enhanced photocatalytic performance [36-38]. Cocatalyst deposition is an effective approach to facilitate the surface reactions and suppresses the backward reactions (Fig. 2d and 2e) [39-41]. There have been some good review articles published focusing from theoretical study to feasibility of large-scale applications and economics [1-4,8,23,24]: Emphasis on photon absorption [1,2], materials synthesis and characterizations [3,4,24], and strategies to optimize the photocatalytic systems [8,23] can be found. Obviously, novel strategies are urgently required and new approaches have been emerged recently. Therefore, in this mini-review, we will focus on some recently reported progresses in this field to highlight on the fundamental underlying principles and current research trends. Over the recent decades, different strategies have been explored to enhance the photocatalytic water splitting performance and will also be briefly discussed. Based on our recent work, it is reported that elevated temperatures can lead to much enhanced photocatalytic water splitting performance due to local polarization of the excitons on the catalyst by enhanced concentrations of H^+ and OH^- at saturated water vapour pressure at high temperatures. It is also demonstrated that the strong local electric field can also be introduced by using polar-faceted support materials which show an extraordinary effect on promoting the separation of photogenerated electron and hole pairs from rapid recombination, which is considered as a facile and versatile approach for photocatalytic water splitting reaction, and also for other systems.

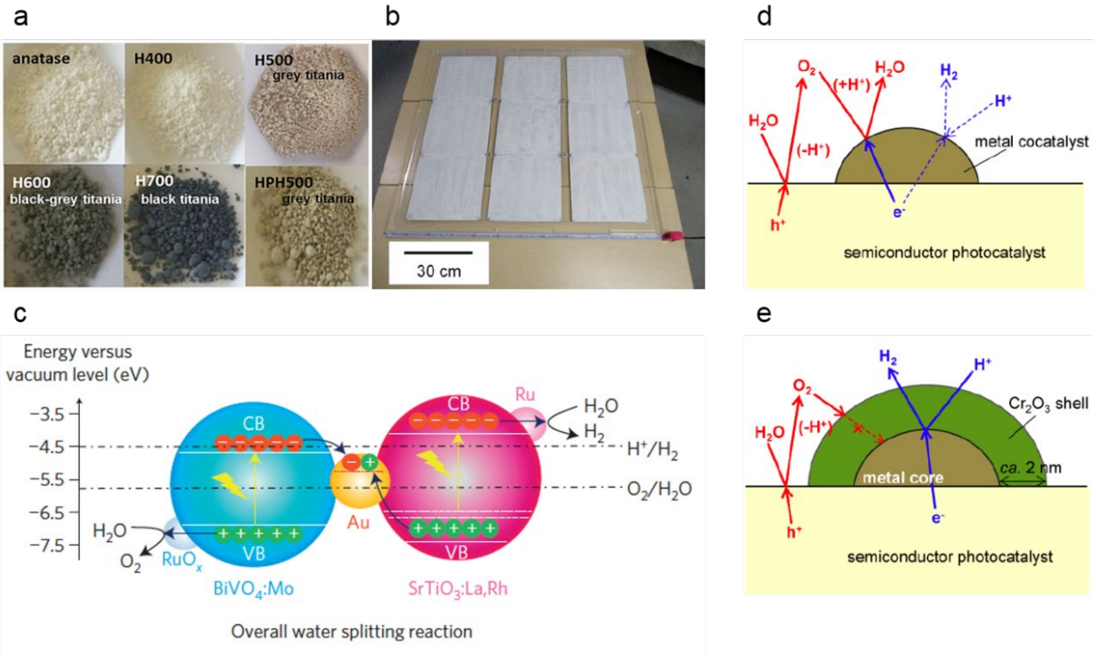

Figure 2. Photographic images of hydrogenated titania with different colours [16] (a) and a $SrTiO_3$:Al panel for photocatalytic water splitting reaction [31] (b); (c) Schematic of overall water splitting on the Ru-modified $SrTiO_3$:La,Rh/Au/$BiVO_4$:Mo sheet [35]; Schematic of the differences of the chemical processes before (d) and after (e) the construction of the core-shell structured cocatalysts [40].

2. Strategies for enhanced photocatalytic performance

As discussed, the overall photocatalytic water splitting reaction performance is influenced by the efficiency of each of the three processes, therefore much effort has been made to gain their understanding, leading to different strategies developed to promote each step. Band structure engineering is a useful technique to narrow the wide band gap materials down to the visible light region to maximize the energy capture [26,27,42-45]. Different methodologies have been used, such as sensitization with organic dyes, where the dye acts as a photosensitizer and injects electrons into the CB [43]. Another methodology is doping with anions or cations which inserts new band levels into the original band gap of the semiconductors or facilitates a band shift to enhance light absorption properties [44,45]. Defects such as oxygen vacancies is also believed to provide intermediate band levels or extra states that can trap electrons, and contribute to enhanced visible light absorption [46-53]. Cocatalysts such as noble metal and metal oxides are often engaged to facilitate the surface chemical reactions, lower the overpotentials for H_2 and O_2 evolution, and suppress the backward water-formation reaction [40,41,54-58]. Besides, methods have also been developed to promote the separation of the photogenerated electrons and holes on catalyst surface and suppress the recombination process, including shape and facet engineering, heterojunction formation and introduction of internal electric fields, etc [37,59-61]. In this section, some prevalent strategies such as defect engineering and cocatalyst deposition will be discussed. The new promising approach to prolong the excitons lifetime by polarization will also be scrutinized in this section.

