The application of perovskite materials in solar water splitting

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Abstract: Solar water splitting is a promising strategy for sustainable production of renewable hydrogen, and solving the crisis of energy and environment in the world. However, large-scale application of this method is hampered by the efficiency and the expense of the solar water splitting systems. Searching for non-toxic, low-cost, efficient and stable photocatalysts is an important way for solar water splitting. Due to the simplicity of structure and the flexibility of composition, perovskite based photocatalysts have recently attracted widespread attention for application in solar water splitting. In this review, the recent developments of perovskite based photocatalysts for water splitting are summarized. An introduction including the structures and properties of perovskite materials, and the fundamentals of solar water splitting is first provided. Then, it specifically focuses on the strategies for designing and modulating perovskite materials to improve their photocatalytic performance for solar water splitting. The current challenges and perspectives of perovskite materials in solar water splitting are also reviewed. The aim of this review is to summarize recent findings and developments of perovskite based photocatalysts and provide some useful guidance for the future research on the design and development of highly efficient perovskite based photocatalysts and the relevant systems for water splitting.

Key words: solar water splitting; perovskite materials; photocatalyst

1. Introduction

Nowadays, the fast-growing energy consumption and increasingly serious environmental pollution are two of the most important issues in the world, so the development of renewable and clean energies is an urgent problem to be solved. As a clean energy, hydrogen gas (H_2) is one of the most promising energy carriers to substitute traditional fossil fuels for solving the environmental issues, which is attribute to that H_2 has many excellent properties such as twice more gravimetric energy density (120 versus 44 MJ/kg) than that of traditional fossil fuels, transportable and storable nature, renewable energy with zero-carbon emission etc[1]. Moreover, hydrogen can serve as a feed-stock for many catalytic reactions, and can be used for producing liquid fuels by fixing carbon dioxide and nitrogen[2]. Due to the sufficient amount of solar energy and high abundance of water in the earth (nearly 71% of the Earth's surface is covered by water)[3–5], water splitting using the solar energy has received rapidly increasing attention with regard to the production of renewable hydrogen. However, there are still many obstacles to construct practical,

complete and large-scale solar water splitting systems to meet mankind's demand for hydrogen.

Among a variety of solar water splitting technologies, the development and design of semiconductor based photocatalytic or photoelectrocatalytic solar water splitting systems have attracted considerable and growing attention in the past few decades[6, 7]. Based on this, tremendous efforts have been taken to develop active, stable and low-cost photocatalysts, and a lot of efficient photocatalytic materials have been found such as TiO_2, ZnO, SnO_2, Fe_2O_3, WO_3, and metal-free materials including graphene based photocatalysts, graphitic carbon nitride (g-C_3N_4) based photocatalysts etc[8–17]. However, the solar to hydrogen (STH) efficiency of the reported solar water splitting system is still far below the target efficiency of 10% for large-scale applications[18]. Therefore, to boost the STH conversion efficiency, it is very necessary to develop new photocatalysts or photoelectrochemical (PEC) systems with high activity and wide light absorption capability. Among a large library of photocatalyst materials, perovskite materials based photocatalysts are very attractive among different kinds of materials for construction of high efficient solar water splitting systems, which is attribute to their good stability, high photocatalytic activity, excellent structural flexibility and simplicity, giving them the potential to design and develop high efficient photocatalysts by precisely adjusting and controlling the composition, morphology, band structure of the materials. Specifically, the ideal perovskite usually has a cu-

bic structure and can be represented by a formula of ABX₃. The A site can be occupied by alkali metal, alkaline-earth metal and rare-earth metal elements, while B site is usually occupied by transition metal elements, and X site is usually occupied by nonmetal elements (O, N etc.)[4, 19, 20]. The rationally combining or partially substituting different elements at A, B or X sites can form diverse perovskite materials and derivatives, which can also modulate the crystal or electronic structures and the related physical and chemical properties of the perovskite materials, offering great potential to regulate the photocatalytic performance of the perovskite based photocatalysts[1, 4, 21, 22]. Thus, developing and designing perovskite based photocatalysts are ideal routes to enhance the STH efficiency of the solar water splitting system, and would finally solve the energy and environmental crisis of the world.

In this paper, the recent developments of perovskite photocatalysts for solar water splitting are comprehensively reviewed. It will focus on the designing and modulating of different perovskite materials to enhance their light absorption capability and the photocatalytic activity for water splitting. The aim of this review is to summarize recent findings and progress on perovskite based photocatalysts and provide some useful guidance for the future research on the design and development of highly efficient perovskite based photocatalysts and systems for solar water splitting. Based on this, the paper is composed of five sections. Section 1 briefly introduces the relationship between hydrogen energy and the crisis of energy and environment in the world and the perovskite materials. In Section 2, the structures and properties of perovskite materials are presented. In Section 3 the fundamentals of solar water splitting including photocatalysis and photoelectrocatalysis are discussed. In Section 4, the recent developments and strategies regarding the design of perovskite catalysts for photocatalytic reactions, including modification of the chemical component, crystal structure and morphology engineering, application of ferroelectric property, construction of heterojunction structure, and construction of plasmonic-based photocatalysts, are comprehensively reviewed. Finally, in Section 5, the current challenges and perspectives for the future research in developing of perovskite based photocatalysts for water splitting are discussed.

2. Structures and properties of perovskite materials

Perovskite materials generally have a same crystal structure as calcium titanate (CaTiO₃), which is initially discovered by the Russian mineralogist Lev Perovski. Later, the "perovskite" is used to represent for a family of materials that have the same type of crystalline unit cell as CaTiO₃[23]. Generally, the chemical composition of perovskite materials can be denoted by a formula of ABX₃, where A and B represent two cations with different sizes, and X is an anion (O^{2-}, I^-, Br^-, Cl^-, etc.) that forms bonds with two cations. The ideal ABX₃ perovskite-type structure is cubic symmetry that has a space group of $Pm3m$-O_h. As shown in Fig. 1, the smaller cation B and anion X can form a BX₆ octahedral structure, where B is located at the center and surrounded by the anion X lie in the corners of octahedra. In this structure, the lager cation A is usually 12-fold cuboctahedral coordinated and the cation B is 6-fold coordinated with the surrounding X anions[21, 24, 25].
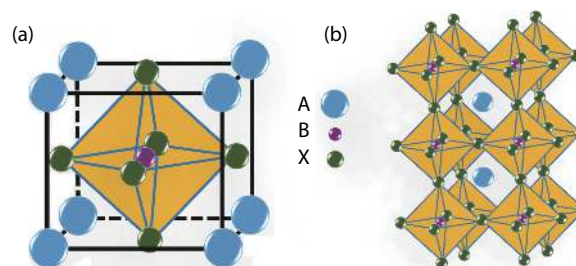

Fig. 1. (Color online) (a) Schematic structure of cubic ABX₃ perovskite unit cell, and (b) the extended tridimensional structure of perovskites formed by the corner-linked octahedral.

As for the perovskite materials, the cations occupying in the A and B site can affect the properties of the materials. More than 90% of metal elements in the periodic table can be stably located in the perovskite lattice, and many kinds of compositions and constituent elements essentially can not change the basic structure. In the ideal cubic symmetry structure, the ionic radii keep the following relationship: $r_A + r_X = \sqrt{2}(r_B + r_X)$, where r_A, r_B and r_X are the ionic radii of elements in A, B and X-site, respectively. However, it is found that the cubic structure is still retained in the perovskite materials even if the actual relationship is not identical to the above[6, 21]. To construct a criterion for the formation of the perovskite structure, Goldschmidt firstly introduced a tolerance factor (t), which is widely accepted and defined by the following equation: $t = (r_A + r_X)/\sqrt{2}(r_B + r_X)$[21, 26, 27]. Although it is generally accepted that the cubic perovskites can be stabilized when the t lies in a range of 0.76 < t < 1.13, Wu $et~al.$ found that the perovskite structures are not stable, even t ranges between 0.8 and 0.9[28]. To further reveal the formation criterion of perovskite structures, the octahedral factor (μ) was then proposed, where $\mu = r_B/r_X$. The formability and stability of the alkali metal halide perovskite can be determined by combining with the above two factors (t and μ)[29]. So the radii of elements play an important role for the structure of perovskites. For the ABX₃ perovskite, the different types and valence states of cations can cause the variation of its radii, which can result in the lattice distortion and the transformation of crystal phases. These variations have a direct impact on the crystal field of perovskites and can cause the variations of the dipole and electronic band structures, which are important for the photocatalytic properties of the materials, as they can influence the excitation, transfer, and redox reaction of the photogenerated charge carriers during the photocatalytic process[24, 30, 31].

The rich compositions and constituent elements of perovskite materials gives rise to the great flexiblility of their electronic structures and band structures, which in turn makes the perovskites a wide variety of diverse physical and chemical properties, such as fine ferroelectricity, superconductivity, colossal magneto resistance, perfect oxygen ion diffusion property, lithium mobility and high catalytic performance (including oxidation of small molecules such as CO and hydrocarbons, photo(electro)chemical splitting of water, and reduction of CO₂ and O₂[4, 23, 32−42]. Above all, the flexibility of the electronic and crystal structure provides an opportunity for the design of multifunctional and high-performance perovskite photocatalytic materials. Through careful and scientific designing of perovskite materials, the electronic structure,
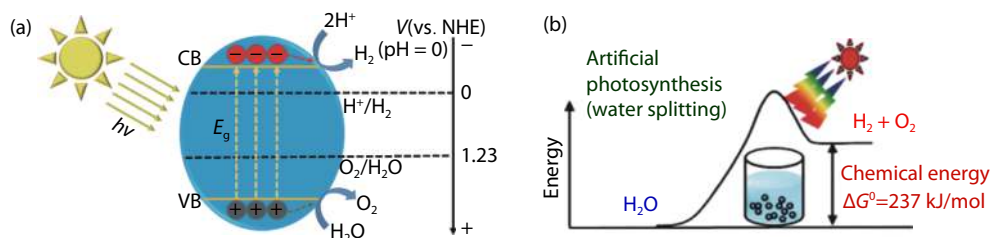
Fig. 2. (Color online) Schematic illustration of the basic reaction mechanism of the overall water splitting on a semiconductor (a), and uphill reaction process of photocatalytic water splitting (b). Reprinted from Ref. [44].

band structure, adsorption properties, crystal structure and crystallite size can be tuned to improve selectivity and stability of catalysis, minimize electrochemical and chemical barriers of different catalytic reactions, and enhance the light absorption capability of the photocatalysts.

