Electronic Engineering of ABO₃ Perovskite Metal Oxides Based on d⁰ Electronic-Configuration Metallic Ions toward Photocatalytic Water Splitting under Visible Light

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Particulate photocatalytic water splitting is considered as one of the most promising and low-cost routes toward green hydrogen production, toward which developing a semiconductor photocatalyst with a wide visible light response and high charge transfer velocity is the key issue. Metal oxides based on d⁰-configuration metal ions, especially those with the perovskite structure, are a group of ideal candidates toward photocatalytic water splitting, benefitting from their high structural stability, suitable conduction band minimum (CBM), and high carrier mobility. However, the main problems staggering the development of highly efficient photocatalysts are from the rather big bandgap of these d⁰-configuration metal oxides to cause limited UV light response and from the flexibly changed valence state of the d⁰-configuration metal cations in the B site of the perovskite structure. Various strategies are developed to address these problems, and the summary on electronic engineering strategies of the d⁰-metal-based perovskite metal oxides toward visible light response and stable photocatalytic performance in this review is focused on. Finally, the construction of the photocatalytic overall water splitting (OWS) system based on these perovskite semiconductors is discussed and outlooked.

1. Introduction

Solar energy is of the largest scale among various kinds of renewable energies, about 120 000 Tw to the Earth’s surface, and nowadays the total global electricity supply is about only 20 Tw.[1] Developing proper systems to convert solar energy (or photon energy) into the molecules that could be stored and transported conveniently is of great significance toward a green and carbon-zero society. The interesting discovery of Fujishima and Honda inspired scientists where the production of H₂ from water splitting driven by solar energy is feasible through introducing a semiconductor.[2] Since then, the concept of photocatalytic water splitting has been developed and the construction of effective photocatalysts with a proper semiconductor has become the focus of this subject.

Semiconductor photocatalysts are the energy conversion centers for the whole photocatalytic process.[3] The excitation of the semiconductor by photon energy to produce photogenerated electrons and holes is the starting step to initiate the subsequent reaction processes. Only a small fraction of the photoexcited electrons and holes could bypass the recombination sites and be successfully transferred from the bulk to the surface of the semiconductor. The electrons and holes that reach the surface may only successfully participate in the surface catalytic reaction at suitable catalytic sites, thus driving the target reaction process and completing the entire light-driven catalytic process.[4,5] The photon energy is first converted into electron energy to initiate the photocatalytic process, which then drives the reaction process into chemical energy into H₂ molecules. The energy conversion efficiency of the whole process (i.e., photocatalytic solar-to-hydrogen [STH] conversion efficiency) depends on how many photons can excite the semiconductor to produce photogenerated carriers, how many photogenerated carriers could be successfully transferred to the catalyst surface, and how many surface photogenerated carriers are involved in the surface catalytic reaction. These efficiencies are defined as the light absorption efficiency (ηla), the photogenerated carrier separation efficiency (ηcs), and the surface catalytic efficiency (ηac), respectively, and the overall efficiency is dependent on all these three efficiencies as $\eta_{\text{STH}} = \eta_{\text{la}} \times \eta_{\text{cs}} \times \eta_{\text{ac}}$.[6] The properties of the semiconductor itself determine the light absorption efficiency and the photogenerated carrier separation efficiency, and the light absorption efficiency is closely related to the bandgap and the extinction coefficient of the semiconductor. A sufficiently small bandgap of the semiconductor could confirm that a sufficient number of photons in the solar spectrum can successfully excite the semiconductor. As the total number of photons distributed in the visible region of the solar spectrum (i.e., from 400 nm to 800 nm) accounts for ≈45% of the total number of photons in the entire
The use of semiconductors that can respond to visible light is the key to ensure sufficiently high light absorption efficiency ($\eta_{\text{abs}}$). In addition, the potential of the photogenerated electrons excited onto the conduction band needs to be more negative than the proton reduction potential (0 V vs reversible hydrogen electrode (RHE)) to drive the hydrogen evolution reaction, and the potential of the photogenerated holes in the valence band (VB) needs to be more positive than the water oxidation potential ($+1.23 \text{V vs RHE}$) to drive the oxygen evolution reaction. Considering that a sufficient overpotential of the surface reaction is required to satisfy the kinetics of the reaction process, a general minimum bandgap of 1.8 eV is required to achieve photocatalytic OWS of the semiconductor.[8]

Metal oxides with TiO$_2$ being the most representative were the first group of inorganic materials to be used in photocatalytic water splitting. TiO$_2$ was constructed as the photoelectrode in 1972 and the photocatalytic water-splitting performance was clearly observed as long as the light was irradiated on the TiO$_2$ photocathode.[2] From then on, the metal oxides based on the transition metal with $d^0$ electronic configuration, including Ti$^{4+}$, Zr$^{4+}$, Ta$^{5+}$, and Nb$^{5+}$, have been drawing explosive attention as photocatalysts for water splitting because of their excellent stability, surface hydrophilicity, and their suitable band edges straddling the water-redox energy levels.[9] However, all of these $d^0$-based metal-oxide photocatalysts, including TiO$_2$, ZrO$_2$, SrTiO$_3$, and NaTaO$_3$, are only UV light responsive with bandgap values above 3.0 eV.[10] Therefore, the development of visible-light-responsive photocatalysts based on metal oxides is of great importance. The ionic doping of metal oxides is an effective method to modulate the bandgap of metal oxides, but the specific effect of doping is closely related to the specific crystal framework of the metal oxide.[11] For example, the crystal framework of the star semiconductor TiO$_2$ with anatase or rutile structure comprises TiO$_6$ octahedrons connected in both the covertex and/or the coedge manner, which leads to big lattice distortion and high concentration of defect sites upon introducing dopants into its crystal lattice,[12] and thus the photocatalytic performance of ion doping of TiO$_2$ with visible light response is not as good as the photocatalytic activity of TiO$_2$ itself.[13,14] In contrast, the perovskite materials with the formula of ABO$_3$ are a class of semiconductors with BO$_6$ octahedrons linked only in a covertex manner, rendering its structure with high flexibility. There are several perovskite derivatives based on ABO$_3$ perovskite materials, including the Dion–Jacobson type, Ruddlesden–Popper type, and Aurivillius type,[15] but all of these perovskite derivatives exhibit layer structures; due to the existence of large layer spacing, the carrier transport between the layers will encounter high resistance, so the charge separation efficiency of these perovskite derivatives is generally low. While the ABO$_3$ perovskite structure materials exhibit much higher carrier transfer efficiency benefiting from their simple covertex connecting structure of BO$_6$ octahedrons, the structure flexibility of ABO$_3$ perovskite oxides provides high inclusiveness of various kinds of doping ions at both A-site or B-site or the oxygen site, thus allowing diverse and efficient modulation of the band structure of the perovskite oxides through ion doping. In addition, codoping with other metal ions at the A-site can stabilize the valence state of the B-site metal ions, thereby improving the photocatalytic stability of the perovskite photocatalyst. In addition, a large class of visible-light-responsive photocatalysts can also be obtained by substitutional doping of the anion O$^{2-}$ of the perovskite structure with N$^{3-}$.[16,17] All of these visible-light-responsive photocatalysts have been properly modulated toward photocatalytic water splitting and have achieved efficient photocatalytic water splitting performance, benefiting from the high carrier mobility that originated from the simple crystal structure framework of perovskite semiconductors.

To date, visible-light-responsive semiconductors with ABO$_3$ perovskite structure have played an important role in the field of photocatalytic water splitting, but there are lack of reviews on the crystal structure, energy band structure, and photocatalytic performance of these materials. The present review focuses on the band structure characteristics and photocatalytic activity of perovskite semiconductors and presents an outlook on the development of visible-light-responsive semiconductors with perovskite structures, hoping to provide guidance for the semiconductor design toward more efficient photocatalytic water splitting.