2.1 Defect engineering

Surface defects, such as vacancies, are ubiquitous in most semiconductor materials, and tailoring the defects is recognized as an effective strategy to manipulate the physical and chemical properties, including electronic structure, surface adsorption properties, charge density, charge separation, etc [62-65]. The vacancy engineering techniques have been widely studied and much progress has been made, especially the oxygen vacancy (V_o) in metal oxides such as TiO_2. V_o exists naturally in most metal oxides in a very low density level, but higher V_o density can be achieved by some simple chemical treatments, such as ion doping [25,49], deeply hydrogen reduction [27], $NaBH_4$ chemical reduction [66,67], plasma treatment [68], and exfoliation to form two-dimensional (2D) materials [69], thermal treatment in NH_3 atmosphere [25,70], etc.

Anion doped TiO_2 was first proposed by Asahi et al. and first-principle calculations were carried out on C, N, F, S and P doped TiO_2 (Fig. 3a), showing that N-doped TiO_2 possesses better visible light absorption [26]. Subsequently, extensive studies were carried out. UV-vis spectroscopy shows that the absorption of N-doped TiO_2 is extended to ca. 500nm. N species is observed by X-ray photoelectron spectroscopy (XPS), showing peaks at 396eV and 400eV attributed to substitutional and interstitial N species, respectively [25,26,70]. Then much attention has been attracted to hydrogen pre-treatment since the pioneering work of Mao et al., in which TiO_2 was treated in a hydrogen atmosphere at 200°C and 20bar for 5 days [27]. The resulting black TiO_2 exhibited largely enhanced light absorption up to 900nm and photocatalytic hydrogen evolution performance (Fig. 3b). Raman spectroscopy is used to examine the black titania, implying that the deeply hydrogenation introduces defects that can activate the zone-edge and otherwise Raman-forbidden modes by breaking the Raman selection rule [27]. VB XPS suggests that the VB of TiO_2 shifts largely by about 2.18eV, resulting in the greatly enhanced visible light absorption and photocatalytic performance (Fig. 3c) [27]. Subsequently, TiO_2 in different colours are developed. Liu et al. synthesized a series of coloured TiO_2 by changing the hydrogenation temperatures and the visible light absorption is extended in different degree [71]. Defects are normally characterized by electron paramagnetic resonance (EPR) spectroscopy. The signals of Ti^{3+} arising from its 3d electrons normally appear in the range of g=1.95-1.98, and O_2 molecule can be trapped at the V_o site to form O_2^- species, resulting in the signals of g=2.00-2.02 [72,73]. Both Ti^{3+} and V_o species are considered to contribute to the enhanced visible light absorption and photocatalytic performance. Other than V_o in TiO_2 based materials, V_o in other materials like CeO_2, perovskite, Fe_2O_3, WO_3 and $BiVO_4$ also show promoting effect on visible light absorption (Fig. 3d and 3e) [62,67,74-76]. Much progress has indeed been achieved in enhancing the visible light absorption by defect engineering techniques, which largely increased the utilization of solar energy. But in our recent study we have found that the surface defects are not stable enough to be maintained throughout the whole catalytic process especially at high temperature and readily replenished in the contact with oxygen or water. Although bulk defects still take up the visible light, surface defects are no longer present, and the lack of surface catalytic activation sites can be harmful to the photocatalytic performance. This observation may also explain the fact that enhanced visible light absorption does not necessarily lead to better photocatalytic water splitting activity or QE [25].