3. Fundamentals of solar water splitting

As a potential candidate for the storage and conversion of solar energy, the photo(electro)catalytic water splitting into hydrogen and oxygen has been regarded as one of the most important methods for the future energy crisis. Since the solar water splitting was firstly discovered by Honda and Fujishima in 1972, which showed that the solar water splitting can be occurred when using single-crystalline TiO_2 as a photoanode under UV light irradiation and Pt as a cathode with an external bias[43]. To date, a large number of good achievements have been made in the field. Moreover, the basic principles of solar water splitting had been presented in many reviews[7, 44–49]. Generally, semiconductor compounds are in different phase with the reactants during the photocatalytic reactions, so they are usually used as heterogeneous photocatalysts and the basic reaction mechanism is shown in Fig. 2(a). When the energy of incident light is larger than the band gap (E_g) of the material, the electrons in the valence band (VB) can be excited to the conduction band (CB) of the heterogeneous photocatalyst, leading to the separation of electrons and holes. The separated electrons and holes can directly react with the water molecules that absorbed in the surface active sites of the photocatalyst and cause H_2 and O_2 production[44].

As shown in Fig. 2(b), the solar water-splitting is an uphill and nonspontaneous reaction because the Gibbs free energy is positive change about 237.3 kJ/mol under standard temperature and pressure[44, 50]. For facilitating the water splitting reaction, the band gap and the potential of the CB edge and the VB of the semiconductor photocatalysts are the key points. The potential of the bottom edge of the CB has to be lower than the redox potential of H^+/H_2 (0 V versus normal hydrogen electrode (NHE)), while the potential of the top edge of the VB has to be higher than the redox potential O_2/H_2O (+1.23 V versus NHE). Accordingly, the minimum band gap to drive water splitting reaction is 1.23 eV that corresponds to a wavelength of about 1000 nm ($\lambda = 1240/E_g$). From the thermodynamic theory, this potential distribution of the photocatalyst with the minimum band gap of 1.23 eV and appropriate band position is necessary and sufficient for solar water splitting. However, the water reduction and oxidation processes are two-electron and four-electron process, respectively. These reaction processes are multi-step reactions and there is

activation barrier between the photocatalyst and water molecules during the charge-transfer process. Therefore, there usually be a high over-voltage in the process of water oxidation and reduction and the energy of the incident photons must greater than the bandgap of photocatalyst, so the minimum band gap of 1.23 eV is not sufficient for driving the whole water splitting, and the practical value is in the range of 1.6–2.4 eV[27, 44, 46, 51].

There are mainly two ways for solar water splitting: the one is using powdered photocatalyst for water splitting and another is PEC method that using photoelectrodes. The basic feature of photocatalytic water splitting using a powdered photocatalyst is shown in Fig. 2(b). The pulverized photocatalyst is well dispersed in a water pool and exposed to sunlight, and then the generated gas from water splitting can be readily got. For the simplicity of powdered photocatalyst system, it is advantageous for large-scale application. However, the dependence on using sacrificial agent for the half-reaction and the difficulty for separation hydrogen and oxygen from the resulting gas mixture are the main challenge of this method. Thus, it is important to develop efficient photocatalyst and design optimized system for practical application of solar water splitting by powdered photocatalyst. In addition, lots of PEC cells have also been developed for solar water splitting[4, 7, 9, 52, 53]. The first PEC cell used for water splitting was reported by Honda and Fujishima in 1972[43]. As shown in Fig. 3, electrons and holes are generated on a TiO_2 electrode while it is irradiated by UV light. Then the photogenerated holes on the TiO_2 electrode can oxidize water to form O_2 while the electrons can be separated from the holes and transferred to the Pt counter electrode under a certain external bias with a power supply to reduce water to form H_2. Another representative study was done by Anpo's group who succeeded in the separation of the generated hydrogen and oxygen with a TiO_2 thin-film photocatalyst compounding with a Pt counter electrode, and the two sides of the compound photoelectrode are in different electrolytes and enclosed with a two-compartment cell[54]. However, the key problem of solar water splitting by PEC cell is the lack of suitable photoelectrode materials with appropriate band structure and high stability.

According to the previous researches[27, 44, 49], the photocatalytic reaction is usually composed of three basic processes. As shown in Fig. 4, the first step is the absorption of effective photons whose energy ($h\nu$) is equal or larger than the band gap of photocatalysts, leading to the generation of photoexcited electron-hole pairs in the bulk of them. In this step, a large number of photogenerated carriers are required for a photocatalyst. However, due to the wide band gap,
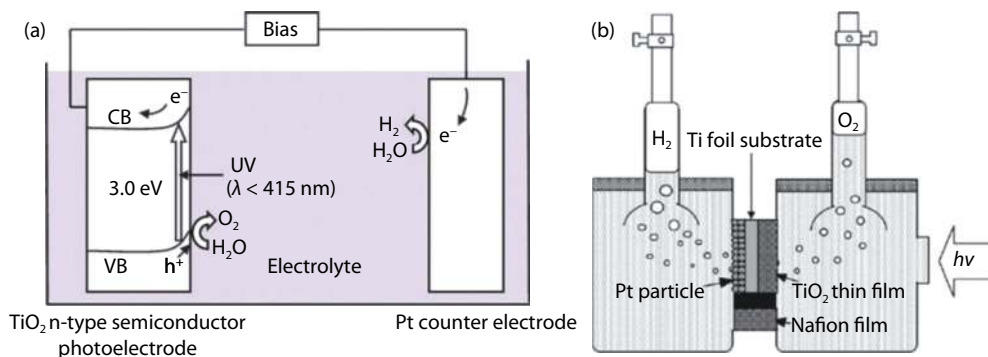
Fig. 3. (Color online) (a) Schematic illustration of water splitting using a TiO_2 photoelectrode. Reprinted from Ref. [44]. (b) H-type glass container for the separate evolution of H_2 and O_2 using a TiO_2 thin film photocatalyst device (TiO_2 side, 1.0 M NaOH aqueous solutions; Pt side, 0.5 M H_2SO_4 aqueous solution). Reprinted from Ref. [54].
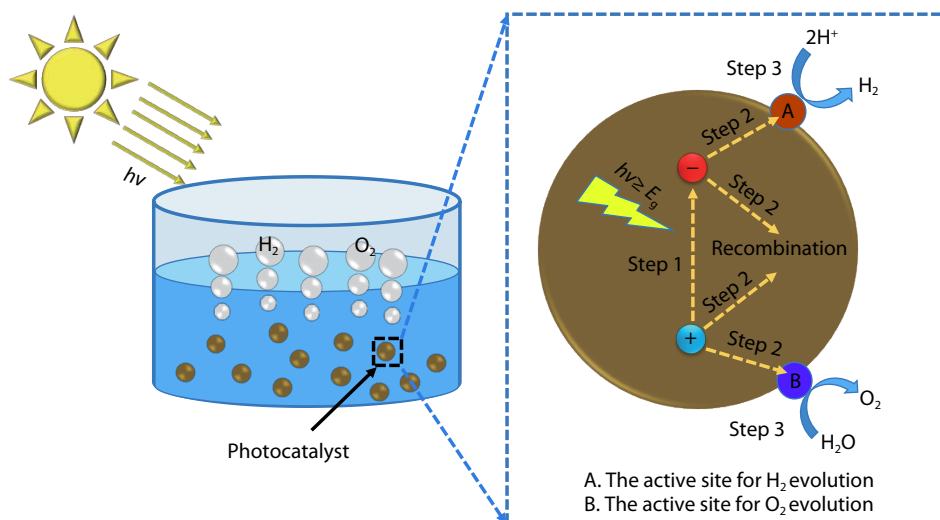

Fig. 4. (Color online) Schematic illustration of the main processes of the photocatalytic overall water splitting reaction.

most of semiconductor photocatalyst materials can only respond to UV light which is only of five percent of the total energy of sunlight. The main component of the solar spectrum (approximately 95%) is composed of visible light (approximately 50%) and infrared light (approximately 45%)[47]. Therefore, a primary goal of the solar water splitting is to develop photocatalysts with efficient visible light response by suitable band engineering. The second step is the separation photogenerated electron-hole pairs and the migration charge carriers. In general, crystal structure, crystallinity and particle size of the photocatalyst have a direct impact on this step. For one thing, the crystallinity affects the density of defects directly. The higher the crystallinity, the less the defect density, which can act as trapping and recombination centers of the photogenerated carriers. For another ting, the large particle size can increase the distance that the separated electrons and holes have to transfer to the catalytic activity sites on the surface of photocatalyst, which can improve the probability of recombination of photocatalytic carriers and reduce the photocatalytic performance of the catalyst[44, 45]. The third step is the process that the photogenerated carriers participate in the surface photocatalytic reactions. The number of active sites and the surface area of photocatalysts are crucial for this step. In order to improve the property of photocatalyst, noble metal or metal oxide is usu-

ally loaded onto the photocatalyst and act as cocatalysts to increase the active sites[44, 55]. Thus, further improvements and optimizations of the aforementioned three processes are crucial for enhancing and obtaining high photocatalytic performance for solar water splitting reactions.