2. Band Structure Engineering Strategies

In general, the conduction bands of metal-oxide semiconductors are strongly influenced by the electronic structure of metal cations, and usually the $d$ orbitals of the metal cations contribute to the conduction band minimum (CBM). The conduction band (CB) which mainly consists of the $d$ orbital of the metal cation should be higher than the reduction potential of H$_2$O to produce H$_2$ ($E_{(H_2/O_2)} = 0 \text{V vs RHE}$), and simultaneously the potential of the VB which mainly consists of O$^{2-}$ orbitals ($\approx +3 \text{eV}$) is considerably more positive than the H$_2$O oxidation potential to produce O$_2$ ($E_{(H_2/O_2)} = +1.23 \text{V vs RHE}$).[9] In that case, the bandgaps of metal oxides with perovskite structures inevitably become much wider than the minimum necessary for water splitting. Band engineering strategies have been developed to modulate the perovskite oxides toward visible light response, and the strategies can be classified into three kinds, as displayed in Figure 1. The first strategy is to introduce the electronic donor level in the bandgap of the metal oxides through doping with transition metal ions. The second is to uplift the VB of the metal oxides by doping or substitution with other anions with a lower electronegativity than that of O$^{2-}$. The third is to construct a solid solution with another low-bandgap semiconductor. With the band engineering strategy being properly carried out on metal oxides based on $d^0$-configuration metals, a large group of visible-light-responsive semiconductors with perovskite structures has been successfully fabricated and developed as efficient photocatalysts toward photocatalytic water splitting.

![Figure 1. Three types of band engineering strategies for the design of visible light-responsive semiconductors.](image-url)
2.1. Doping with Transition Metal Ions

Both SrTiO$_3$ and NaTaO$_3$ are typical ABO$_3$ perovskite structure oxides, and their crystal structure and energy band structure are shown schematically in Figure 2. As the bandgaps of SrTiO$_3$ and NaTaO$_3$ are 3.2 and 4.0 eV, respectively, both of them can only respond to UV light, and an efficient OWS activity under UV light was achieved on both SrTiO$_3$ and NaTaO$_3$, as shown in Table 1. For SrTiO$_3$ and NaTaO$_3$, the Ti3$d$ or Ta4$d$ orbital of the B-site metal ion contribute to their CBM, and their CBM potentials are high enough to drive the proton reduction and their VBM positions have an overpotential enrichment of more than 1.0 eV relative to the oxygen production potential from water oxidation. Therefore, to make the cationic doping of SrTiO$_3$ and NaTaO$_3$ meet the hydrogen production potential, the effective B-site metal-ion doping should raise the top of the VB of SrTiO$_3$ and NaTaO$_3$ or form a doping energy level (donor level) near their VB maximum (VBM). Doping SrTiO$_3$ and NaTaO$_3$ with transition metal ions is an effective strategy to extend their visible light absorption.

The ionic radius of the transition metal ions, such as Cr$^{3+}$, Ni$^{2+}$, Co$^{3+}$, Cu$^{2+}$, Rh$^{3+}$, Mn$^{2+}$, and Fe$^{3+}$, is close to that of the B-site metal ions, making them be more easily doped into the B-site of SrTiO$_3$ and NaTaO$_3$.

Based on calculations, Zhou et al. show that the above transition metal ions are all in a configuration where the outermost d-orbitals are partially filled with electrons, and these transition metal ion doping tends to introduce new energy levels close to the VB edge positions or even in the bandgap of the perovskite oxides, resulting in an electronic excitation from the doping energy levels to the conduction band and thus rendering SrTiO$_3$ and NaTaO$_3$ to be visible light responsive.

The TM (TM = Ni, Cu, Fe, and Mn) doped SrTiO$_3$ nanocrystal with the dopant concentrations of 0.44, 1.24, 1.70, and 1.05 mol %, respectively, was synthesized with the hydrothermal method by Ma et al. The d orbital of the transition metal splits into two cleavage energy levels of $t_{2g}$ and $e_g$ as well as these TMs taking the place of Ti and forming an MO$_6$ octahedral unit in the perovskite due to the Jahn–Teller effect.

The $t_{2g}$ and $e_g$ as shown in Figure 3c forms a discontinuous energy level above the VBM of SrTiO$_3$, which can respond to visible light and the electrons are excited from the $t_{2g}$ to the conduction band. The energy gaps between $t_{2g}$ and CBM for example of these TM-doped SrTiO$_3$ were exhibited as Ni:SrTiO$_3$ < Mn:SrTiO$_3$ < Cu$^{2+}$:SrTiO$_3$ < Fe$^{2+}$:SrTiO$_3$, with the values of 2.4 eV, 2.45 eV, 2.7, 2.8, and 3.2 eV, respectively (Figure 3c).

Among these transition metal dopants, Cr$^{3+}$ ions have been proved to be the most efficient dopants. As revealed by Xu et al., the Cr-doped SrTiO$_3$ with various doping concentrations could be synthesized with the simple solid-state reaction (SSR) method, and the material showed an efficient hydrogen evolution activity under visible light. The visible light absorption of SrTi$_{1-x}$Cr$_x$O$_3$ was revealed by theoretical calculations to be caused mainly by the electronic excitation from the Cr3$d$ orbital introduced by Cr doping to the empty mixed orbitals of Cr3$d$ and Ti3$d$. Wang et al. found that the Cr dopant also has the potential to occupy the A-site of SrTiO$_3$ and that the sample with Cr occupying the Sr site (Sr$_{0.95}$Cr$_{0.05}$)TiO$_3$ has more than 100 times the hydrogen-producing activity than that of the sample with Cr occupying the Ti site Sr(Ti$_{0.95}$Cr$_{0.05}$)O$_3$. Further studies showed that Cr occupying the Sr site in Cr:SrTiO$_3$ exists mainly in the form of Cr$^{3+}$, while Cr occupying the Ti site exhibits both trivalent and hexavalent. It is the presence of Cr$^{6+}$ that leads to the extremely low hydrogen production activity of SrTi$_{0.95}$Cr$_{0.05}$O$_3$, as Cr$^{6+}$ forms a shallow energy level under the CBM of SrTiO$_3$ that traps electrons and thus decreases the proton reduction activity. Subsequently, it was shown that the partial photoreduction of Cr$^{6+}$ to Cr$^{3+}$ could be achieved using a high-pressure mercury lamp and a significant increase in hydrogen production activity was observed. The energy band structure before and after photoreduction is shown in Figure 4.

The shallow energy levels formed by Cr$^{6+}$ are below the proton reduction potential, and therefore these shallow energy levels bind the excited electrons and render SrTiO$_3$ essentially inert for photocatalytic hydrogen production. A suitable electron regulation to inhibit the transition of doped metal ions to higher valence states should be the key to enhance the photocatalytic hydrogen production activity of SrTiO$_3$.

In addition to transition metal dopants, the noble metal dopants (like Ru, Rh, or Ir) can also modulate the band structure of SrTiO$_3$ and contribute to its visible light-responsive ability. The visible light absorption performance of the noble metal-doped SrTiO$_3$ is attributed to the excitation of electrons on the donor energy levels closing to the VBM of SrTiO$_3$, and thus contributing to the conduction band of SrTiO$_3$. The Rh-doped SrTiO$_3$ with a bandgap of only 2.3 eV shows a quantum efficiency of 0.71% for hydrogen production under...
visible light irradiation, while SrTiO$_3$ doped with other noble metal ions shows much lower quantum efficiency for hydrogen production ($\approx$0.02%).$^{[24]}$ The visible light absorption band possessed by Rh-doped SrTiO$_3$ is absent from pure SrTiO$_3$. The electronic conversion at 400 nm occurs from the electron donor level of Rh$^{4+}$ to the CB level of SrTiO$_3$, while at 600 nm the conversion occurs from the VB level of SrTiO$_3$ to the acceptor level of Rh$^{3+}$.$^{[25,26]}$ The Rh valence state ($\pm$3 or $\pm$4) in Rh: SrTiO$_3$ was found to obviously affect both the electron lifetime and the electron transfer kinetics. The occupied donor levels close to the SrTiO$_3$ VBM that contribute to the visible light response of Rh: SrTiO$_3$ were suggested to be originated from both Rh$^{4+}$ and Rh$^{3+}$ dopants. However, the unfavorable effect is that an unoccupied midgap acceptor state originating from Rh$^{4+}$ was also formed and located at about 1.5 eV below the CBM of SrTiO$_3$ (Figure 5). The in-gap Rh$^{4+}$ acceptor state should essentially act as an electron sink, for about 80% of the photogenerated electrons were revealed to be deeply trapped to the in-gap Rh$^{4+}$ acceptor state in $\approx$0.14 ps. The time constant for electron transfer from Rh$^{4+}$:SrTiO$_3$ to Ru was calculated to be 0.29 ps based on a theoretical model.$^{[27]}$ Thus, the fast and prompt electron quenching should result in a kinetic competition between the electron trapping and the electron transfer to the Ru cocatalyst. As a result, Rh$^{4+}$ is detrimental to the photocatalytic performance of Rh: SrTiO$_3$ and inhibiting the oxidation of Rh$^{3+}$ should be considered to improve the photocatalytic stability of Rh: SrTiO$_3$.