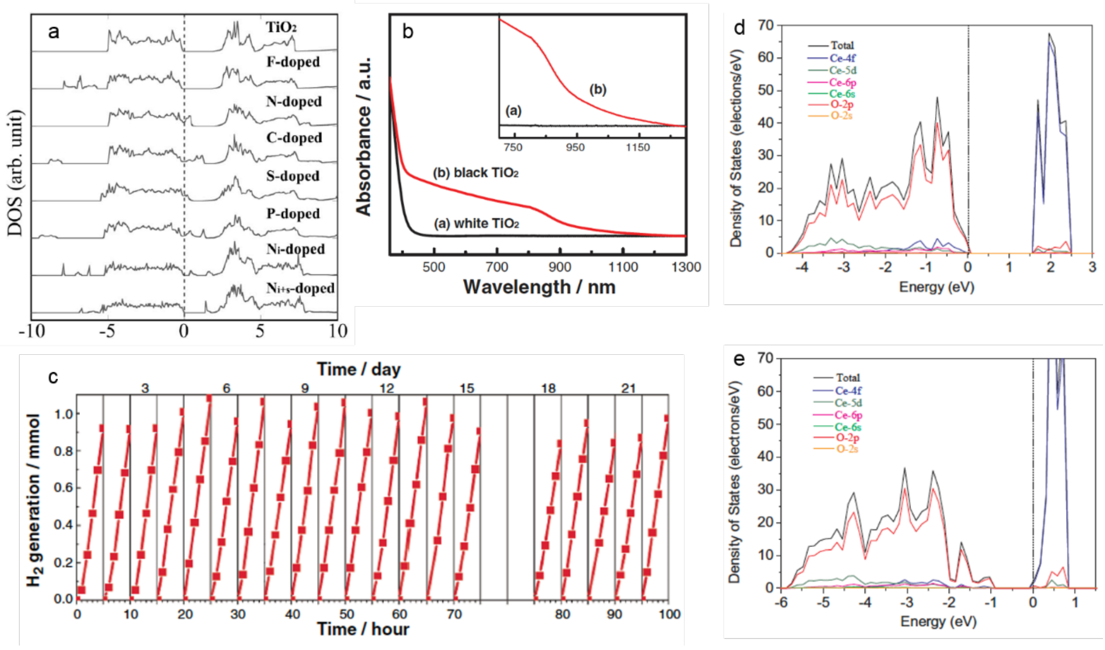

Figure 3. (a) Total DOSs of the doped TiO_2 [26]; (b) Spectral absorbance of the white and black TiO_2 nanocrystals. The inset enlarges the absorption spectrum in the range from approximately 750-1200 nm [27]; (c) Cycling measurements of hydrogen gas generation through direct photocatalytic water splitting with disorder-engineered black TiO_2 nanocrystals under simulated solar light [27]; Total DOS and projected density of states (PDOS) of (d) perfect CeO_2(110) and (e) oxygen-defective CeO_2(110). The dotted lines at energy zero represent the Fermi level [62].

2.2 Decoration with cocatalysts

Cocatalysts are of great interest in the field of photocatalytic water splitting, and have been extensively explored. A cocatalyst is capable of promoting charge separation and suppressing the charge recombination by extracting the photo-excited electrons or holes dependent on the nature of the cocatalyst used. Besides, it is widely believed that in a photocatalytic water splitting system, photo-reduction of protons for hydrogen evolution is kinetic facile process, but oxygen evolution from OH^- is a slow fundamental step where four electrons are involved [5]. Therefore, cocatalysts are often engaged to promote the surface H_2 or O_2 evolution reaction by lowering the activation energy. Generally, metals such as Pt, Pd, Au, Ru, Ni and Rh are considered as H_2-evolutoion cocatalysts, while the metal oxides of Ir, Mn, Co and Ru function as the O_2-evolution cocatalysts [77].

H_2 evolution cocatalysts such as Pt are widely used and much progress has been made. Recently, our laboratory have also found that Au nanoparticle introduced by photoreduction method shows a strong promoting effect in an N-doped TiO_2 photocatalytic water splitting system, leading to a 90%

increase in the H_2 evolution rate [25]. It is also reported that H_2 evolution cocatalysts also accelerate the thermodynamically favourable reverse reaction, the water formation reaction, therefore bimetallic cocatalyst systems have also been developed to suppress the backward reaction at the same time promoting the forward reaction [77]. Domen group reported a Rh@Cr_2O_3 core-shell structure synthesized by selective photoreduction, the Cr_2O_3 species of their catalyst kinetically prevented the O_2 from reaching the metal surface, therefore limited the possibility of the evolved O_2 to be reduced again [40,78]. TEM showed that the core-shell structure was successfully achieved by photo-deposition method; XPS and EXAFS also confirmed the core and the shell consisting of metallic Rh and Cr_2O_3, respectively. It was later shown that GaN:ZnO loaded with Rh@Cr_2O_3 exhibited an enhanced water splitting activity due to the suppressed backward reaction. Other noble metals such as Pt and Ir as the metal core can also lead to similar performance [40]. In a subsequent study, a similar modification method was developed to effectively promote overall water splitting [78]. Amorphous oxyhydroxides of group IV and V transition metals (Ti, Nb, Ta) were introduced to a semiconductor photocatalyst. In this method, amorphous oxyhydroxide covered the whole photocatalyst particles, created a core-shell structure. Overall water splitting performance was successfully enhanced after the surface modification, resulting from the prevention of the reverse reaction. The amorphous oxyhydroxide layers were believed to function as molecular sieves which selectively filter the reactant and product molecules. The core-shell structures were confirmed by TEM and SEM, and the permeation behaviour on the core-shell structures was also studied in detail. It was demonstrated that this structure was effective for overall water splitting even when the active sites were covered by the coating, due to the selective permeation behaviour: H_2O was allowed to permeate in, while the produced gases were allowed to permeate out. And this permeation property enabled the prevention of the reverse reaction without suppressing the forward reaction, leading to efficient water splitting.