4. Strategies to apply perovskite materials for solar water splitting

To design a photocatalyst with excellent performance, the generation, migration and reaction of the photogenerated charge carriers, which are three major steps during the whole process of photocatalytic reaction, must be considered. Perovskite can be used as a new category of ideal photocatalyst for solar water splitting because it has many advantageous properties different from other conventional photocatalytic materials. Firstly, some of perovskites have suitable band structure that are favorable for either half reaction or the overall water splitting. Secondly, the flexible compositions and constituent elements of perovskite materials in A site or B site offer its adjustable electronic structure and the according band structure. Last but not least, some of perovskites have ferroelectric and/or piezoelectric properties which can further enhance their photocatalytic abilities for water splitting[56–58]. However, the large band gap of most perovskite materials impedes them used as high efficient pho-
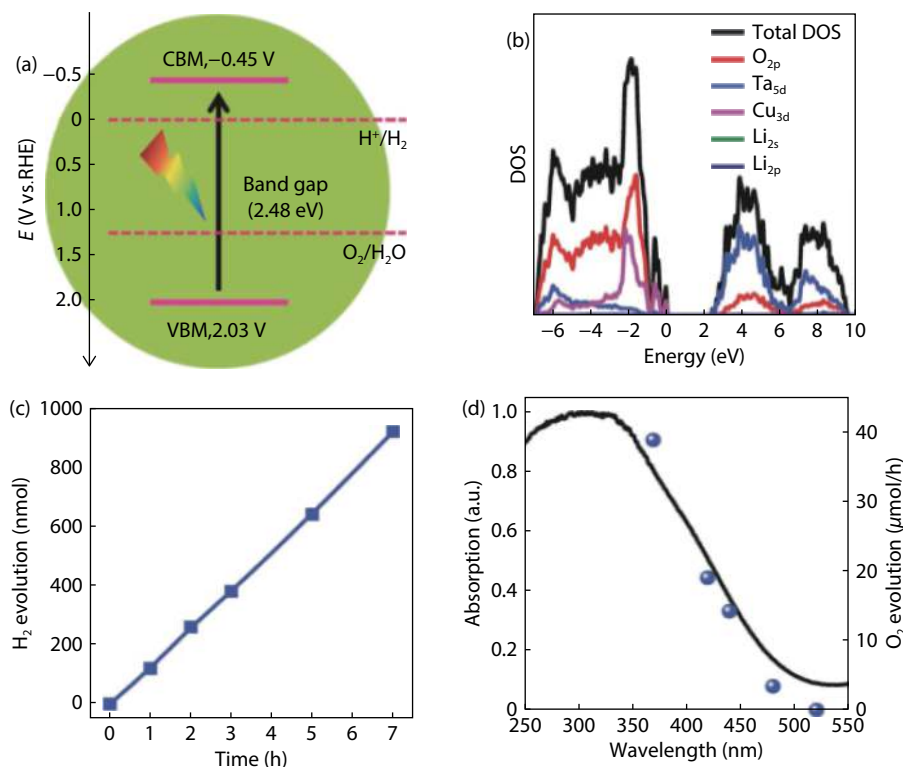
Fig. 5. (Color online) Schematic illustration of (a) the band structure and (b) DOS (density of states) plots of LCTO, (c) typical time course of photocatalytic H_2 evolution reaction, (d) photocatalytic O_2 evolution rate as a function of the cutoff wavelength of incident light. Reprinted from Ref. [69].

tocatalysts, because it's hard for them to utilize the visible and infrared light of solar spectrum which is the main part of sunlight and contains almost 95% of the whole solar energy. Different strategies have been developed to optimize the three key processes (generation of photoexcited electron-hole pairs, the separation of electron-hole pairs and the migration of charge carriers, and the surface photocatalytic reactions initiated by photogenerated carriers) of photocatalytic reaction that use perovskite materials as photocatalysts for water splitting. In this review, we will focus on five key strategies: (1) modification of the chemical component, (2) crystal structure and morphology engineering, (3) application of ferroelectric property, (4) construction of heterojunction structure, and (5) construction of plasmonic-based photocatalysts.

4.1. Modification of the chemical component

As the electronic band structures of perovskite materials are directly related to their chemical component, the strategy to modify the chemical component is mainly for the purpose of adjusting the electronic structures and enhancing the solar light response of the photocatalytic materials. The electronic band structures of a perovskite photocatalyst can be designed and modified by doping of foreign element. Generally, the CB of most perovskite materials is mainly consisted of d_0 transition metal orbits and the bottom edge of CB is much lower than the redox potential of H^+/H_2 (0 V vs. NHE). The VB is mainly consisted of O_{2p} atomic obits and the top edge of the VB energy levels is much higher than the redox potential of H_2O/O_2. The large band gap can be altered in two main ways: introducing new mid-gap state between the VB and CB through modifying the chemical component of per-

ovskite material, and altering the VB or CB position of perovskite material through the mixing of energy levels of the foreign elements and host elements[57, 59, 60]. Therefore, it is an effective way to manipulate the band structure of perovskite material by doping of suitable foreign elements, which can make perovskite material become a visible light response photocatalyst and enhance its photocatalytic activity.

In the past few years, numerous doped perovskite photocatalysts have been explored for potential applications in the field of photocatalysis, and the most common materials for solar water splitting under UV and visible lights are Ti, Ta, and Nb-based perovskite oxides[61]. Take the typical $SrTiO_3$ perovskite as an example, $SrTiO_3$ has a broad band gap of 3.2 eV, which limits it act as a visible light response photocatalyst. However, when it is doped with forigen elements, such as Fe, Rh, Ru, Ir, and Mn, the band gap of the compound material is decreased and it apparently becomes a visible-light responses photocatalyst[62–64]. Akihiko et al. found that the Mn-, Ru-, Rh-, and Ir-doped $SrTiO_3$ can enhance the solar light response range to visible light region, which is due to electronic transition from the discontinuous donor levels formed by the dopants to the CB band of the host $SrTiO_3$. Moreover, the $SrTiO_3$:Rh photocatalyst indicates the highest H_2 evolution rate among all the doped photocatalysts due to the doped Rh as a Rh^{3+} on the B-site which can serves as the visible light absorption center and the surface reaction center. In addition, Cr-doped $SrTiO_3$ is also a promising visible light response photocatalyst for solar water splitting. Due to the formation of a new mid-gap state that lies about 1.0 eV above the top of the valence band, the band gap of $SrTiO_3$ is narrowed to about 2.48 eV[65]. Besides, the band gap energy of perovskite photocatalyst can be manipulated by doping

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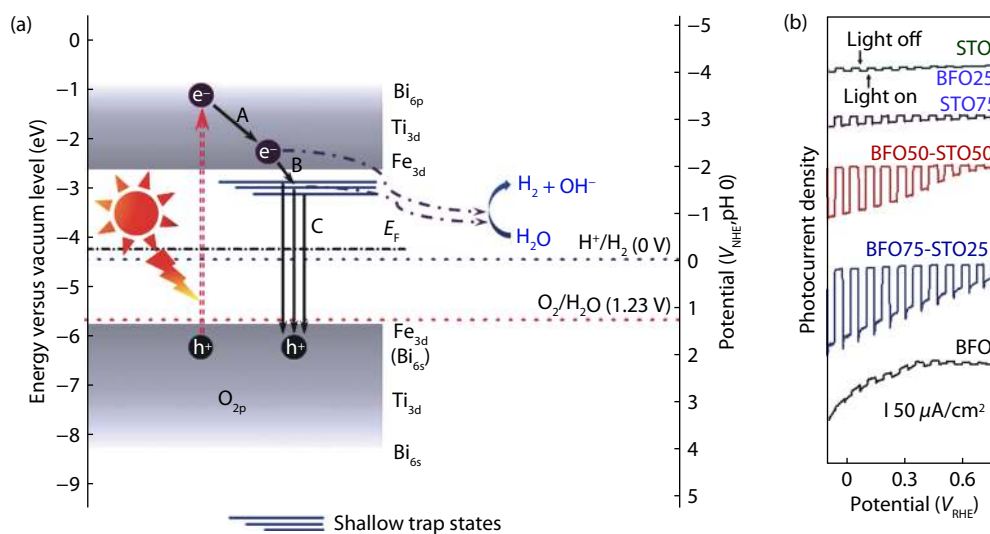
Fig. 6. (Color online) (a) Schematic diagram of band positions relative to the vacuum level and NHE for the BFO50-STO50 film. A, B, and C represent the photoexcited carriers relaxation and recombination processes. (b) Current density-potential curves of BFO, BFO75-STO25, BFO50-STO50, BFO25-STO75, and STO films. Reprinted from Ref. [81].

of A-site elements. The modified $SrTiO_3$ and $BaTiO_3$ perovskites were synthesized by Guo *et al.* among which the A-sites were partially substituted by Zn^{2+}. It was calculated that the top of VBs was mainly consisted of O_{2p} orbitals and the bottom of the CBs was derived from Ti_{3d} and Zn_{3d}. The bottom of CBs is moved down with increasing the Zn content which causes the decrease of band gap of perovskites[66]. Furthermore, some researchers have also studied tantalate and niobate based perovskites by modifying the A-site cations, such as dual doping of A-site for $MLnTa_2O_7$ (M = Cs, Na, Rb, H; Ln = Pr, La, Nd, and Sm) and doping of A-site for $MIn_{0.5}Nb_{0.5}O_3$ (M = Ca, Sr, and Ba) to change the band gap[67, 68]. Recently, Dong *et al.* prepared a novel perovskite-like photocatalyst $LiCuTa_3O_9$ (LCTO) with A-sites partially occupied by Li^+ or Cu^{2+} cations and B-sites occupied by Ta^{5+} cations. As shown in Fig. 5, due to the hybridization of O_{2p} and Cu_{3d} orbits, the VB position of the perovskite was greatly enhanced and it show a visible-light-responded dual functions for water reduction and oxidation[69]. These results indicate that the band structures and crystal structures could be changed by doping of A-site with foreign elements. In addition, doping of X-site of perovskites has also attracted considerable attentions to reduce the band gap for water splitting. In these materials, perovskite oxynitrides are a kind of materials that can absorb visible light for water splitting since the doped N can form a new VB, which leads to upward shift of the top of VB and reduces the band gap[27]. Moreover, the anion doping of O-site for titanates has also been reported to enhance the photoactivity for water splitting. The calculated and experimental results indicate that S/N-doped $NaTaO_3$ shows the remarkably reduced band gap since the new p orbital energies formed by the dopant are higher than the O_{2p} orbits[70, 71].