2.1. Codoping of Multiple Metallic Ions

The doping of SrTiO$_3$ with a single metal ion, such as Rh$^{4+}$ and Cr$^{3+}$, allows SrTiO$_3$ to respond to visible light and obtain excellent photocatalytic hydrogen evolution activity. However, there are some negative effects caused by dopants to inhibit the further enhancement of the photocatalytic activity. On the one hand, the valence state of doping ions will change easily during the photodoping reaction, and on the other hand, the doping of these lower-valence metal ions at the B-site of SrTiO$_3$ will lead to the generation of anionic vacancies. Doping the B-site with a higher-valence metal ion, like Ta$^{5+}$ or Sb$^{5+}$, can effectively promote the charge balance and inhibit the oxidation of Rh$^{3+}$ or Cr$^{3+}$ to a higher valence state. This process of using multiple exogenous metal ions as dopants is known as codoping. For example, Rh and Ta codoped SrTiO$_3$ photocatalysts displayed a much higher photocatalytic hydrogen evolution activity than that of the sole Rh-doped SrTiO$_3$. The charge imbalance between Rh$^{3+}$ and Ti$^{4+}$ was greatly mediated through the codoping of Ta$^{5+}$ and thus the production of Rh$^{4+}$ was largely suppressed. Similarly, the Cr/Ta codoped SrTiO$_3$ photocatalysts were fabricated with the polymerization complexation method (PCM) or the SSR method.$^{[29,30]}$ As the ionic radius of Ta$^{5+}$ (64 pm) is similar to that of Ti$^{4+}$ (61 pm), Ta-doped SrTiO$_3$ is structurally modeled with Ta$^{5+}$ replacing the lattice sites of Ti$^{4+}$. Theoretical calculations show that the bandgap together with...
with the VBM and CBM positions of Ta-doped SrTiO$_3$ remains essentially unchanged after its doping, but the Ta$^{5d}$ energy level is involved in constituting the CB of SrTiO$_3$. In addition, the theoretical calculation results indicate that a gap energy level consisting of the hybridization of Cr$^{3d}$ and O$^{2p}$ is formed between the VBM and CBM of Cr and Ta codoped SrTiO$_3$, and the difference from the gap energy level to CBM is about 1.0 eV.$^{[31]}$ Incident photons can excite the electrons on the gap energy level to the vacant Ti$^{3d}$ orbital and subsequently participate in the photocatalytic reaction on the surface to reduce H$^+$ to H$_2$. It was found that the photocatalytic H$_2$ production activity of Cr and Ta codoped SrTiO$_3$ synthesized by the PC method was ten times higher than that of the sample synthesized by the SSR method. Among them, Cr and Ta codoped SrTiO$_3$ with a doping amount of 2% showed the highest photocatalytic performance in the visible region with a H$_2$ evolution rate of 122.6 $\mu$mol h$^{-1}/$C$_0$ at 420 nm, corresponding to an apparent quantum efficiency (AQY) of 2.6%.$^{[30]}$

In addition, doping the A-site of SrTiO$_3$ with metal ions of a higher valence relative to Sr$^{2+}$ also has a charge balancing effect.
La$^{3+}$ with an ionic radius closer to that of $\text{Sr}^{2+}$ at the A-site is usually used as a codoping ion to stabilize the valence of $\text{Rh}^{3+}$ and $\text{Cr}^{3+}$ and thus enhance the activity and stability of the photocatalyst. The La–Cr codoped SrTiO$_3$ nanoparticles were synthesized through a single-step microwave-assisted method, based on which SrTiO$_3$ with a broad visible spectra response was obtained by finely tuning the doping amount of La and Cr. As the ionic radii of La and Cr are close to that of Sr and Ti, respectively, the Cr–SrTiO$_3$, La–SrTiO$_3$, and La–Cr–SrTiO$_3$ samples have diffraction peaks that are essentially the same as those of pure SrTiO$_3$, confirming that no impurities are generated in La, Cr, and La–Cr codoped SrTiO$_3$. However, the bandgap of SrTiO$_3$ decreases from $3.20$ to $2.80$ eV before and after doping, resulting in a broad visible spectra response. By controlling the amount of La and Cr doping, the atomic ratio of La–Cr/Sr varied from 1% to 75% and could optimize the photocatalytic $\text{H}_2$ production activity, with the highest photocatalytic $\text{H}_2$ production rate reached at about 90 μmol g$^{-1}$ h$^{-1}$. The density functional theory (DFT) calculations revealed that La is the most effective dopant ion among all n-type dopant ions (e.g., Ta, Sb, Nb, La, and Y) that can stabilize $\text{Cr}^{3+}$. In addition, the photocatalytic hydrogen production efficiency of $\text{Sr}^{2+}$/Cr/SrTiO$_3$ (10.2 μmol h$^{-1}$) was lower than that of La/ Cr:SrTiO$_3$ (29.2 μmol h$^{-1}$), but higher than that of Nb/Cr:SrTiO$_3$ (6.8 μmol h$^{-1}$) and $\text{Y}/\text{Cr}:\text{SrTiO}_3$ (9.6 μmol h$^{-1}$), and hydrogen production activity decreased with increasing irradiation time. Thus, La/Cr:SrTiO$_3$ was considered to be a highly active photocatalyst in the visible range, with a maximum AQY value of 25.6% at 425 nm.

It has also been demonstrated that even La and Cr codoping of the SrTiO$_3$ crystal structure with concentrations of up to 10% did not lead to significant distortion of the BO$_6$ octahedra, which mainly stems from the high flexibility and acceptability of its perovskite crystal structure. UV-vis absorption spectra show that the absorption at 550 nm is originated from the $\text{Cr}^{4+}$ species in Cr:SrTiO$_3$, while La/ Cr:SrTiO$_3$ essentially suppresses the oxidation of $\text{Cr}^{4+}$. The bandgap values for these materials are in the order SrTiO$_3$ > Cr:SrTiO$_3$ > La/Cr, corresponding to a bandgap value of 3.25 > 3.31 > 2.11 eV.

In addition, the addition of La to the perovskite structure increases its surface basicity and hydrophilicity. Wang et al. synthesized La and Rh codoped SrTiO$_3$ by a conventional two-step SSR method. According to the diffuse reflection spectra (DRS), $\text{Rh}^{4+}$ species generated in Rh:SrTiO$_3$ leads to an electronic excitation from the VB to the $\text{Rh}^{4+}$ impurity energy level and corresponds to the 550–800 nm range of visible light absorption. In addition, the absorption of the $\text{Rh}^{4+}$ species in the visible region below 520 nm contributes part of the excited electrons involved in the hydrogen production by proton reduction. The absorption spectra of La/Rh codoped SrTiO$_3$ show that the ion concentrations of $\text{Rh}^{4+}$ and $\text{Rh}^{4+}$ fluctuate. In addition, the codoping of Rh and La reduces the electron-hole recombination as it suppresses the generation of oxygen vacancies and inactive $\text{Rh}^{4+}$ species.

Under visible light irradiation ($\lambda = 420$ nm), the photocatalytic $\text{H}_2$ evolution velocity of Rh/La:SrTiO$_3$ in methanol solution was 3.5 times higher than that of Rh:SrTiO$_3$, mainly due to the higher concentration of $\text{Rh}^{4+}$ ions in Rh/La:SrTiO$_3$ to suppress the production of $\text{Rh}^{4+}$. Deep trapping of photoexcited electrons by defective states (e.g., oxygen vacancies) was found in Rh$^{4+}$:SrTiO$_3$ (4 mol.% La). Despite the simultaneous deep trapping of electrons, the time constant for electron transfer to the Ru catalyst was only 1.6 ps and its quantum efficiency was as high as 14.7%. When the amount of the La codopant increased from 4 to 10 mol%, the lifetime of its free electrons was substantially extended and meanwhile the deep-trapping electrons were reduced. However, the efficiency of the photodeposited Ru cocatalyst on the (Rh$^{4+}$+10 mol% La):SrTiO$_3$ surface is very low, so loading Ru by photodeposition exhibits almost no photocatalytic activity.

2.1.2. Codoping of Metal Ion and Anion

Introducing $\text{N}^{3-}$, which is a n-type dopant as the codoping ion for metal ions with a valence state of +3 (like $\text{Cr}^{3+}$, $\text{Sb}^{3+}$, $\text{La}^{3+}$, $\text{Ce}^{3+}$, $\text{Pr}^{3+}$, and $\text{Nd}^{3+}$) could enhance the charge balance and inhibit the formation of anion vacancies. In addition, both theoretical calculation and experimental results have revealed that the codoped metal ions are in favor of the incorporation of N and reduce the formation of oxygen vacancies in N/M-codoped SrTiO$_3$ with the metal ion (M) located at Sr site. The Cr and N codoped SrTiO$_3$ shows much higher photocatalytic hydrogen production activity, with the highest photocatalytic $\text{H}_2$ production activity reached at about 90 μmol g$^{-1}$ h$^{-1}$. 