2.3 Photocatalysis at elevated temperatures

Photocatalytic water splitting reaction have been studied mainly at room temperature for decades, however, it is well known that elevated temperatures can lead to enhanced performance of endothermic reactions both thermodynamically and kinetically. Thermolysis of water requires extremely high temperature of more than 1000 ^{o}C [79] which is not practical, but photocatalysis promoted by elevated temperatures is presumably able to provide a novel alternative for the solar energy utilization especially the heat is also provided by the solar means. Moreover, infra-red contributes almost half in the solar spectrum and can provide the required heat by thermal radiation instead of using electric heating devices [23]. Han and Hu have reported recently a temperature-induced photocatalytic hydrogen production system, of which the QE can reach 65.7% in the visible light range at 280 ^{o}C in the presence of methanol as sacrificial reagent [15]. It is claimed that elevated temperatures add to the thermal energy of the reactants and subsequently increase the kinetic driving force, leading to enhanced hydrogen evolution rate and QE. It should be noted that the thermal decomposition of methanol also contributes to the overall hydrogen production, and inevitably results in unwanted carbon emission, which also hinders its practical application. But the idea of using elevated temperatures in photocatalytic water splitting is worthy further exploring. Tian et al. also reported a photocatalytic water splitting system over black phosphorous nanosheets at elevated temperature [80]. It was shown that amorphous cobalt phosphide supported black phosphorous exhibited around nine times enhancement of photocatalytic water splitting performance at 353K compared with that of room temperature, showing a QE of 42.55% at 430nm. There was no addition of sacrificial reagent in the photocatalytic system; however, oxygen was not detected stoichiometrically, suggesting the existence of photo-corrosion of the phosphide catalyst. It should be noted that the water dissociation to H^+ and OH^- when at equilibrium is also temperature-dependent, which can be promoted by about 25 times compared with that at room temperature (about 1×10^{-14}) and peaks at around 270 °C before rapidly declines [81]. Obviously, enhanced concentrations of H^+ and OH^- are beneficial to the photocatalytic water splitting performance kinetically. However, the photocatalytic water splitting at elevated temperatures is not often reported.

Enlightened by these previous works on temperature-promoted photocatalytic water splitting systems, we have recently reported an extraordinary QE of 81.8% at 437nm at 270 °C over a TiO_2-based photocatalyst, and it is noteworthy that a QE of 3.2% was also obtained at even 1000nm, which is nearly the theoretical threshold of photocatalytic water splitting reaction [25]. For photocatalysis, charge carriers that can reach the surface of the photocatalyst are more important than those remain in the bulk. With the help of EPR measurements, it is found that after the sample was exposed to air at ambient conditions, the surface oxygen vacancies gradually disappeared and only less than a quarter remained after one day. This is attributed to the fact that oxygen from the air (i.e. O_2 and H_2O), when in contact with the particle surface, may gradually replenish the surface oxygen vacancies and redistribute the electrons. However, we also noticed that when the samples were treated at elevated temperatures, no matter in N_2, liquid water or water vapour, the EPR signals of these materials re-emerge and become even larger, implying that more surface oxygen vacancies can be regenerated at elevated temperatures. Thus, the surface oxygen vacancies formed in N-doped TiO_2 are vulnerable to oxygen sources at room temperature, but at elevated temperatures, the faster subsequent reactions can regenerate them to sustain the surface photocatalytic processes. As a result, this also gives the major advantage of performing high-temperature photocatalysis to facilitate the water splitting reaction.