In addition to one element or one site doped of perovskite materials, many two elements doped perovskite photocatalysts with strong visible light absorption have been reported. For example, Cr, B-codoped-$SrTiO_3$ had been synthesized by Yu *et al.* The narrowed band gap of this material with strong visible light absorption is due to strong p-d repulsion

of doped B_{2p} orbits with Cr_{3d} orbits. The results offer a novel route that co-doping of two elements can also modify the band structure of perovskite materials[72]. Similarly, Luo *et al.* studied the effects of B and Fe co-doping on the ability of visible light absorption and the activity of $SrTiO_3$ photocatalyst[73]. It is confirmed that the two elements are successfully doped into the $SrTiO_3$ matrix where B substituted O anions, while Fe substituted Ti cations, which leads to the band gap of $SrTiO_3$ significantly reduced from 3.4 to 1.9 eV. Recently, Domen *et al.* discovered $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ solid solutions that could realize overall water splitting under visible light irradiation when the compounds with $x \geqslant 0.33$. The experimental results revealed that co-substitution of Mg^{2+} for Ta^{5+} and O^{2-} for N^{3-}, respectively, could tune the band position of the compounds especially for the valence band position. When increasing the oxygen content of the compounds, the top of VB would shift toward the more positive potential which is benefit for water oxidation to realize overall water splitting[74].

Some researchers have also investigated the solid solutions that are composed of two different perovskite materials to overcome the limitations of wide band gap for solar water splitting, including $Na_{0.5}La_{0.5}TiO_3$-$LaCrO_3$, $AgNbO_3$-$SrTiO_3$, $SrTiO_3$-$LaTiO_2N$, and $BiFeO_3$-$SrTiO_3$ (BFO-STO)[75–79]. In these materials, the band structure can be effectively modified by doping with nonmetal elements (e.g., C, N, and S), 3d transition elements, and cations with d^0 or d^{10} or $d^{10}s^2$ electronic structures[6, 20, 27, 67, 80]. Driscoll *et al.* have explored the underlying mechanism of enhanced solar water splitting ability by constructing a thin film system of BFO-STO[81]. As shown in Fig. 6, the bottom of CB is raised and an exponential tail of trap states is formed near the CB edge by hybridizing of Ti_{3d} and Fe_{3d} orbits, and the new trap states can strongly suppress the fast recombination of photon-generated carriers and enlarge the absorption of the compounds to visible-light region.

4.2. Crystal structure and morphology engineering

In general, the crystal structure, crystallinity, particle shape and size of the photocatalyst are directly related to the
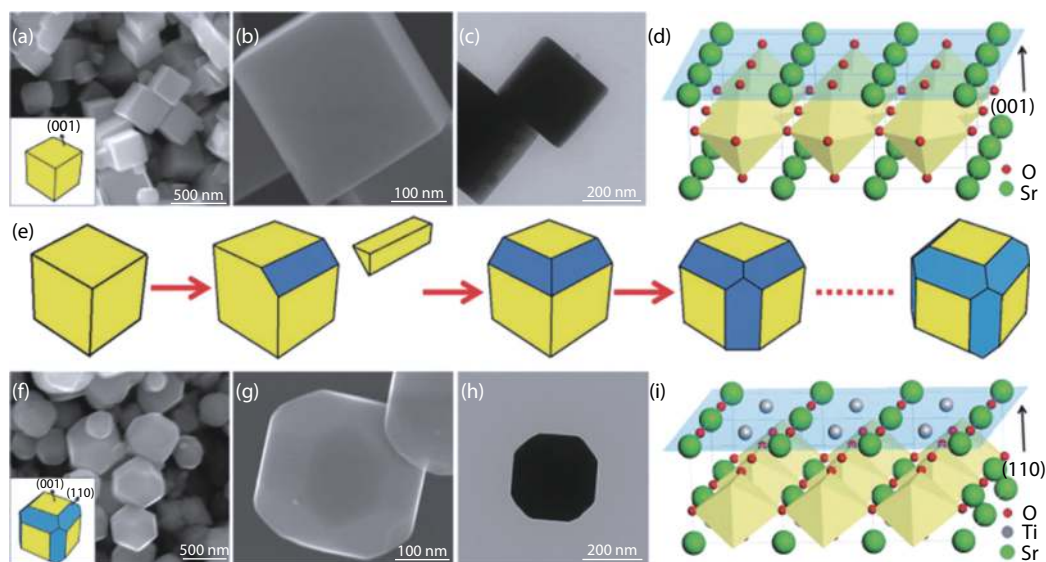
Fig. 7. (Color online) The morphology engineering strategy for SrTiO$_3$ nanocrystals. (a–c) The morphology of 6-facet SrTiO$_3$ nanocrystals. (d) The structure of the {001} facet of SrTiO$_3$. (e) The schematic description of changing SrTiO$_3$ nanocrystals from 6-facet to 18-facet. (f–h) The morphology of 18-facet SrTiO$_3$ nanocrystals. (i) The structure of the {110} facet of SrTiO$_3$. Reprinted from Ref. [85].

surface area of photocatalysts and the diffusion pathway of charge carriers, which can directly affect the photocatalytic activity of the photocatalysts[82, 83]. Although modifying the crystal structure and morphology of the perovskite photocatalysts may not make influence on altering the electronic structures and the spectral response range of the parent materials, it can affect the separation and migration efficiency of photogenerated carriers, which is one of the most important steps in solar water splitting. The photogenerated carriers can be separated effectively between different facets, which can be realized by modulating the morphology of the perovskite photocatalysts. Therefore, the exposed facets of crystals are important for the photocatalytic performance of the photocatalysts especially for the low symmetry nanocrystals. SrTiO$_3$ is a very common cubic phase perovskite photocatalyst for solar water splitting[84]. As shown in Fig. 7, by controlling the nucleation and growth process of nanocrystal, Mu *et al.* successfully tailored the morphology and constructed a 18-facet SrTiO$_3$, which realized the exposed facets of high symmetry SrTiO$_3$ nanocrystals from isotropic facets (6-facet SrTiO$_3$) to anisotropic facets (18-facet SrTiO$_3$). Interestingly, they found that the distribution of the reduction and oxidation catalytic sites on the two nanocrystals was different. For the 6-facet SrTiO$_3$, the reduction and oxidation catalytic sites are randomly distributed on the isotropic facets. However, for the 18-facet SrTiO$_3$, the two different catalytic sites are regularly distributed on the different anisotropic facets, respectively. Based on this performance, by selectively depositing the reduction and oxidation cocatalysts on the different anisotropic facets of 18-facet SrTiO$_3$ nanocrystals, the photogenerated carriers can be separated effectively between the anisotropic facets and the photocatalytic performance of the photocatalyst can be greatly improved[85]. Moreover, a BaTiO$_3$ nanocubes supported CdSe quantum dots (QDs) compound structure is reported by Zhong *et al.*, and used as the model to investigate the the synergetic effect of different exposed facets on the activity of heterogeneous catalyst system. By a simple solvothermal method, BaTiO$_3$ exposed with different facets was synthes-

ized, and CdSe QDs were successfully deposited on isotropic facets of 6-facet cubic BaTiO$_3$ and anisotropic facets of 30-facet varietal cubic BaTiO$_3$ by a novel chemical bath strategy. Interestingly, due to the high efficiency of charge separation between BaTiO$_3$ and CdSe QDs and the synergetic effects of {001} and {230} facets on inhibiting the recombination of photogenerated carriers, the CdSe QDs deposited on 30-facet BaTiO$_3$ demonstrated enhancement of apparent photocurrent and superior performance compared to CdSe QDs sensitized cubic 6-facet BaTiO$_3$[86]. These findings suggest that modulating the morphology of perovskites can change its exposed crystal facets, which can make a great effect on the separation efficiency of charge carriers, resulting in improving the photocatalytic activity of the perovskite photocatalysts.