Figure 5. a) The UV-vis absorption spectrum of Rh:SrTiO$_3$ and b) the band-edge diagram of Rh:SrTiO$_3$. Reproduced with permission. Copyright 2012, American Chemical Society. c) The diagram of carrier transfer kinetics of Rh:SrTiO$_3$, Reproduced with permission.
evolution activity under visible light compared with the Cr monodoped SrTiO$_3$.[38] This is mainly due to the smaller bandgap and much less vacancy defects in Cr/N-SrTiO$_3$. The smaller bandgap arrives from the largely upraised VB of Cr/N-SrTiO$_3$ comprising the hybridization of N2p and Cr3d orbits (Figure 6).

A comparative study for determining the electronic structure and photocatalytic performance of rare-Earth (RE) (La, Nd, Ce, or Pr)-N codoped SrTiO$_3$ where RE acted as the donor and N as an acceptor for bandgap modulation was carried out with first-principle calculations.[39] Among these RE elements, the 4f orbital of Nd or Pr exhibits a greater effect in narrowing the band structure for Nd or Pr monodoped SrTiO$_3$.[40] Furthermore, 4f orbitals of Pr and Ce are located mainly in CB and 4f orbitals of Nd are positioned between the VB and CB of SrTiO$_3$. The calculated energy of CB and VB indicates that these RE monodoped SrTiO$_3$ have the potential to drive water reduction. Moreover, the calculated binding energies of Nd–N, Pr–N, Ce–N, and La–N were 1.11, 1.91, 1.34, and 1.84 eV, respectively, in which the codoping of Pr–N and La–N was more stable for SrTiO$_3$. In case of the electronic structure of RE (La, Nd, Ce, or Pr)-N codoped SrTiO$_3$, La–N, Ce–N, and Pr–N codoped SrTiO$_3$ exhibit direct bandgaps of 2.02, 2.01, and 1.99 eV, respectively. Afterward, the precise band edges of RE–N-codoped SrTiO$_3$ were calculated to find suitable codoping ion pairs and the CBMs of La–N, Pr–N, and Ce–N codoped SrTiO$_3$ are positioned just out of the normal hydrogen electrode (NHE) potential. Therefore, the Nd–N codoped SrTiO$_3$ was predicted as the best candidate as an efficient photocatalyst among all RE–N codoped SrTiO$_3$. With a much wider bandgap than that of SrTiO$_3$, the doping strategy on NaTaO$_2$ to induce its visible light-responsive ability was rarely reported and the codoping of multiple anions with smaller electronegativity than that of O$_2^-$ was suggested to be applicable to elevate its conduction band and reduce its bandgap. The DFT calculation indicates that codoping with N–N, C–S, and N–P could obviously reduce the bandgap of NaTaO$_2$ but lose its water oxidation ability.[41] The S,N-codoped NaTaO$_2$ was experimentally exploited through a facile polymerized complex method and visible light degradation of rhodamine B was achieved, indicating the codoping with multiple anions is useful to narrow the bandgap of NaTaO$_2$.[42]

### 2.2. Perovskite Oxynitrides: Substitution of O$^{2-}$ with N$^{3-}$

In addition to B-site doping of perovskites with transition metal ions to broaden their light absorption range, the introduction of other anions at the oxygen site of ABO$_3$ perovskite oxides can also modulate the band structure to achieve a visible light response. The substitutional doping of N$^{3-}$ at the O$^{2-}$ position of the metal oxide through a high-temperature nitridation process can induce the formation of oxynitrides with AB(O,N)$_3$ perovskite structure, which is exhibited as stable B(O,N)$_6$ octahedron connected with a covertex mode. The smaller B-site metal cation constitutes the B(O,N)$_6$ octahedron surrounding the larger A-site metal cation to form a cubic structure or orthotetragonal structure. As the N2p orbital energy is higher than that of the O2p orbital energy, the replacement of the O2p by N2p contributing to the VB of the semiconductor can substantially raise the VB of the semiconductor and thus narrow the bandgap, rendering the oxynitride a broad visible light response. The oxynitrides widely used in photocatalytic water splitting are all based on d$^0$-configuration metal ions, mainly because the d orbitals of the d$^0$-configuration metal ions have a higher energy value of the e$_g$ orbitals originating from the Jahn–Taylor effect. The e$_g$ orbitals contribute to the conduction band of the semiconductor, endowing the d$^0$-based (such as Ti$^{4+}$, Ta$^{5+}$, Nb$^{5+}$, Zr$^{4+}$, and Hf$^{4+}$) oxynitrides a higher CBM than the proton reduction potential. Therefore, perovskite oxynitrides based on d$^0$-configuration metals are potentially efficient toward photocatalytic H$_2$ evolution.

The ionic radius of the A- and B-site metal ions needs to satisfy the basic criterion to satisfy the structural stability of ABO$_3$ perovskite, that is, the equation of the tolerance factor $t_{IR} = (r_A + r_B^t) / \{r_A + r_B^s\}$ ($r_A$ denotes as the ion radius of the A-site metal ion, $r_B$ denotes as the ion radius of the B-site metal ion, $r_B^t$ denotes as the average ion radius of O$_2^-$ and N$_3^-$).[43,44] Of which the tolerance factor (denoted as $t_{IR}$) should be in the range of 0.8–1.1. Therefore, the available A-site metal ions mainly include alkaline Earth metal ions (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and lanthanide metal ions (La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, etc.). Among them, only lanthanide metal ions with positive trivalent can be used to form perovskite oxynitrides with Ti$^{4+}$, Zr$^{4+}$, and Hf$^{4+}$ because the divalent alkaline Earth metal ions can only form structurally stable ABO$_3$-type perovskite pure oxides. For the metal ions Ta$^{5+}$ and Nb$^{5+}$, they can form oxynitrides with the fixed chemical formula ABO$_2$N with the alkaline Earth metal ions as well as with the trivalent lanthanide metal ions with the fixed chemical formula ABON$_2$. The tolerance factors for the AB(O,N)$_x$-type oxynitrides formed from the above ions are shown in Table 2, where the already reported oxynitrides with stable structures. The band-edge positions of these oxynitrides span the values of the proton reduction potential and water oxidation potential. Moreover, their bandgaps are small enough to respond to a broad visible light spectrum of the solar light, suggesting AB(O,N)$_3$ perovskite oxynitrides to be a class of promising semiconductors for photocatalytic water splitting.

#### 2.2.1. Perovskite Oxynitrides Based on Ta

The stable valence state of Ta in the oxynitrides based on Ta is +5. The metal ions that can form bimetallic oxynitrides with Ta
are the alkaline Earth metal ions (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) with a valence state of +2 and the RE metal ions (La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, etc.) with a valence state of +3. Among them, the alkaline Earth metal ions form a stable perovskite structure with Ta$^{5+}$ and exhibit the chemical formula of ATaO$_2$N and the RE metal ions form a stable perovskite structure with Ta$^{5+}$ and exhibit the chemical formula of RTaON$_2$. The crystal structure parameters of these oxynitrides are shown in Figure 7b. As the ionic radius of the A-site ion increases from 134 pm of Ca$^{2+}$ to 161 pm of Ba$^{2+}$, the symmetry of its corresponding perovskite oxynitride increases and the bandgap value decreases (Figure 7b). Through theoretical calculations and characterization techniques, Sniezana Balaz et al. revealed that the position of the conduction band edge is closely linked to the Ta—O/N—Ta bond angles and hence the tilting of the octahedra, whereas the position of the VB edge is more sensitive to the oxygen-to-nitrogen ratio. In comparison, the bandgap values of the lanthanides as A-site metal elements are very close to those of the perovskite oxynitrides with Ta, probably because the outermost electron energy of the La elements is so high that the valence electrons of the lanthanides have less influence on the energy band structure of the perovskite oxynitrides. The relative energy band positions of LaTaON$_2$ and PrTaON$_2$ are shown in Figure 7a. The bandgap values are nearly the same, whereas the VBM of PrTaON$_2$ and CBM of LaTaON$_2$ are both more negative than that of LaTaON$_2$. Other lanthanides after Pr displayed smaller ionic radii and greater electropositivity than La and Pr, and no perovskite oxynitrides that comprised lanthanides after Pr and Ta were reported in photocatalysis, which mainly resulted from that formation of a large number of anion vacancies and Ta$^{4+}$ defects during the nitridation process in consideration of the fact that much higher temperature and longer nitration time were needed to synthesize the oxynitrides LnTaON$_2$ (Ln = Nd, Sm, Gd). [47]