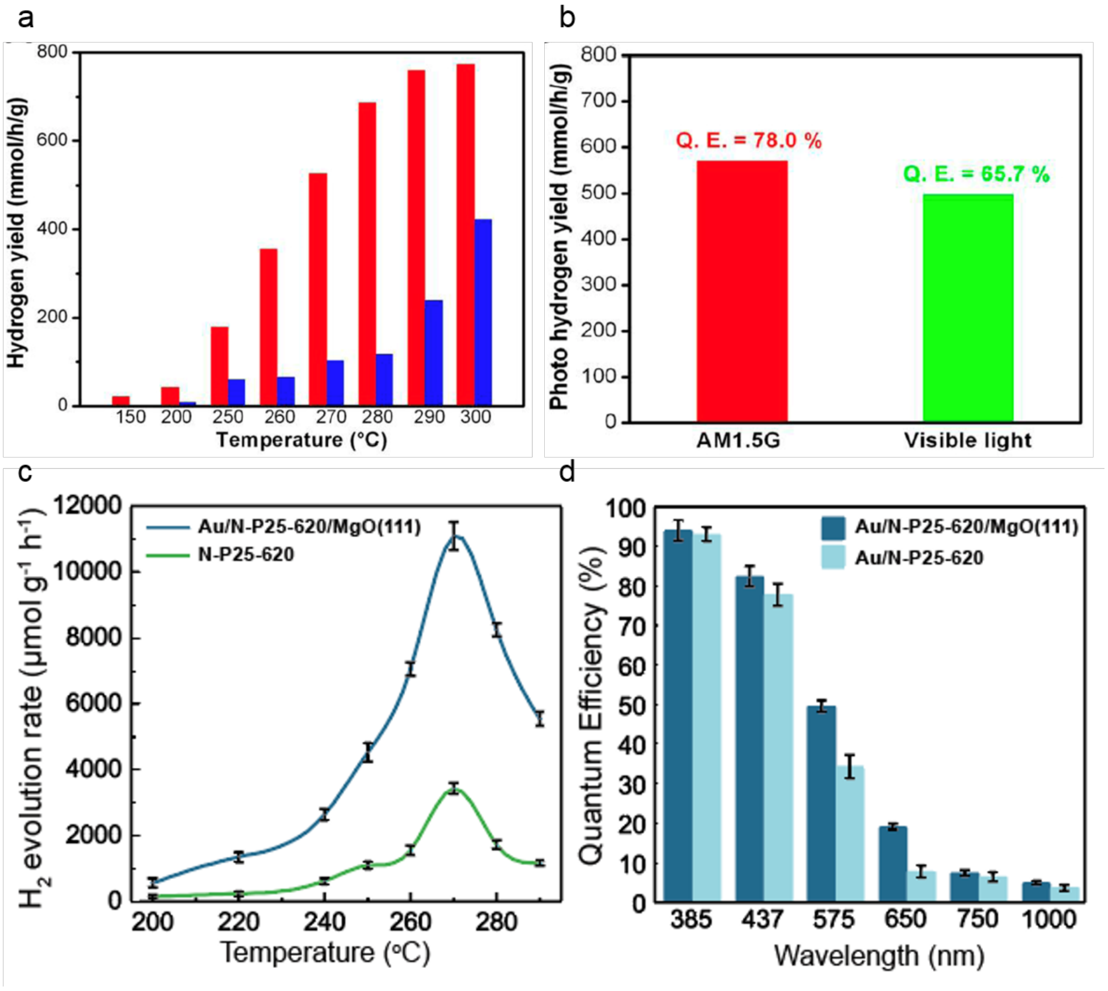

Figure 4. (a) Temperature-enhanced photocatalytic hydrogen production from H_2O with a sacrificial agent (30% methanol) without light illumination (blue bar) and with AM 1.5 global sunlight illumination (red bar) and (b) apparent quantum efficiencies of visible light and AM 1.5 global sunlight over black Pt/TiO_2 catalyst at 280 ºC [15]; (c) Photocatalytic activities of N-P25-620 and Au/N-P25-620 with MgO (111) at different temperatures; (d) QE of different wavelengths over Au/N-P25-620 with and without MgO (111) photocatalysts at 270 ºC [25].

Time-resolved photoluminescence (TRPL) spectroscopy can be used to probe the recombination rate of photo-excited electron-hole pairs. Although no obvious change was observed when the TRPL experiments were conducted in air without water at different elevated temperatures, it was interesting to find that the exciton lifetime varies with the pH change [25]. Bearing in mind that the water dissociation constant increases with the temperature and peaks at 270 ºC, which presumably contribute to the enhanced photocatalytic performance at elevated temperatures. As a result, TRPL measurements were subsequently carried out in different H^+ and OH^- concentrations by soaking the N-TiO_2 sample in solutions with various pH at ambient temperature to mimic the high temperature conditions. As expected, the exciton lifetimes increased dramatically, and the fastest recombination rate was obtained at pH= 7 where there were the lowest concentrations of H^+ and OH^-, and the exciton lifetimes apparently increased presumably with higher concentrations of H^+ or OH^-, Clearly, the adsorption of H^+ or/and OH^- near the surface of the semiconductor could create a local electric field (LEF) which can attract the counter charged electron or hole species hence suppressing their recombination rate and enhancing the overall photocatalytic activity. As stated, dissociation of H^+ and OH^- from water becomes more favourable at higher temperatures and peaked at around 270 °C. Consequently, at elevated temperatures the exciton lifetime is prolonged compared to that at room temperature due to the simultaneously enhanced H^+ and OH^- concentrations, which allows chemical reactions to take place more efficiently. It should be noted that simply adding acid or alkali to the catalytic system may prolong the exciton lifetime, but it also concomitantly decreases the concentration of counter ions (OH^- or H^+) due to ionization equilibrium at room temperature, which is unfavourable for the overall kinetics of photocatalysis. In contrast, the use of high temperatures can increase both H^+ and OH^- concentrations at the same time by the raising the water ionization constant, which is a promising and efficient way to promote the photocatalytic water splitting performances.