Some researchers have also investigated the effects of restructuring the crystal structure of the perovskite on the electronic structure and the according photocatalytic performance of photocatalyst for solar water splitting. By means of systematic density functional theory (DFT) computations, Qiao *et al.* introduced a two-dimensional photocatalyst of monolayer PdSeO$_3$, which has a moderate band gap of 2.84 eV and has rather pronounced optical absorption both in the visible and ultraviolet regions of the solar spectrum. Remarkably, the valence and conduction bands of PdSeO$_3$ perfectly engulf the redox potentials of water, which make it can be utilized as a highly efficient photocatalyst for direct overall water splitting without using sacrificial reagents and cocatalysts[87]. In addition, Li *et al.* fabricated two kinds of NaNbO$_3$ with different crystal structures of cubic and orthorhombic phase, respectively. As shown in Fig. 8, the orthorhombic NaNbO$_3$ showed a larger band gap than the cubic NaNbO$_3$. Correspondingly, the photocatalytic hydrogen production activity of cubic NaNbO$_3$ was nearly two times higher than that of orthorhombic NaNbO$_3$[31]. The DFT calculation demonstrated that the higher photocatalytic performance of cubic NaNbO$_3$ could be attributed to its unique electronic structure with high symmetry, which was beneficial to the excitation and transfer process of photogenerated carriers.
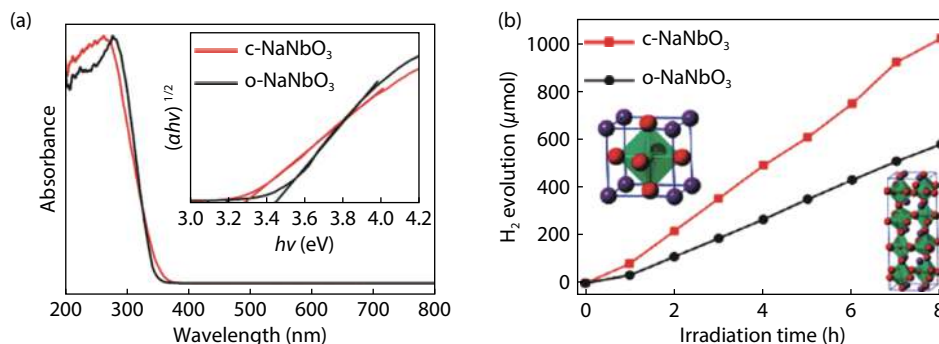
Fig. 8. (Color online) (a) UV–vis absorption spectra and (b) typical time course of photocatalytic H_2 evolution reaction of c-NaNbO$_3$ (cubic NaNbO$_3$) and o-NaNbO$_3$ (orthorhombic NaNbO$_3$) samples. Reprinted from Ref. [31].

Moreover, four distinct types of Lead Magnesium Titanate (PMT) perovskites including the shapes of spheres, flakes, hierarchical flower and thin microbelts had been synthesized by Chandrasekaran et al.[88]. Owing to the remarkable structural features of the microbelts such as a large surface area, high optical absorbance, more active sites and high interface area, which provided large contact areas of the electrolyte with highly active materials and a rapid route for charge transfer, the PMT perovskite with the thin microbelt structure showed the highest photoconversion efficiency for water splitting.

Particle size can also influence the photocatalytic activity. Since the smaller particles have a larger specific surface area and smaller period for migration of the photogenerated carriers to the surface of photocatalysts, which could reduce the probability of charge recombination and improve the photocatalytic activity of photocatalysts. Parida et al. synthesized LaFeO$_3$ NPs with different particle sizes by a sol-gel method under different activated temperatures from 500 to 900 °C for 2 h[89]. All the prepared photocatalysts exhibited visible light activity for solar water splitting, and the samples calcined at 500 °C showed the highest amount of H$_2$ and O$_2$ evolution. The enhanced photocatalytic activity of LaFeO$_3$ calcined at 500 °C was consistent with the small particle size and the according larger BET-surface. Tijare et al. also compared the photocatalytic activities of the LaFeO$_3$ samples synthesized by the sol-gel method and the solid state route, respectively[90]. The results showed that due to the higher surface area and nanosized particle morphology of the sol-gel-generated LaFeO$_3$, it exhibited higher photocatalytic activity for water splitting than the samples with the same composition synthesized by the solid state route under visible light irradiation. A similar results was reported for SrSnO$_3$ where peanut-shaped SrSnO$_3$ synthesized using the aqueous peroxide route exhibited much higher photocatalytic activity than the samples synthesized via a solid-state reaction, which is due to the different structural order, surface area and particle size of the two kinds of samples[91]. Krtil et al. demonstrated that the size and shape of SrTiO$_3$ have a strong influence on its PEC activity. The different samples were synthesized by tuning the content of gelatin, which determines the size and band gap of the perovskite nano-cubes. The results showed that all the samples were active in PEC water splitting, and their specific activity decreases with decreasing particle size and drops exponentially with crystal size below 20 nm[92]. In addition, the crystalline quality of the photocatalyst can strongly affect its photocatalytic activity. Due to the strong negative cor-

relation between crystalline quality and the amount of defects, the higher crystalline quality can decrease the amount of defects which can operate as trapping and recombination centers of photogenerated electrons and holes and then reduce the photocatalytic activity[44]. Kudo et al. found that the high calcination temperature can increase the crystallinity of SrTiO$_3$ and enhance its photocatalytic activity because the number of defects decreases with the increase of crystallinity[93].

4.3. Application of ferroelectric property

Due to their unique performances in the separation and migration photoexcited charge carriers, the application of ferroelectric materials for solar water splitting is another potentially efficient approach to overcome the limits of the traditional semiconductors[94]. Ferroelectric perovskite materials, such as BiFeO$_3$ (BFO) and Pb(Zr,Ti)O$_3$ (PZT)[95–98], usually have a large, stable and tunable remnant ferroelectric polarization which can produces a permanent electrical polarization field. This internal electric field is useful for separating the photoexcited charge carriers and switching the charge-transfer directions. Interestingly, the orientation and intensities of the polarization field can be controlled by external applied voltages, which is useful for solar water splitting with a photoelectrode because the controllable field of a ferroelectric photoelectrode can make it as both a photocathode and a photoanode, giving a highly realizable possibility to drive both water oxidation and reduction just by a ferroelectric photoelectrode through tuning the orientation of remnant polarization. Based on this, our group fabricated a series of polycrystalline BFO photoelectrodes by a cost-advantageous spin-coating technology. As shown in Figs. 9(a)–9(d), due to the distinct ferroelectric performance of the ferroelectric perovskite materials, the orientations of the band bending for BFO at the BFO/electrolyte can be switched from up with –8 V poling pretreatment to down after –8 V poling pretreatment. Accordingly, the external quantum efficiency and photocurrent of the photoelectrodes are changed with different polarization states. Moreover, the systematical PEC investigations indicate that the charge-transfer directions of photoexcited charges both in the BFO and in the surface modifiers, such as molecular dyes and CdSe QDs can be tuned by changing the poling conditions of the ferrroeletric photoelectrodes. These results demonstrate the adjustable polarization field of ferroelectric perovskite materials can be used for PEC reaction, which provides a new strategy to design smart PEC systems for driving both water oxidation and reduction on a single
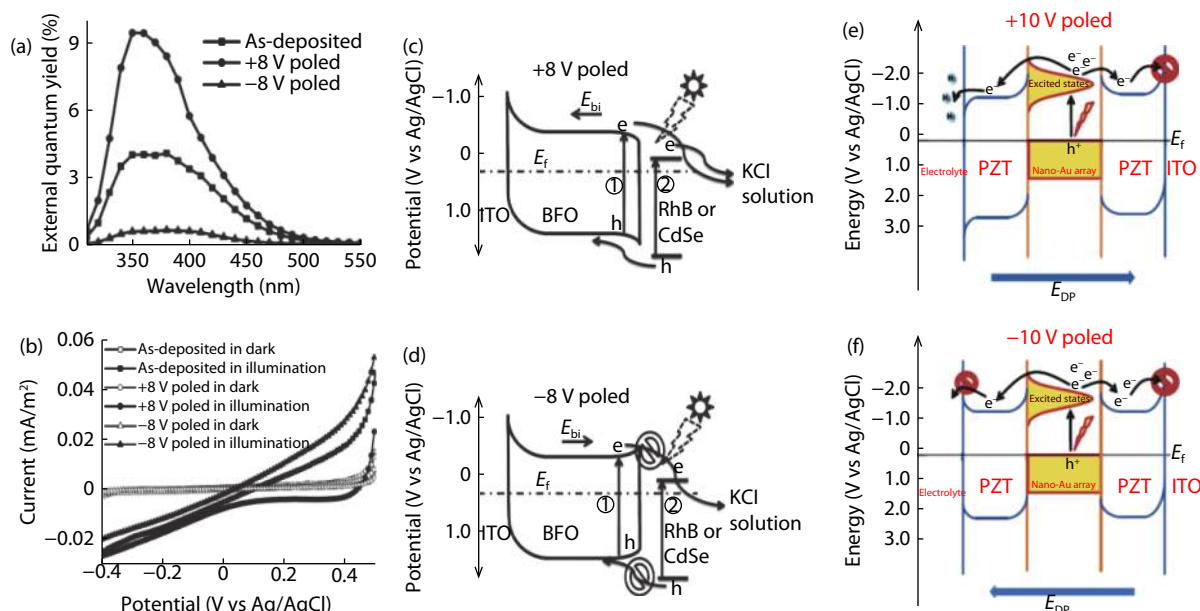
Fig. 9. (Color online) (a) External quantum yield spectra measured for BFO electrodes before poling and after + 8 and –8 V poling. (b) Photocurrent-potential characteristics of the photoelectrodes with different polarization states. Schematic illustrations of the mechanisms in photoexcited charge transfer from BFO films to the electrolyte and from excited surface modifiers to the BFO films after the BFO films were (c) positively and (d) negatively poled. Reprinted from Ref. [99]. (e, f) Schematic electronic band structure and the mechanisms for the injected hot-electron transfer from PZT films to the electrolyte for the two poling configurations. Reprinted from Ref. [101].

photoelectrode[99]. Recently, another typical example that used ferroelectric perovskite materials for PEC water splitting was reported by Song et al., who systematically summarized the effects of ferroelectric switching under different polarization states on PEC behaviors[100]. The different polarization states can induce different band bending which is important for the migration and separation of charge carries, and influences the PEC performances of the photoelectrodes. In addition, our group employed a ferroelectric perovskite material and constructed nano-Au based photoelectrodes to study and manipulate the hot-electrons transfer in the plasmonic hybrids. The results indicate that the PEC properties of the hybrids can be effectively manipulated by switching the direction of the depolarization field in the employed ferroelectric perovskite material, which provides a flexible platform to freely manipulate the injection and transfer of hot-electrons generated by the plasmonic hybrids. As described in Figs. 9(e) and 9(f), the orientation of the associated depolarization electric field (E_{DP}) is towards the ITO substrate after + 10 V poling pretreatment, and the formed downward band bending for PZT at the interface with electrolyte is favorable for transferring hot electrons to the surface to drive water reduction reaction. However, after –10 V poling pretreatment, the orientation of E_{DP} is switched towards the interface of PZT and electrolyte, and the formed upward band bending for PZT at the interface blocks the hot electrons transferring to the surface to drive the reaction. In this case, the transferred hot electrons are trapped in the bulk of PZT films, leaving the hot holes to drive PEC oxidation reactions[101].