Both the VBM and the CBM of these oxynitrides are positioned to satisfy the corresponding potential requirements for oxygen production from water oxidation and hydrogen production from proton reduction, so they have the potential to drive the semireactive activity of photocatalytic hydrogen and oxygen production. Modified with suitable cocatalysts, these Ta-based oxynitrides all exhibit efficient photocatalytic hydrogen evolution activity, as displayed in Table 1. In contrast, the photocatalytic oxygen evolution activity of the Ta-based oxynitride is superior to their photocatalytic hydrogen evolution performance, which should be ascribed to the greater oxygen production overpotential provided by the VB position of these oxynitrides.

| A B | T$^{4+}$ (61 pm) | Zr$^{4+}$ (72 pm) | Hf$^{4+}$ (76 pm) | Nb$^{5+}$ (64 pm) | Ta$^{5+}$ (64 pm) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ca$^{2+}$ | (134 pm) | – | – | – | 0.95$^{(5)}$ |
| Sr$^{2+}$ | (144 pm) | – | – | – | 0.98$^{(5)}$ |
| Ba$^{2+}$ | (161 pm) | – | – | – | 1.04$^{(5)}$ |
| La$^{3+}$ | (136 pm) | 0.97$^{(5)}$ | 0.92$^{(5)}$ | 0.90$^{(5)}$ | 0.95$^{(5)}$ |
| Pr$^{3+}$ | (118 pm) | 0.91$^{(5)}$ | 0.86$^{(5)}$ | 0.84 | 0.89$^{(5)}$ |
| Nd$^{3+}$ | (127 pm) | 0.94$^{(5)}$ | 0.89$^{(5)}$ | 0.87$^{(5)}$ | 0.92$^{(5)}$ |
| Sm$^{3+}$ | (124 pm) | 0.93$^{(5)}$ | 0.88$^{(5)}$ | 0.86$^{(5)}$ | 0.91$^{(5)}$ |
| Cd$^{2+}$ | (105 pm) | 0.86 | 0.81 | 0.79 | 0.85 |

$^{(5)}$ Already reported oxynitrides with stable structures.
nitridation time under 1223 K and thus leads to the formation of a large concentration of Ti$^{4+}$ which inhibits its photocatalytic performance.\cite{49} Recently, Zhang and co-workers carried out the Na$^+$ volatilization-assisted nitridation strategy on a layer-structure precursor NaSmTiO$_4$ to construct SmTiO$_2$N with lower defect density and applied it in the semireactions of both photocatalytic hydrogen production and photocatalytic oxygen production for the first time, and a rather high AQE of water oxidation on the photocatalyst CoO$_2$/SmTiO$_2$N was achieved.\cite{50,51} As an element with the same period to Ti, only the lanthanide elements (Ln = La, Pr, Nd, Sm) can form the perovskite-structure oxynitrides with Zr and all these oxynitrides LnZrO$_2$N (Ln = La, Pr, Nd, Sm) have been successfully synthesized through an extremely harsh nitridation condition.\cite{52,53} Only the oxynitride LaZrO$_2$N had been tested toward photocatalytic water oxidation with the O$_2$ evolution rates reaching about 1 $\mu$mol h$^{-1}$.\cite{52} The much poor photocatalytic performance of the oxynitrides based on Zr should be originated from their wider bandgaps than oxynitrides based on Ti and their high concentration of defect sites which formed during the harsh nitridation process. To fabricate highly efficient photocatalysts from these oxynitrides, new fabrication strategies focusing on the inhibition of defect formation should be developed.

\subsubsection*{2.2.4. Cationic Doping to Inhibit Defect Formation}

A high concentration of metallic ions with lower valence is easily formed due to the charge imbalance between O$^{2-}$ and N$^{3-}$ and the highly reductive ability of ammonia gas as the insertion of N$^{3-}$ into the crystal lattice of metal oxides usually requires a high-temperature nitridation process. Doping is a widely used and efficient strategy to modulate the electronic structure of the semiconductor photocatalyst and promote its carrier separation.\cite{54} Due to the diverse elemental composition and structural stability of the perovskite structure, a variety of metal ions are available for doping. The electronic structure of the dopant ion should match the electronic structure of the parent metal ion in the oxynitride. The specific reason is that if the radius of the dopant ion is too large or too small, then the lattice distortion near the doping site will be very violent and defects caused by the lattice distortion will be formed, thus forming a defect state that is not conducive to carrier transport in the bulk phase. If the electronic structure of the valence layer of the dopant ion differs greatly from that of the parent metal ion in the oxynitride, the corresponding impurity energy levels will be formed in the bandgap of the semiconductor, which are mostly detrimental to the separation of photogenerated carriers. Combined with the previous research results, various kinds of $d^0$-configuration metallic ions (as shown in Table 3) with the ionic radius between 60 and 75 pm can be used as dopants for the perovskite oxynitrides with its B-site based on $d^0$-configuration metallic ions. Among them, the doped metal ions have a lower valence state than that of the B-site parent metal ion of the oxynitride. Such metal ion doping can protect the B-site metal ion from being reduced and inhibit the generation of B-site metal ion defects with lower valence state, thus promoting carrier separation. The doping ions with higher valence, such as Mo$^{6+}$ and W$^{6+}$, in the nitridation precursors will be reduced in preference to the B-site parent metal ions during nitridation, thus inhibiting semiconductor as revealed by the much higher UV–vis absorption tail of BaNbO$_2$N also leads to a lower photocatalytic hydrogen evolution activity (Figure 8). The bandgap of the perovskite structure oxynitride comprising La and Nb is even smaller, $\approx$1.6 eV, which is supposed to be caused by the higher nitrogen content in LaNbO$_2$N and the lower energy of the Nd4d electronic state. As the CBM of LaNbO$_2$N is lower than the proton reduction potential for hydrogen production, only the photocatalytic oxygen production activity can be achieved on LaNbO$_2$N. Wang et al. synthesized shell-coated LaNbO$_2$N with low defect concentrations in the outer layer of LaKNaNbO$_5$ by nitriding LaKNaNbO$_3$, which exhibited a photocatalytic oxygen evolution activity of 100 $\mu$mol h$^{-1}$ after loading with CoO$_2$ as the cocatalyst.\cite{48} The synthesis of perovskite oxynitride comprising Nb and lanthanide after La requires harsher nitridation conditions, which lead to the formation of an extremely high defect concentration of Nb$^{6+}$ and Nb$^{4+}$, and thus the photocatalytic applications of these Nb-based oxynitrides have rarely been reported.

\subsection*{2.2.3. Perovskite Oxynitrides Based on Ti and Zr}

The highest valence state of Ti is +4 and it can only form perovskite-structure oxynitrides with lanthanides (Ln = La, Pr, Nd, Sm).\cite{49} The successful synthesis of LnTiO$_2$N (Ln = La, Pr, Nd, Sm) has been reported. In contrast, the ionic radius of Gd after Gd requires harsher nitridation conditions, which lead to the formation of an extremely high defect concentration of Nb$^{4+}$ and Nb$^{6+}$, and thus the photocatalytic applications of these Nb-based oxynitrides have rarely been reported.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure8.png}
\caption{The Kubelka-Munk function of UV–vis diffuse reflectance spectra of a) BaNbO$_2$N, b) BaNb$_{0.75}$Ta$_{0.25}$O$_2$N, c) BaNb$_{0.5}$Ta$_{0.5}$O$_2$N, d) BaNb$_{0.25}$Ta$_{0.75}$O$_2$N, and e) BaTaO$_2$N crystals. Reproduced with permission. Copyright 2016, The Royal Society of Chemistry.}
\end{figure}

The much poor photocatalytic performance of the oxynitrides based on Zr should be originated from their wider bandgaps than oxynitrides based on Ti and their high concentration of defect sites which formed during the harsh nitridation process. To fabricate highly efficient photocatalysts from these oxynitrides, new fabrication strategies focusing on the inhibition of defect formation should be developed.
the generation of the defects of low-valence B-site metal ion to some extent. In summary, metal ion doping of perovskite oxynitride is effective for the suppression of defect generation in oxynitride semiconductors. In addition, the effect of doping on carrier concentration in the semiconductor may also be important to enhance its photogenerated carrier separation efficiency. The concentration of cationic dopant is also a key parameter as the doping concentration should usually be below 5%, as excessive metal ion doping may form impurity phases. For example, the doping amount of Mo and W should be below 5 at% to avoid the formation of the impurity phase of BaMoO₄ or BaWO₄, when Mo and W are used as dopants for BaTaO₄. Recently, the metal oxide Ba(Zn₁₋ₓTaₓ/3)O₃ with a similar perovskite structure to that of BaTaO₂N was used as the nitridation precursor to synthesize BaTaO₄N doped with a large amount of Zn²⁺, in which the Zn²⁺ doping amount was up to 30 at% and its photocatalytic hydrogen production activity was promoted more than five times compared with that of BaTaO₂N synthesized by the conventional nitridation route. Zn²⁺ with the d⁰ electronic configuration is preferentially reduced to form metallic Zn during the nitridation process, thus protecting the B-site metal ion Ta⁵⁺ from being reduced and fabricating BaTaO₂N free from the Ta⁵⁺ defects.