2.4 Polarization field engineering at elevated temperature

Following the light absorption, the charge carriers travel across the photocatalyst to reach the surface. And in terms of the time scales of each process, the photo-excited electron-hole pairs are generated in femtoseconds after the light irradiation, while the separation and migration of the charge carriers normally take hundreds of femtoseconds or even picoseconds to take place. Instead of migrating to the surface and reacting with chemical species, the electrons and holes will recombine to give out the energy in the form of heat, and this process generally take place in several picoseconds. However, the interfacial charge transfer to the chemical species is relatively slow compared with the above steps, which takes place from hundreds of picoseconds to even microseconds, leading to the fact that most photo-excited electrons and holes favour recombination with each other instead of migration to the surface [24,82]. As a consequence, although the visible light absorption is largely enhanced for many photocatalysts, only a few electrons and holes can travel through the photocatalyst and reach the surface, leading to the poor QEs. Apparently, the photo-generated electron-hole (exciton) pairs must possess a sufficient lifetime to capture both H^+ and OH^- species derived from the water molecules to allow efficient photocatalysis to take place [5,25]. In order to suppress the electron-hole recombination on surface, it is important to enhance the local polarization within the same particle to facilitate the separation of photo-excited electrons and holes. The introduction of an electric field to enhance the polarization has recently been demonstrated to be an efficient approach for improving the charge separation both in bulk and on surface of the photocatalysts [36-38]. Zhang's group reported a new strategy to introduce an internal electric field to Bi_3O_4Cl by carbon incorporation [37]. The resulting C-doped Bi_3O_4Cl achieved a bulk-charge separation efficiency of 80%, therefore the exciton lifetime was prolonged from less than 500ps to around 4000ps (Fig. 5a and 5b), which is attributed to the strong internal electric field (Fig. 5c). This catalyst enabled photocatalytic water oxidation under visible light in the absence of sacrificial reagents; however, hydrogen was scarcely detected because the CB is more positive than the hydrogen-evolving potential. Likewise, the same research group also reported a Janus Cl_2-$Bi_{12}O_{17}$-MoS_2 bilayer junction photocatalyst with strong internal electric field for hydrogen evolution (Fig. 5d and 5e), in which case the carrier lifetime was claimed to be 3446 ns and a hydrogen evolution rate of 33mmol $g^{-1}h^{-1}$ was obtained with ascorbic acid as the hole scavengers [38].

A facile and versatile method to tune the local electric field (LEF) with the help of polar-faceted materials is recently developed in our group, in which a strong LEF is obtained by engaging polar-faceted MgO (111) as support. Polarity effects have long been studied in catalysis since late 20th century, and the studies covered semiconductor surfaces, oxide surfaces, ultra-thin oxide films and oxide interfaces [83-85]. For polar surfaces, the orientation is such that each repeat unit grows in the direction perpendicular to the surface, resulting in a non-zero dipole moment on the surfaces. Thus, electric fields and electrostatic forces are generated on polar surfaces [83]. Due to the presence of a macroscopic dipole, their surface properties and local environment strongly differ from those in the bulk or their non-polar counterparts. High surface energy makes the polar surfaces have great tendency to cancel out the polarity, by charge transfer or introduction of compensating charges in the outer plane [84]. However, the rigidity of some oxides hampers such processes and leaves considerable polarity and electrostatic forces on the polar surfaces, which we suppose can be good candidates for our local polarization effect study. Typical polar surfaces include MgO (111), ZnO (0001), Al_2O_3 (0001) and NiO (111), etc. [85]. As is well known, polar MgO (111) nanocrystals give both negative (O^{2-}) and positive (Mg^{2+}) terminated surfaces [86,87], giving a strong LEF to the catalyst particles. Solid state NMR and TEM were used to confirm the surface polarity of crystalline MgO (111) facets inducing significant chemical shifts [25]. After combined with N-doped TiO_2, TRPL measurements were carried out, which showed that MgO (111) prolongs the exciton lifetime of N-doped TiO_2 from 2.56 ns to 5.76 ns. Non-polar MgO (100) and MgO (110) were also tested, following the same procedure, which showed no apparent influence. Accordingly, the photocatalytic activity of the MgO (111) promoted Au/N-doped TiO_2 gave a much enhanced and stable hydrogen evolution rate of 11092 μmol $g^{-1}h^{-1}$ at 270°C, while non-polar Au/N-doped TiO_2/MgO (100) or (110) showed no rate promotion compared to that without the MgO support. The QEs of 81.8% at 437 nm and 3.2% at 1000 nm were also achieved with the inclusion of MgO (111). EPR experiments were also carried out to exclude the influence of the oxygen vacancies. We believe that the use of polar faceted MgO (111) can introduce an LEF, which prolongs the exciton lifetimes and therefore enhances the photocatalytic water splitting activities. To rule out the effect of different sizes and morphologies of the MgO supports, N-doped TiO_2 of different sizes were mixed with the same MgO (111) support. And it was observed that smaller particle sizes led to more obvious enhancement of activities caused by LEF. Subsequently, other polar-faceted oxides such as CeO_2 (100) nanocubes (NCs) and ZnO (0001) nanoplates (NPs) were also used to study the LEF effect, which showed similar behaviour as the MgO (111), while their non-polar counterparts barely show any effect. Additionally, it should be noted that the enhancement well correlated with the polarity of the polar faceted oxides in almost a linear manner. We thus believe the above experiments clearly indicate that the LEF effect although anticipated to be localized, it still can be clearly observed and optimized using polar support material under the general catalyst-support interaction in catalysis.