Since there are many inherent limitations in the light absorption and the catalytic performance of the ferroelectric perovskite materials when they are used alone for solar water splitting, many recent studies that using ferroelectric material as a part of the heterojunction structures have been repor-

ted. According to the previous studies, the tunable remnant ferroelectric polarization in the ferroelectric material of the ferroelectric-based heterojunction could redistribute the charge carriers in the ferroelectric materials and its adjacent semiconductor. Thus, utilizing tunable ferroelectric polarization of ferroelectric material could change the band structure and modulate the performance of the ferroelectric-based heterojunction[102]. Huang et al. combined the metal-sulfide nanoparticles (CdS) and ferroelectric nano-materials (BaTiO₃) to construct a ferroelectric-based heterojunction. The results demonstrated that the hydrogen production activity of the composite photocatalyst can be greatly improved by the employed BaTiO₃. The mechanistic study revealed that the dipolar fields in the BaTiO₃ could enhance the separation and transfer process of charge carriers generated in CdS, and thus improved the hydrogen production efficiency of the composite photocatalyst[103]. Yang et al. reported a ferroelectric BaTiO₃/TiO₂ heterojunction structure, which showed marked improvement in water oxidation reactions as the result of the increased band bending of TiO₂ nanowires and the enhanced separation of photogenerated charge carriers induced by the spontaneous electrical polarization of BaTiO₃[104]. Similarly, Li et al. constructed a PbTiO₃ based ferroelectric heterojunction by tunable epitaxial growth of TiO₂ on the selective polar surface of single-crystal and single-domain ferroelectric PbTiO₃ nanoplates. The heterostructures demonstrated a polarization dependent photocatalytic performance for photodegradation and water splitting, due to the crucial role of ferroelectric polarization effects[105]. In addition, BaTiO₃/TiO₂[106], SrTiO₃/TiO₂[107] and BiFeO₃/BiVO₄[108] heterojunctions were also reported to investigate the ferroelectric effect of ferroelectric perovskite materials on the oxygen evolution reaction (OER) performance. The experimental and calculational results revealed that the ferroelectric polarization effect has positive im-
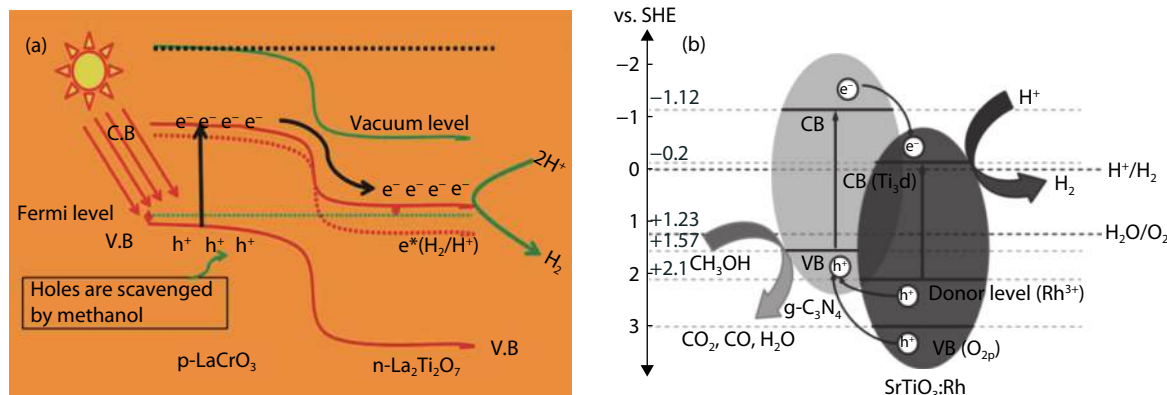
Fig. 10. (Color online) Schematic illustration of the (a) electron–hole separation of $La_2Ti_2O_7/LaCrO_3$ heterojunction and (b) g-$C_3N_4/SrTiO_3$:Rh composite under visible light irradiation. Reprinted from Refs. [111, 113], respectively.

pact on the heterojunction and could enhance their activity for solar water oxidation. All these results indicate that the internal field induced by the ferroelectric polarization effect can enhance the separation and migration of the photogenerated electrons and holes. However, there are many limiting factors, such as high dielectric constant and insulativity of ferroelectric materials, thus it needs to intensively study for applying the ferroelectric materials in photocatalytic water splitting[56, 57].

4.4. Construction of heterojunction structure

The approach of construction of heterojunction structure is another effective strategy for improving photocatalytic activity of perovskite materials for solar water splitting. A suitable heterojunction nano-architecture, where the formed band structure is favorable for the charge carriers generation in one semiconductor and transport them to the adjacent materials vectorially, which can result in efficient charge separation and fast charge migration, and can expand the light absorption range of the wide bandgap perovskite materials when combining them with a narrow bandgap semiconductor[109, 110]. Many perovskite-based heterojunction structures have been reported to explore their effect on solar water splitting. Most of them are type-II heterojunctions. As shown in Fig. 10(a), Nashim *et al.* prepared a series of $La_2Ti_2O_7/LaCrO_3$ heterojunction based photocatalysts through a solid state method. The prepared photocatalysts showed a great boost in the photocatalytic activity of solar water splitting under visible light irradiation, which is mainly because of the synergetic effect of the visible light activation of $La_2Ti_2O_7$ and retarded recombination rate of charge carriers by the formed heterojunctions[111]. Xu *et al.* synthesized a g-$C_3N_4/SrTiO_3$ composite photocatalyst by simply decomposing urea in the presence of $SrTiO_3$ at 400 °C. Due to the formed heterojunction structure, the g-C_3N_4 and $SrTiO_3$ were closely connected and the photogenerated electrons and holes were effectively separated, thus, the catalyst exhibited an improved photocatalytic activity for H_2 production under visible light irradiation[112]. Similarly, as shown in Fig. 10(b), Kang *et al.* also constructed a g-$C_3N_4/SrTiO_3$:Rh composite photocatalyst to improve the hydrogen evolution rate from the viable-light driven solar water splitting. The highest hydrogen evolution rate was attained when combining 20 wt% g-C_3N_4 with $SrTiO_3$:Rh, which was mainly attributed to the efficient electron-hole separa-

tion and transportation in the heterojunctions of the organic and inorganic materials under visible light irradiation[113]. In addition, to investigate the synergistic effects of the coupled graphene oxide (GO) sheet and foreign element loaded on the $NaNbO_3$, Opoku *et al.* designed a bi-functional GO/V-doped $NaNbO_3$ heterostructure photocatalyst and detected the effect on the photocatalytic performance of $NaNbO_3$ with wide band gap using dispersion-corrected hybrid DFT calculations. The hetero-structure photocatalyst demonstrates a high stability and activity for hydrogen generation during water splitting process. The systematic studies reveal that the improved photocatalytic activity of hydrogen evolution is mostly ascribed to the loading of GO sheet and V binary cocatalysts on the $NaNbO_3$, where the formed type-II heterojunction between GO sheet and $NaNbO_3$ can promote the interfacial charge carriers separation and restrain the recombination of them. Moreover, GO sheet with high electrical conductivity and specific surface area can provide efficient electron channels for the separation of charge carriers, hence further improve the photocatalytic performance of the composite catalyst[114].

Some new strategies that systematically investigate the synergistic effects of heterojunction and other modifications such as changing of crystal structure and doping of foreign elements have been used to construct perovskite based catalysts for water splitting reaction. For example, Jia *et al.* constructed a $BiVO_4$-Ru/$SrTiO_3$:Rh composite Z-scheme photocatalyst by an impregnation method and a liquid-solid state reaction. The suitable contact was formed between $BiVO_4$ and Ru/$SrTiO_3$:Rh, which resulted in efficient electron transfer at interface, and the present composite photocatalyst demonstrated a high activity for water splitting under visible light irradiation. The indepth study showed that the crystallinity and morphology of $BiVO_4$ could also have effects on the photocatalytic activity of the composite[115]. Similarly, Dong *et al.* constructed a visible-light response Z-scheme photocatalyst using ultrathin 2D $BiVO_4$ nanosheets (NSs) as the oxygen evolving photocatalys, Ru/$SrTiO_3$:Rh as the hydrogen evolving photocatalyst, Fe^{2+}/Fe^{3+} as the redox mediator, respectively. The study reveals that the superior photocatalytic activity of the as-prepared $BiVO_4$ NSs is attributed to its unique morphology and crystal phase with ligand-free surfaces, large-scale exposed {010} planes, and widely distributed VO in a crystalline structure[116]. In order to use the
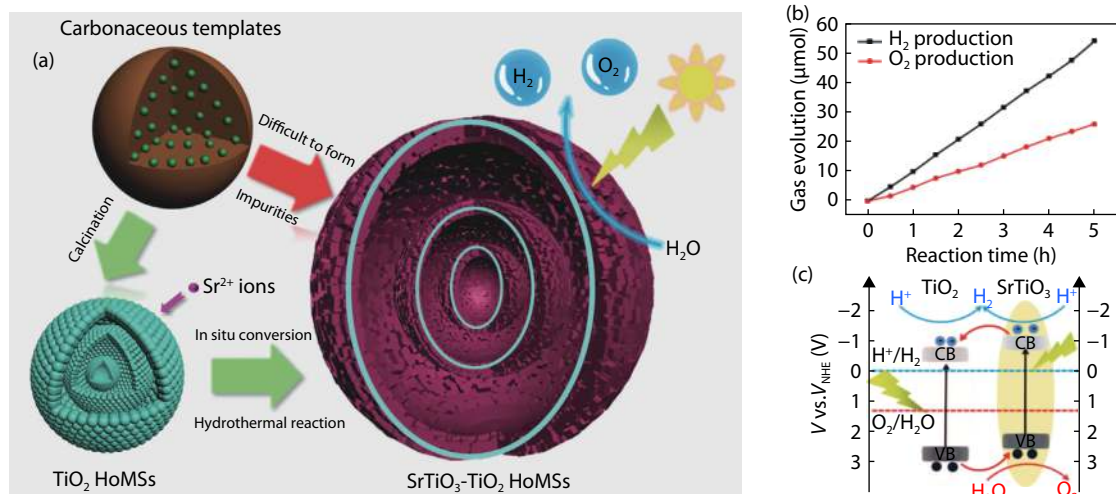
Fig. 11. (Color online) (a) Synthesis route of SrTiO₃/TiO₂ HoMs from hydrothermal reaction. (b) Typical time course of photocatalytic H₂ and O₂ evolution reaction of triple shelled SrTiO₃/TiO₂ HoMs photocatalyst. (c) Possible band structure diagram for SrTiO₃/TiO₂ HoMs. Reprinted from Ref. [118].