2.3. Constructing Perovskite Solid Solution

In addition to the doping of transition metal ions in the A-site or B-site of perovskite oxides and the doping of N³⁻ in the oxygen site of perovskite oxides to construct perovskite semiconductors with visible light response, constructing a solid solution is another useful band engineering strategy. Due to the diversity of perovskite structure materials and the inclusiveness of perovskite structure materials to various elements, the construction of solid solution comprising a perovskite structure oxide and a perovskite structure oxynitride is a simple and widely used strategy. The solid-solution strategy allows the construction of a series of oxynitrides with a bandgap that is adjustable with the solid-solution ratio, and the defect density of the solid-solution oxynitride is generally low. In addition, the suitable solid-solution ratio can be adjusted to obtain a significant increase in the photocatalytic performance of perovskite-structure oxynitride. As shown in Table 4, the formation of solid-solution photocatalysts from a perovskite oxynitride and a perovskite oxide is applicable for most d⁰-metal-based oxynitrides. The new bandgap of the perovskite solid solution decreases as the component ratio of the oxynitride increases. In addition, the lattice distortion of the solid solution also changes with the solid-solution ratio, but there is no linear relationship between the lattice distortion and the solid-solution ratio. Combining the effects of light absorption, lattice distortion, and defect density on carrier transport properties, there is an optimum value for the solid-solution ratio of the oxynitride for the final photocatalytic performance, as shown in Table 4.

Benefitting from the high lattice match between the ABO₃ perovskite structures, there is generally a very high probability that each group of two perovskite semiconductors can form a solid solution. However, due to the limitation of oxynitride synthesis conditions, the choice of the perovskite oxide has to ensure that the structural stability can be maintained during the high-temperature nitridation process, and therefore a structurally stable oxide is generally chosen. The polymerized complex process is mainly used to ensure adequate mixing of each element in spite of the negative effect of C residues caused by organic precursors. The development of more versatile routes for solid-solution synthesis is of high priority for the extending of solid-solution oxynitride systems. In addition, the solid-solution strategy needs to ensure that no new interstitial energy levels are introduced in the bandgap of the oxynitride, and the perovskite oxides with its B-site metal based on d⁰-metals (such as Ti⁴⁺, Zr⁴⁺, and Ta⁵⁺) are generally selected. The band structure of the solid solution varies with the solid-solution ratio and is generally linearly tuned between the band structure of the pure oxynitride and the band structure of the pure oxide with the varying of the ratio of each component, as displayed in Figure 9c,d. Combining the advantage of the solid-solution strategy to linearly modify the energy band structure of the material and the

Table 3. Summary of the cationic doping studies of perovskite (oxy)nitrides.

| (Oxy)nitrides     | Dopant | Ionic radius [pm] | Dopant conc [atomic ratio, %] | Enhancement factor | Reaction condition | References |
|------------------|--------|------------------|-------------------------------|--------------------|--------------------|------------|
| SrTaO₄N          | La⁵⁺  | 9                 | 20                            | ≈10 (HER)² 4 µmol h⁻¹0.4 µmol h⁻¹ | 0.5%Pt loaded, (λ > 420 nm) | [94]       |
| BaTaO₂N          | Ca²⁺  | 134               | 10                            | 2.75 [OER]⁵ (110 µmol @ 5 h|40 µmol @ 5 h) | CoO loaded, (λ > 420 nm) | [95]       |
|                  |        |                  |                               | 5 [OER] (107 µmol@10 h|20 µmol@10 h) | IrO₂ loaded, (λ > 420 nm) | [55]       |
|                  | W⁶⁺   | 60                | 5                             | 4.61 [HER] 15.2 µmol h⁻¹3.3 µmol h⁻¹ | Pt loaded, (λ > 420 nm) | [56]       |
|                  | Zn²⁺  | 74                | ≈30                           | 2.35 [OER] (100.1 µmol h⁻¹)24.6 µmol h⁻¹ | CoO loaded, (λ > 420 nm) | [96]       |
| CaNbO₂N          | Mg⁷⁺  | 72                | 10                            | 7.36 [OER] (65.19 µmol h⁻¹8.86 µmol h⁻¹) | CoO loaded, (λ > 420 nm) | [97]       |
| SnO₂N            |        |                  |                               | 17 [OER] ≈17|1 µmol h⁻¹ | CoO loaded, (λ > 400 nm) | [98]       |
| BaNbO₂N          | Ti⁴⁺  | 61                | 4                             | 2.45 [Photoanode] 0.71 mA cm⁻²0.29 mA cm⁻² | CoO loaded, (λ > 400 nm) | [99]       |
|                  | Zr⁴⁺  | 72                | 3                             | 1.93 [Photoanode] 0.56 mA cm⁻²0.29 mA cm⁻² | CoO loaded, (λ > 400 nm) | [100]      |
| LaTaON₂          | Zr⁴⁺  | 72                | 10                            | 2.92 [OER] (35 µmol @ 2.5 h|12 µmol @ 2.5 h) | CoO loaded, (λ > 420 nm) | [101]      |
|                  |        |                  |                               | 8.89 [HER] (40 µmol @ 2.5 h|4.5 µmol @ 2.5 h) | Pt-loaded, (λ > 420 nm) | [102]      |
| LaTiO₂N          | Ca²⁺  | 134               | 5                             | 1.82 [OER] (40 µmol h⁻¹22 µmol h⁻¹) | CoO loaded, (λ > 420 nm) | [103]      |
|                  | W⁶⁺   | 60                | 5                             | 2.83 [OER] (31 µmol h⁻¹18 µmol h⁻¹) | CoO loaded, (λ > 420 nm) | [104]      |

*The HER denotes hydrogen evolution reaction; OER denotes oxygen evolution reaction.*
advantage of optimizing the carrier mobility by reasonably varying the lattice distortion of the perovskite solid solution as displayed in Figure 9a, Pan et al. achieved a one-step OWS on the solid-solution sample (LaMg$_{2/3}$Ta$_{1/3}$O$_{3}$)$_{1/2}$[LaTaON$_3$]$_{1/2}$.[58] The perovskite solid solution can also be constructed from two oxynitrides, and two key points, that is the enough high lattice match and the similar nitridation condition, should be carefully considered toward the successful construction. Both the oxynitrides LaTaON$_3$ and CaTaO$_N$ can be successfully synthesized under the nitridation of 1223 K and 15 h and they exhibit a highly matched crystal framework, as displayed in Figure 9b. A linear modulation of the bandgap of the solid-solution sample (LaTaON$_3$)$_{1-x}$[CaTaO$_N$]$_x$ was carried out through modulating the ratio of the solid solution (Figure 9d).[59] and the photocatalyst La$_{0.7}$Ca$_{0.3}$TaO$_{1.7}$N$_{1.12}$ (x = 0.9) realized an OWS activity with a stoichiometric H$_2$/O$_2$ ratio of 2:1 under visible light. The key parameters including Ta—O/N bond length, Ta—O/N—Ta bond angle, defects concentration, bandgap, and band-edge alignments could be properly modulated through the construction of the solid solution (LaTaON$_3$)$_{1-x}$[CaTaO$_N$]$_x$, and these optimized parameters were revealed to substantially promote the separation of photogenerated charge carriers with sufficient energetics for water oxidation and proton reduction. The global merits of the solid solution with perovskite structure make it a promising strategy for the photocatalyst fabrication toward OWS.