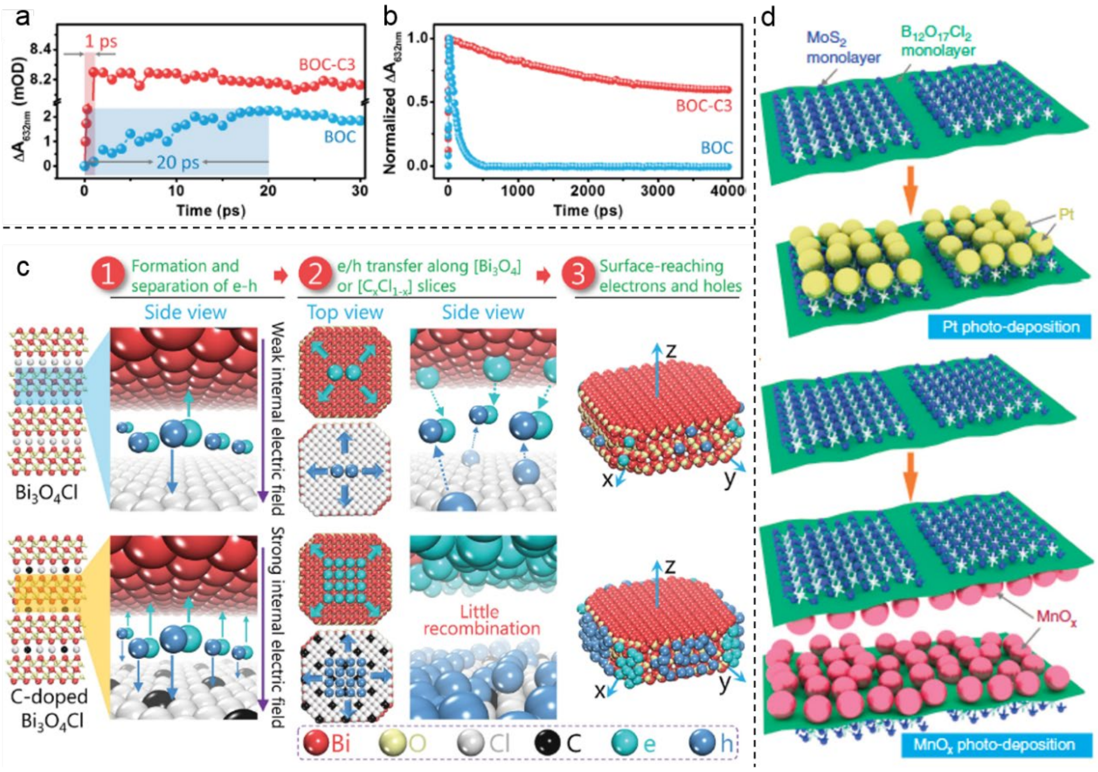

Figure 5. (a) Kinetic traces (probed at 632 nm) as a function of probe delay time and (b) their corresponding normalized traces. All these data were recorded with a 400 nm laser pulse (120 fs) [37]; (c) Schematic illustration of the separation and migration of electrons and holes in the bulk of the pure and C-doped Bi_3O_4Cl [37]; Schematic illustration of Pt (d) and MnO_x (e) photo-depositions on BOC-MS [38].

Apart from metal oxides, metal chalcogenides are also particularly promising candidates for visible light driven photocatalysis because their VBs typically consisting of p orbitals of chalcogenides, which are shallower than O 2p orbitals. [23] Two-dimensional (2D) materials like single layer MoS_2 (SL-MoS_2) are attracting wide attention toward hydrogen evolution reaction (HER) recently, due to its good photocatalytic performance and visible light absorption [88-90]. Upon the exfoliation of MoS_2, the optical, electronic and magnetic properties change dramatically, and the sulphur vacancies created via this process can serve as catalytic active sites or anchoring sites of metal atoms or chemical species, which lead to enhanced hydrogen evolution performance [91-93]. Such properties also make SL-MoS_2 an ideal photocatalyst to study the polarization effect considering the electric field introduced by the polar-faceted materials is quite localized, and the structural flexibility of SL-MoS_2 leads to strong interaction with the support hence giving high sensitivity to the LEF exerted by the polar support. In another work, we investigated the LEF effect with SL-MoS_2. SL-MoS_2 was chemically exfoliated and doped with Ru via a hydrothermal process [94]. XRD suggested that SL-MoS_2 kept as single layer and no obvious stacking happened during the hydrothermal treatment. Likewise, the SL-MoS_2 is combined with different polar-faceted metal oxide supports as mentioned before, including CeO_2 (100) nanocubes (NCs), MgO (111) and ZnO (0001) nanoplates (NPs). As expected, the photocatalytic activities of Ru:SL-MoS_2 are greatly improved after blended with the polar-faceted oxides. The Ru:SL-MoS_2/CeO_2 NCs shows a high hydrogen evolution rate of 2977 μmol $g^{-1}h^{-1}$ under visible light irradiation. In the other hand, their non-polar counterparts show no obvious improvement on the photocatalytic activities of overall water splitting reaction. It is noteworthy that there has been nearly 4 times promotion in activity when blended with polar CeO_2 NCs support. TRPL spectroscopy confirmed the changes of exciton lifetimes of the photocatalysts, which show nearly the same trend as the photocatalytic water splitting activities. Therefore, the remarkable enhancement of photocatalytic activities is attributed to the prolonged exciton lifetimes. Strong LEF is exerted to the catalyst by the surface of the polar-faceted oxide supports, and such polarization effect facilitates the separation of photo-excited electron-hole pairs on the catalyst surface at the interface and therefore suppresses the recombination process.