layered perovskite-type wide-gap semiconductor $La_2Ti_2O_7$ (LTO) to construct a visible-light-driven photocatalyst, Ma *et al.* had constructed g-C_3N_4-based heterojunction model and systematically investigated the synergistic effect of doping and heterojunction on enhancing visible light absorption and photogenerated carriers separation. The results of DFT calculations showed that the doping N or S into the LTO surface could notably decrease the band gap and enhance the light absorption efficiency of it. Moreover, the formed type-II band alignment between the doped LTO and g-C_3N_4 can efficiently separate the charge carriers. The results suggest that S-doped LTO/g-C_3N_4 composite would be a potential photocatalyst for solar water splitting[117].

In addition to the construction of Z-scheme photocatalyst, using the effect of structure engineering and heterojunction synergistically can also improve the activity of photocatalyst. As shown in Fig. 11, Wei *et al.* constructed a hollow multi-shelled (HoMs) SrTiO₃/TiO₂ heterojunction by a hydrothermal crystallization method. The broccoli-like SrTiO₃/TiO₂ heterogeneous HoMs structures exhibited a fourfold higher overall water splitting performance than that of bare SrTiO₃, which could be attributed to the special HoMs structures and the fabricated heterojunctions. It was reported that the HoMs structures could increase the light absorption ability of the composite photocatalysts and the constructed heterojunctions could boost the transfer and separation efficiency of the photogenerated electrons and holes. Therefore, the HoMs structures are helpful for enhancing the photocatalytic activity of the SrTiO₃/TiO₂ heterojunctions[118]. Chang *et al.* also constructed a ternary CdS/Au/3DOM-SrTiO₃ composite photocatalyst, which showed a dramatically improved photocatalytic activity for water reduction. The remarkably enhanced photocatalytic performance was mainly due to the slow photon region of 3DOM-SrTiO₃, which was well matched the optical absorption band of the composite and could significantly enhance the light absorption efficiency of the ternary composite[119].

4.5. Construction of plasmonic-based photocatalysts

The decoration of semiconductors with plasmonic metals

and construction of plasmonic-based photocatalysts is another promising way to improve the photocatalytic performance of photocatalysts for solar water splitting. Generally, there are four main mechanisms of plasmonic effects on the photocatalytic process of solar water splitting, including: i) the improvement of light absorption efficiency by either trapping or scattering light into the semiconductors using the plasmonic metal nanoparticles (NPs); ii) hot-electrons injection; iii) plasmon-induced resonance energy transfer (PIRET) and iv) the role of cocatalysis[120, 121]. Based on these effects, many different plasmonic NPs/perovskite composite catalysts have been developed for solar water splitting, such as $Ag/KTaO_3$, $Ag/NaTaO_3$, $Ag/SrTiO_3$, $Au/SrTiO_3$[122–124]. Our group has introduced a well-known catalyst, $LaCoO_3$, to the community of water splitting using solar energy. As shown in Fig. 12(a), by combining with Au NPs, the plasmonic-based hot electrons injection from Au NPs to $LaCoO_3$ is responsible for amplifying the photocatalytic efficiency while the well-known thermal-stimulus for driving chemical transformations is not observed to be influential. Such charge transportation process is crucial for promoting the subsequent water splitting and HCHO decomposition reactions. For the first time, we have differentiated the contributions of hot charge transfer from thermal-stimulus in excited plasmonic materials to the PEC efficiency improvement of the composite devices[125]. Moreover, we have constructed a plasmon-based $Au/LaFeO_3$ composite photocatalyst to investigate the complex roles of hot electrons and holes for solar water splitting. Benefiting from the formation of Schottky junction and surface plasmon resonance effect of the Au NPs, the synthesized photocatalyst exhibits an excellent photocatalytic activity for solar water splitting. The in-depth investigation reveals that the improved hydrogen evolution is caused by the hot electrons injection from Au to $LaFeO_3$, and the hot holes in Au induced by the separation of hot charges can initiate the water oxidation directly on the surface of gold[126]. To broaden the light absorption range of photocatalysts for solar water splitting, Cai *et al.* designed an Au nano-rods (NRs) modified $La_2Ti_2O_7$ nano-steps (Au-LTO NSP) by loading the visible and NIR plasmonic absorption responded Au NRs on the surface of LTO NSP. As shown
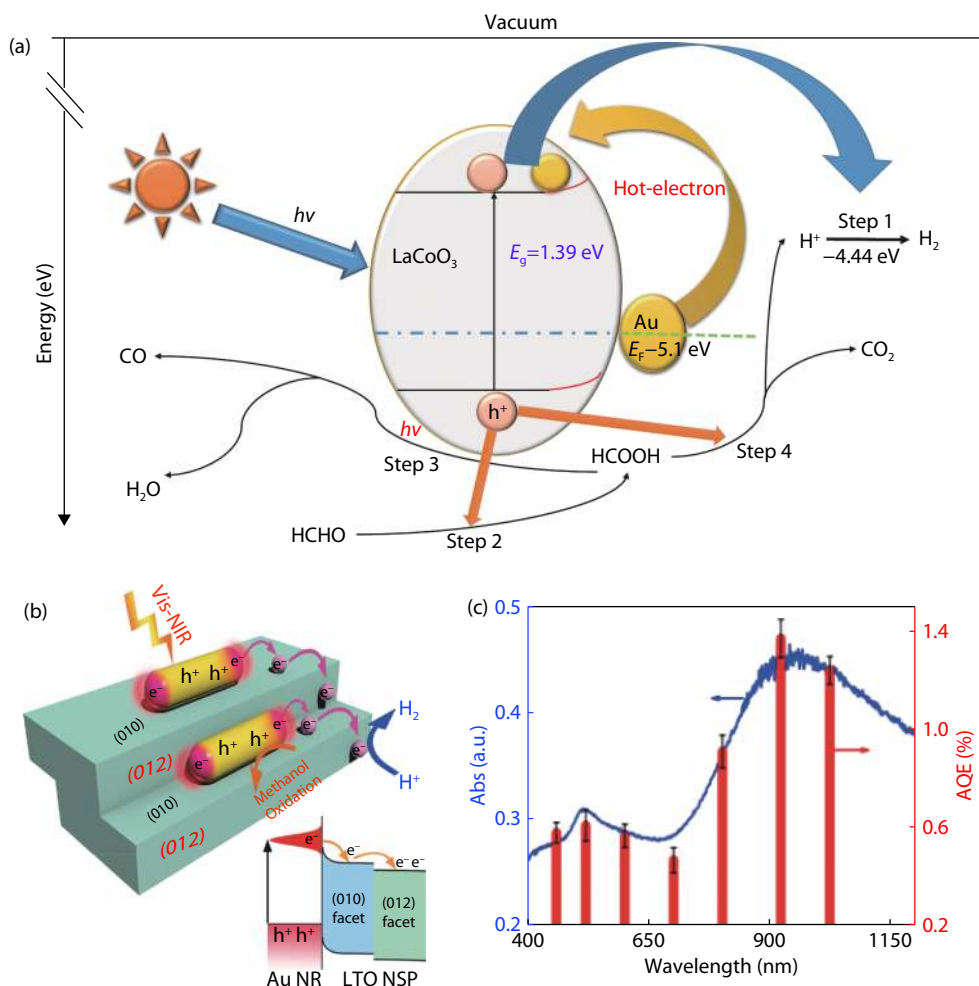
Fig. 12. (Color online) Schematic illustration of (a) the photogenerated charge transfer and catalytic reaction mechanisms of the fabricated La-CoO$_3$/Au nano-composite (Reprinted from Ref. [125]), and (b) the prepared Au/LTO NSP. (c) The diffuse reflectance spectra (left axis, blue line) and apparent quantum efficiency (right axis, red column) of Au-LTO NSP under vis-NIR (λ > 420 nm) light irradiation. Reprinted from Ref. [127].

in Figs. 12(b) and 12(c), the Au-LTO NSP composite exhibited significantly high photocatalytic activity for hydrogen generation when irradiated by the light with wavelengths longer than 420 and 780 nm. The single-particle fluorescence measurements indicated that the plasmonic-induced hot electrons injection of Au NRs increased the number of electrons transfer to LTO NSP, realizing the more efficient utilization of the long-wavelength solar light for the composite in the redox reaction[127]. Moreover, Shi *et al.* has developed a type of nonmetallic plasmonic perovskite semiconductor with plasmon-enhanced activity for solar water splitting. Due to the high charge carrier density induced by oxygen vacancies, the constructed SrTiO$_3$ photoelectrode with a crystalline-core@amorphous-shell structure shows an intense localized surface plasmon resonance (LSPR) in the visible light region and displays much higher plasmon-induced PEC water splitting performance than the pristine SrTiO$_3$ photoelectrode[128]. To promote the efficiency of water splitting system, Zhong *et al.* constructed an Au based water splitting device by using of both sides of the same SrTiO$_3$ single-crystal substrate. The study indicated that the chemical bias was significantly reduced by the plasmonic effects and the catalytic reaction spectrum corresponds to the plasmonic absorption spectrum closely, which suggested that the plasmon-induced charge separation at the Au/SrTiO$_3$ interface could improve

both the water oxidation and reduction[129].