3. Constructing the Photocatalytic OWS System

Although most of the above-reported perovskite structure oxynitrides are capable of achieving the photocatalytic semireaction of both the hydrogen production and the oxygen production in a sacrificial agent-containing system, the industrial application of photocatalytic water splitting must be carried out in a sacrificial agent-free system with both hydrogen and oxygen produced simultaneously. The main challenges that need to be overcome for the OWS include first, hydrogen production cocatalysts (e.g., Pt, Ir, Rh, etc.) that can generally catalyze the reaction of H$_2$ and O$_2$ to generate H$_2$O at the same time with high efficiency, thus inhibiting the photocatalytic water splitting activity; second, the separation efficiency of electrons and holes on the surface of the photocatalyst is poor, and the activity of simultaneous hydrogen and oxygen production is relatively low in a single photocatalyst. In response to the earlier problems, the development of multiple types of photocatalytic OWS systems without sacrificial agents is on the road.

3.1. One-Step OWS

Two big problems, that are the oxidative corrosion of the dopant ions in the surface lattice and the severe reverse reaction on the cocatalyst, have impeded the photocatalytic OWS on a single-perovskite photocatalyst. To address the problem of N$^{3-}$ oxidation in the surface lattice of perovskite oxynitrides, the inert oxide can be coated on the surface of the oxynitrides and constructed as a surface-protecting layer. Such oxide layers need to isolate the surface of the oxynitride from the reaction solution and at the same time should avoid blocking the transport of photogenerated electrons and holes to the surface of the photocatalyst. Therefore, the layer thickness should be sufficiently small to ensure that the metal oxide layer is capable of transporting both electrons and holes. For example, Chen et al. modified the surface of the photocatalyst Ta$_3$N$_5$ with a thin layer of MgO by a simple grinding method to protect the surface of Ta$_3$N$_5$ from being oxidized.[60,61] In addition, the MgO protection layer could promote the dispersion of the cocatalyst Pt and CoO$_x$, thus enhancing both the photocatalytic hydrogen and oxygen production activities of Ta$_3$N$_5$. Although the thickness of the MgO protection layer cannot be regulated by grinding, a sufficiently thin MgO layer is essential to ensure that the photogenerated electrons and photogenerated holes can be effectively transported to the surface of Ta$_3$N$_5$. Domen and co-workers developed a photocatalyst deposition method to modify TiO$_2$H layers on the surface of oxynitrides, and the TiO$_2$H protection layer modified by this method is uniformly distributed on the surface, which can effectively enhance the resistance of oxynitrides to photocorrosion.[58,62] To address the problem of severe reverse reaction on the proton reduction cocatalyst, the core idea is to create a barrier between H$_2$ and O$_2$ molecules on the cocatalyst. One approach is to spatially separate the hydrogen evolution cocatalyst from the oxygen evolution cocatalyst so that H$_2$ and O$_2$ are produced in different regions of the catalyst. However, the synthesis process for the spatially separate cocatalyst loading is long and complex, exposing the oxynitride photocatalyst to the risk of destruction. Another type of method is to cover the surface of the hydrogen evolution cocatalyst with a blocking layer which impedes the contact of O$_2$ to the surface of the cocatalyst. For example, the hydrogen evolution cocatalysts RhCrO$_x$ are immune to the reverse reaction of H$_2$O production from H$_2$ and O$_2$, benefiting from the ability

| Table 4. Summary of the perovskite semiconductors constructed from the solid solution. |
| Solid solution | Optical value of x | Bandgap [eV] | H$_2$ [μmol·h$^{-1}$] | O$_2$ [μmol·h$^{-1}$] | References |
|---------------|-------------------|---------------|-----------------|-----------------|------------|
| (SrTiO$_3$)$_{1-x}$[LaTiO$_2$N$_x$] | 0.25 | 2.0–3.2 | 10 | 8 | [103] |
| (BaZrO$_3$)[BaTaO$_2$N$_x$] (x ≤ 0.1) | 0.05 | 1.7–1.8 | 14.1 | 0 | [104] |
| (SrTiO$_3$)$_2$[LaTaON$_3$]$_{1-x}$ | 0.5 | 2.0–2.3 | 7.2 | 104 | [57] |
| (SrZrO$_3$)$_{1-x}$[LaTaON$_3$]$_x$ | 0.6 | 1.9–2.8 | – | 23 | [105] |
| (BaTaO$_2$N$_x$)[Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_y$Na$_{1/3}$Ta$_{1/3}$O$_x$] | – | 1.8 | – | 699 | [106] |
| (LaTaON$_3$)$_{1-x}$[CaTaO$_N$]$_x$ | 0.9 | 1.9–2.4 | ≈1.2 | ≈0.6 | [59] |
| (LaMg$_{2/3}$Ta$_{1/3}$O$_{3}$)$_{1/2}$[LaTaON$_3$]$_{1/2}$ (x ≤ 2/3) | 1/3 | 1.9–4.6 | ≈1.0 | ≈0.5 | [58] |
of the CrO$_x$ layer near Rh to allow the penetration of H$_2$ and block the O$_2$ molecules, as explained by Maeda and co-workers.$^{63}$ A general strategy of compounding or mixing CrO$_x$ with hydrogen production cocatalysts (like Ru, Pd, Pt) to form an antireverse
reaction cocatalyst was developed from then on.\(^{[64-66]}\) By modifying the surface of the perovskite structure oxynitride LaMg\(_{1-x}\)Ta\(_{1/2}\)O\(_{1+x}\)N\(_{2-x}\) \((x = 1/3)\) with a TiO\(_{2}\) protection layer and loading the RhCrO\(_x\) hydrogen production cocatalyst, Domen and co-workers achieved the one-step OWS on the oxynitride photocatalyst with an absorption edge of 600 nm in a non-sacrificial agent system.\(^{[62]}\)

### 3.2. Z-Scheme OWS

Although single-photon-excited OWS can be achieved on perovskite photocatalysts by multistep surface or interface modification, their photocatalytic OWS activity is still low. It is of great interest to take advantage of the high efficiency of perovskite-structure photocatalysts to drive hydrogen production in a two-photon excitation system by simulating the electron chain transfer coupling process of two major photoacceptor proteins in photosynthesis. The two-step OWS based on a pair of photocatalysts and the redox mediators (Figure 10a) which mimics the natural photosynthesis is intriguing for hydrogen production from water, and the H\(_2\)-evolving photocatalyst (HEP) based on (oxy)nitrides has been widely fabricated.

One of the key points to construct such Z-scheme OWS (Z-OWS) processes is to develop efficient electron transfer chains, that is, redox electron pairs. Currently, there are many types of redox electron pairs that act as the electron transfer chain and their working pH as well as working concentration are displayed in Table 5. Among them, IO\(_3^-/I^-\) is the earliest and most widely used redox electron pair, mainly because of its wide working pH range and the fact that both IO\(_3^-\) and I\(^-\) are colorless and do not interfere with the light absorption of the photocatalyst.\(^{[67]}\) Sayama et al. constructed a Z-OWS system using Pt-loaded Cr,Ta: SrTiO\(_3\) (Pt-SrTiO\(_3\); Cr,Ta) as HEP, Pt/WO\(_3\) as the O\(_2\)-evolving photocatalyst (OEP), and IO\(_3^-/I^-\) as redox ion pair, respectively.\(^{[68]}\) IO\(_3^-\) was revealed to be selectively reduced on Pt/WO\(_3\) and I\(^-\) was selectively oxidized on Cr,Ta: SrTiO\(_3\), and the production of H\(_2\) and O\(_2\) with a stoichiometric ratio of 2:1 was performed on Cr,Ta: SrTiO\(_3\) and Pt/WO\(_3\), respectively. The effect of cation doping on the photocatalytic activity of Cr,Ta: SrTiO\(_3\) is bidirectional and the doping concentration needs to be optimized to enhance the photocatalytic activity. Cr\(^{3+}\) and Ta\(^{5+}\) are more likely to replace the Ti\(^{4+}\) ion occupancy in the B-site of SrTiO\(_3\) lattice as both the ionic radii of Cr\(^{3+}\) and Ta\(^{5+}\) are close to that of Ti\(^{4+}\); therefore, an equal doping amount of Cr\(^{3+}\) and Ta\(^{5+}\) can effectively maintain the charge balance. The photocatalytic OWS performance of SrTiO\(_3\) in the IO\(_3^-/I^-\) redox system can be substantially enhanced when the doping concentrations of Cr\(^{3+}\) and Ta\(^{5+}\) are close to 1%, and its photocatalytic stability was improved simultaneously.\(^{[30]}\) The visible light-responsive oxynitrides were also revealed to be a potentially efficient HEP, as the photocatalysts Pt/CaTaO\(_2\)N and Pt/BaTaO\(_2\)N were able to drive the