The intensity of the LEF introduced by the polar-faceted materials is obviously related to the electronegativity difference of the metal and oxygen, so lower electronegativity of the metal gives higher polarity near the surface. And interestingly, when plotting against the polarity, both the photocatalytic activities and exciton lifetimes show apparent linear relationships within experimental errors. Such observation confirms that combining with polar-faceted materials is an effective approach to facilitate the separation of the photogenerated charge carriers, therefore result in enhanced photocatalytic performance. Similar phenomenon is observed as well when Ru:SL-MoS_2 is combined with layered double hydroxides (LDHs), which are also well-defined layer-structured materials and are able to introduce a local electric field via the surface polarity. Among various LDHs, MgAl-LDH showed the highest enhancement effect, leading to a hydrogen evolution rate of 1811 μmol $g^{-1}h^{-1}$ and a prolonged exciton lifetime of 2.62 ns. Total polarity is developed by taking into account the contribution of each element of the metal oxides or LDHs [94]. The photocatalytic activities and exciton lifetimes of the Ru:SL-MoS_2 based materials are in a linear relationship with the total polarities, which further confirms that the local polarization effect contributes to the separation of the photo-excited electron-hole pairs, leading to prolonged exciton lifetimes and largely enhanced photocatalytic activities and QEs. This simple and versatile approach may contribute to the rational design of the photocatalysts with suppressed recombination, for not only the water splitting system, but also other valuable photocatalytic processes.

3. Conclusion and prospective

In this review, the fundamental thermodynamic and kinetic considerations of photocatalytic water splitting reaction have been presented. Electron-hole pairs (excitons) are generated after the light irradiation, and then they separate from each other and migrate to the surface trapping sites before the surface chemical reactions for H_2 and O_2 evolution. For the stoichiometric production of H_2 and O_2, a photocatalyst needs to meet some prerequisites, such as having a bandgap wider than 1.23eV but narrower than 3.1eV, and also appropriate VBM and CBM positions. Besides, the photogenerated electrons and holes must have long enough lifetime to travel through the photocatalyst and reach the surface, before the surface chemical reactions are able to happen. For the solar-light-driven water splitting reaction to be a competitive approach for the hydrogen production, the quantum efficiency needs to undergo a substantial increase.

This is apparently a challenging goal, and in this mini-review, some effective and promising strategies have been summarized and discussed. Defect engineering has long been considered as a simple and strong technique to modify the bandgap structure of semiconductors. The deposition of co-catalysts facilitates the surface chemical reactions very efficiently and hinders the backward reaction when in an appropriate structure. However, the suppression of charge recombination remains to be the most difficult problem. Some methods have been developed previously and also reviewed here, which manage to prolong the exciton lifetimes by forming an internal electric field. Based on our recent work, some new strategies have also been demonstrated. First, elevated temperatures are found to be excitingly effective to enhance the photocatalytic water splitting performance provided that the heat required is provided by solar means. At elevated temperatures, the ionic dissociation of water is largely promoted which provide higher concentrations of H^+ and OH^-, and these species can prolong the exciton lifetimes of the photocatalysts by constructing LEF near the surface region. Further improvement of the LEF can be achieved by introduction of polar-faceted support materials, such as polar-faceted oxides or LDH, which are strongly polarized on the surface. This is proved to be able to suppress the charge carrier recombination, resulting in much enhanced QEs.

Particulate photocatalytic water splitting system has the advantage of simplicity and low cost over other solar energy conversion techniques, such as photovoltaic-electrolysis systems and photoelectrochemical devices, however, the highest solar to hydrogen conversion efficiency reported so far is only around 1% [35]. There is no doubt that the future work should be focusing on improving this efficiency to approximately 5% to meet the practical application requirement [77]. Therefore, new strategies to harness the visible or even infrared light are still desirable. Novel approaches to suppress the charge carriers recombination and the backward reactions are also required. The following inter-related processes such as separation, purification, transportation, and utilization of the hydrogen fuel remain challenging as well. All these aspects are tremendously essential to realize the efficient and sustainable production of hydrogen via solar-light-driven water splitting.

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