Additionally, some studies on using the synergistic effect of plasmonic enhancement and other strategies have been reported to improve the activity of catalyst to an unprecedentedly high level for solar water splitting. Our group has combined the plasmon resonance effect with the ferroelectric enhancement, and designed a plasmonic-ferroelectric hybrid PEC photoelectrode. As shown in Fig. 13, we explored the charge transfer and transport in nano-Au/PZT hybrids by constructing three nanostructures including ITO/Au/PZT, ITO/PZT/Au/PZT, and ITO/PZT/Au, and by poling the PZT films with different potentials. Due to the LSPR effect of the nano-Au, the nano-Au/PZT hybrids could broaden the light absorbance to the NIR range (800 nm). The spatial distribution of the electric field intensity around the square dot was obtained by the finite difference time domain (FDTD) method under 800 nm light illumination. It indicated that the strong field was located at the edge of the Au square and the hot spots might increase the probability of the hot charge carriers transfer from Au to the nearby materials. Moreover, using the ITO/PZT/nano-Au/PZT electrodes, we demonstrated the tunable photocurrent by changing the pre-poling bias from −10 to +10 V. This is attributed to the ferroelectric performance of the PZT, which can form different band bending at PZT/electrolyte interface under different pre-poling bias and

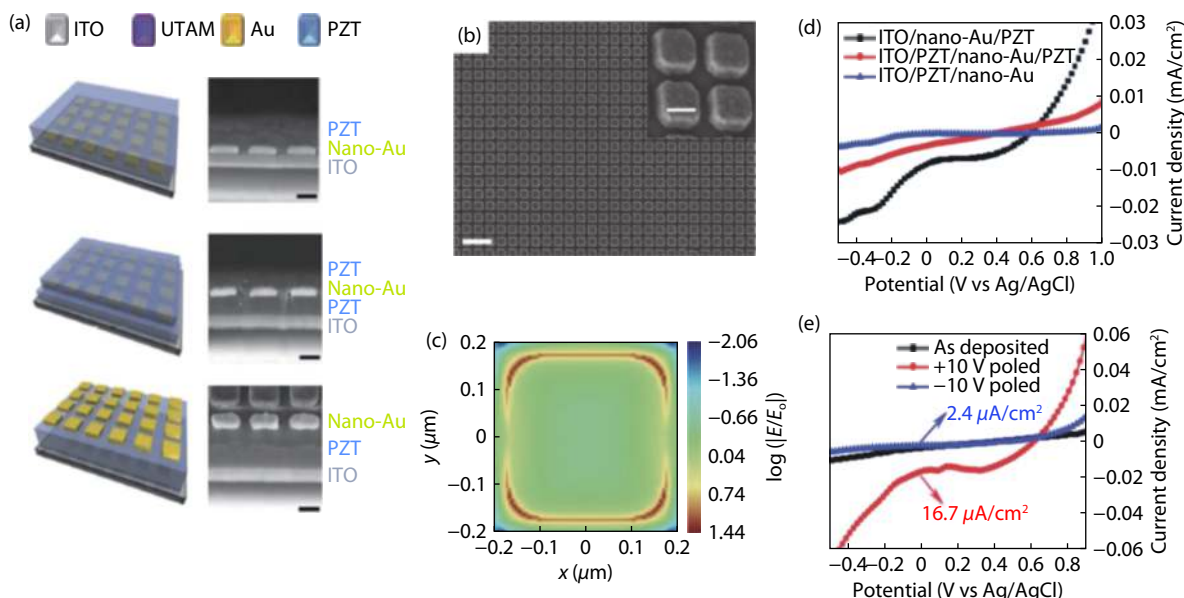**Y B Huang et al.: The application of perovskite materials in solar water splitting**

Fig. 13. (Color online) (a) Schematics and cross-section of scanning electron microscope (SEM) of the fabricated ITO/PZT/Au, ITO/PZT/Au/PZT, and ITO/Au/PZT electrodes. (b) Top-view SEM image of nano-Au array fabricated on ITO glass; scale bar, 1 μm. The inset zooms in one part of the SEM; scale bar, 200 nm. (c) FDTD-simulated spatial distribution of the electric field intensity around the square dot illuminated by 800 nm light. (d) Photocurrent-potential measurements of ITO/nano-Au/PZT(black), ITO/PZT/nano-Au/PZT (red) and ITO/PZT/nano-Au (blue) under the white-light excitation (filtered, > 450 nm). (e) Photocurrent-potential measurements of the ITO/PZT/nano-Au/PZT (the as-grown (black), + 10 V (red) and –10 V (blue) poled) under the white-light excitation (filtered, > 450 nm). Reprinted from Ref. [101].

affect the hot electron transfer from Au to PZT. The femtosecond transient absorbance results even more confirmed the hot charge transfer from Au NPs to PZT[101]. Similarly, Au/BFO, Ag/BFO, and Ag/PZT were also constructed to utilize the SPR effect and ferroelectric performance synergistically for improving the catalytic activity of the PEC systems[98, 130, 131]. Furthermore, to improve the utilization efficiency of solar energy and achieve highly efficient STH conversion, Zhu *et al.* combined the Au/LTO with black phosphorus (BP) to design a broadband solar response photocatalyst. The composite photocatalyst shows 74 and 60 fold higher of photocatalytic activities than the pristine component of BP and LTO at wavelengths longer than 420 and 780 nm, respectively. Time-resolved diffuse reflectance spectroscopy revealed that the efficient electron transfers caused by the broad absorption of BP and SPR enhancement effect of plasmonic Au in the visible and NIR light regions, and the formed intimate heterojunction of BP and Au/LTO, were contributed to the improved photocatalytic performance of the composite photocatalyst[132]. Chang *et al.* developed a ternary composite by the three dimensionally ordered macroporous (3DOM) SrTiO₃, Au and CdS nano materials. Duo to the synergistic effects of Au SPR, efficient carrier separation of the formed heterojunction and slow photon effect of the 3DOM-SrTiO₃, the CdS/Au/3DOM-SrTiO₃ composite showed an extraordinarily high hydrogen evolution rate when depositing Pt NPs on the composite as a co-catalyst[119].

5. Conclusions and perspectives

In this review, we reviewed recent progress and the design strategies in the field of solar water splitting based on the perovskite materials. Our aims were to provide some useful guidance for future research on the design of perovskite-based photocatalysts and systems for water splitting reaction. Although some great progress in the construction of perovskite-based photocatalysts and systems for water splitting have also been made by implementing different design strategies, such as adjustment of the chemical component, crystal structure and morphology engineering, application of ferroelectric property, construction of heterojunction structure and plasmonic-based photocatalysts, etc. However, the STH conversion efficiency of the current water splitting systems is still very low (about 2%) for large-scale applications of H₂ generation[133]. Therefore, the new materials and strategies are required to improve the STH conversion efficiency. The main problems and perspectives are shown below.

(1) The selection and doping of A, B and X sites elements in the perovskite are proved to effectively reduce the band gap and improve the catalytic activity. However, the low light harvesting ability is still a critical problem of most perovskite-based catalysts for solar water splitting. The development of experimental techniques are needed to precisely control the position, element and concentration of the dopants. Moreover, co-doping of metal and non-metal elements would be a useful strategy to modify the band structures of perovskites to meet the highly efficient solar water splitting.

(2) Surface engineering, crystal structure, morphology engineering, and construction of heterojunction structure have been proved to be four valid strategies for modifying perovskite materials to improve the photo/photoelectrocatalytic activity by facilitating surface reactions, suppressing charge carriers recombination, reducing the particle size and increasing the surface areas, etc. However, the interaction mechanism and the synergetic effect of the different components of the perovskite-based composites have not been clearly addressed. The further efforts such as using the new experimental methods and theoretical calculations should be taken to

clarify the problem, which could be the effective directions.

(3) There is an activation barrier for H_2 and O_2 evolution reactions and most of the perovskite based photocatalysts are broad-band gap materials (> 2 eV), thus, designing and finding the optimal photocatalyst with the best activity and suitable band structure is still the challenge for overall water splitting. Therefore, much more efforts should be taken to develop the photocatalyst with multifunctionality that has wide light absorption range, efficient photogenerated charge carriers separation ability, sufficient catalytic active sites, high stability, and appropriate band structure for water redox reactions. Moreover, utilization of different enhancement effects and some advanced synthetic techniques synergistically to develop the high efficiency photocatalysts and systems could be an effective direction.

(4) In addition to the development of photocatalysts and systems with high activity, systematic investigation of the working mechanisms and reaction mechanisms of the perovskite based photo/photoelectrocatalytic systems should be another critical issue to be addressed. The comprehensively experimental and theoretical studies should be designed and conducted to investigate the intrinsic mechanism of the system in the future, especially for the compound photocatalysts and the complex systems. It may be beneficial for the future research and can provide useful guidance for design of perovskite based photocatalytic system with superior photo/photoelectrocatalytic activity and stability. Therefore, more efficient experimental and computational methods need to be developed in the future to overcome these problems.

Acknowledgement

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