![Figure 10. Z-scheme OWS on particulate photocatalysts with a) ion pair as the electron mediator and b) solid conductor as the electron mediator. c) The all-solid-state Z-scheme systems with Ru/SrTiO\(_3\); La,Rh as HEP, CoO\(_x\)/Ta\(_3\)N\(_5\) as OEP, and the nanometal Ir as the electron conductor. Reproduced with permission.\(^{[35]}\) Copyright 2014, American Chemical Society. d) The photoreduced graphene oxide performed as a fast electron transfer mediator in the all-solid-state Z-scheme system. Reproduced with permission.\(^{[78]}\) Copyright 2011, American Chemical Society.](https://www.small-structures.com)
photocatalytic H₂ production in a solution of 5 mM NaI and the oxidation product IO₃⁻ was obviously detected.\(^{[69]}\) Using the low-defect BaTaO₂N prepared from the SrCl₂-assisted nitridation method as the HEP and IO₃⁻/I⁻ as the redox mediator, the Z-OWS system with a breakthrough AQE of 6.8% at 420 nm and STH of 0.24% was achieved on the perovskite BaTaO₂N.\(^{[70]}\)

Similar to the IO₃⁻/I⁻ redox pair, the Fe³⁺/Fe²⁺ redox ion pair was another traditional shuttle ion pair used in the early days of the Z-scheme system. Due to its single-electron transfer properties, Fe³⁺/Fe²⁺ is often used as an effective sacrificial reagent (electron acceptor) for photocatalytic water oxidation because of its reaction kinetic advantage.\(^{[71]}\) The effectiveness of Fe³⁺/Fe²⁺ as a redox electron pair was demonstrated in earlier work that uses BiVO₄ as OEP, Ru/SrTiO₃:Rh as HEP, and Fe³⁺/Fe²⁺ as a redox electron pair to obtain OWS activity with STH up to 0.1%.\(^{[72]}\) Using FeCl₃ as an electron sacrificial agent, BiVO₄ can easily oxidize water to O₂ and simultaneously reduce Fe³⁺ to Fe²⁺. Fe²⁺ will be oxidized to Fe³⁺ by holes on Ru/SrTiO₃:Rh and thus complete the corresponding redox. The photocatalytic OWS of the system exhibited an AQY of 0.3% and its long-term operational stability reached 70 h.\(^{[73]}\) However, the pH environment for Fe³⁺/Fe²⁺ redox is acidiﬁed at the region of 2–3, rendering most of the photocatalysts, especially those containing nitrogen atoms, unstable. Further, the ligand ions of Fe, [Fe(CN)₆]³⁻/⁴⁻, were revealed to be stable in the neutral aqueous solution and they also exhibit the single-electron transfer character during the redox.\(^{[74]}\) With the photocatalyst Ru/SrTiO₃:Rh constructed as the HEP, an efficient H₂ evolution activity was observed when the ligand ion [Fe(CN)₆]³⁻ was used as the sacrificial agent. A successful Z-OWS system was constructed after introducing the Fe and Cs codoped WO₃ as the OEP and the ion pair of [Fe(CN)₆]³⁻/⁴⁻ and [Co(phen)]³⁺/²⁺ as the electron transfer mediator; a stable and efﬁcient evolution activity of both H₂ and O₂ was achieved with the STH reaching about 0.04%.\(^{[75]}\)

In addition to these conventional redox ion pairs with simple structure, coordination compounds of transition metals (such as the cobalt-based coordination compounds [Co(bpy)]³⁺/²⁺ and [Co(phen)]³⁺/²⁺) show excellent potential for driving the Z-OWS system because of their adjustable standard potentials over a wide pH range and their convenient reversibility.\(^{[76]}\) The HEP which consists of SrTiO₃:Rh monolithic photocatalyst loading with platinum or ruthenium as cocatalysts is among the few photocatalysts in the list that is capable of producing H₂ in the aqueous solutions of [Co(bpy)]³⁺/²⁺ or [Co(phen)]³⁺/²⁺.\(^{[77]}\) The main reason for this is that SrTiO₃ itself is essentially unable to drive the oxidation of Co³⁺ ions to Co⁴⁺, resulting in no photocatalytic hydrogen production performance of SrTiO₃ in Co-based ion-pair solutions. In contrast, the photocatalyst SrTiO₃:Rh could efﬁciently drive the oxidation of [Co(bpy)]³⁺ or [Co(phen)]³⁺, indicating that the interstitial doping of Rh plays an important role in promoting the oxidation of Co-based ions. It should be noted that the disadvantage of using ion pairs as electron transport chains is the competitive reactions of ion pairs, that is, the reduction of oxidative ions on the HEP and the oxidation of the reductive ions on the OEP. In that case, the working concentration of the ion pair should be as low as possible. However, the second key point is that the reaction rates of the ion pair should be matched to the reaction rates of water oxidation and/or proton reduction. Therefore, the working concentrations of these ion pairs should be modulated to optimize the working efﬁciency of the Z-OWS system and their common working concentrations are shown in Table 3.

A solid conductor could also be used as the electron transport medium in the two-step photoexcitation system instead of the need for ion pairs and no adverse effects of competitive reactions as that of the ion pairs were introduced (Figure 10b). Precious metals, as highly conductive materials, can be used as electron transfer media in direct Z-scheme systems. Solid electron transfer media have vector electron transfer properties and can also be used as a medium for isolated photocatalysts. With high electron mobility, iridium (Ir) can be constructed as the electron transfer medium and is capable of driving electron transfer in the all-solid-state Z-scheme systems, as displayed in Figure 10c, which fabricates Ru/SrTiO₃:La:Rh as HEP and CoO₃/Ta₃N₅ as OEP.\(^{[78]}\) A cascade electron transfer occurs in the La:Rh-SrTiO₃:Ir/CoO₃/Ta₃N₅ triplet system, where electrons in the Ta₃N₅ conduction band are transferred to the VB of SrTiO₃:La:Rh through the Ir–semiconductor ohmic contact interface. The La and Rh ions codoped in the SrTiO₃ lattice could induce the formation of oxygen vacancies to replace some of the Ti⁴⁺ sites in SrTiO₃, thereby compensating for charge balance. The presence of oxygen vacancies leads to the formation of Gap energy levels, which narrow the bandgap of the semiconductor, and SrTiO₃:La:Rh exhibits light absorption up to 700 nm. Visible light-driven photocatalytic OWS was observed on the La:Rh-SrTiO₃:Ir/CoO₃/Ta₃N₅ all-solid-state Z-scheme system with AQY and STH of 1.1% and 0.037%, respectively. The ability of this Z-scheme system to perform photocatalytic water splitting without the sacrificial agent is a direct indication of the efﬁciency of this solid electron transfer medium.

Not only the metallic conductors can be used as efﬁcient electron transport media for all-solid-state Z-scheme system, but also the inexpensive carbon-based materials being used as electron transport media are beginning to receive increasing attention due to their versatility and extraordinary electronic properties.\(^{[79]}\) Iwase et al. first incorporated RGO as an electron transport medium in the Z-scheme system, and the reduction of GO was obtained by the photoreduction process of GO on Ru/SrTiO₃:Rh or BiVO₄.\(^{[80]}\) The reduction of GO on Ru/SrTiO₃:

| Mediators        | pH   | Working concentration | Potential (V vs NHE) | References |
|------------------|------|-----------------------|---------------------|------------|
| IO₃⁻/I⁻          | 6–11 | 1–2 mM                | 1.085–0.059× pH     | [67]       |
| I⁺/I⁻            | 4.5  | 1–2 mM                | 0.536               |            |
| Fe³⁺/Fe²⁺        | 2–3  | 1–8 mM                | 0.771               | [107–109]  |
| [Fe(CN)₆]³⁻⁻/⁴⁻⁻ | 6–7  | 10 mM                 | 0.358               | [73]       |
| [Co(bpy)]³⁺⁻/²⁺⁻ | 3.8  | 0.5 mM                | 0.30                | [76]       |
| [Co(phen)]³⁺⁻/²⁺⁻ | 7    | 0.5 mM                | 0.36                | [76]       |
| VO₂⁻/VO²⁺⁻      | 2.4  | 100–200 mM            | 1.0 (pH = 0)        | [110]      |

\(^{a)}\)NHE = normal hydrogen electrode, bby = 5-(7-bromo-1,3-benzodioxol-5-yl)-1-methyl-1 H-pyrazol-3-amine, phen = 1,10 phenanthroline.
Rh is more pronounced than that on BiVO₄ due to the stronger reduction of the conduction band electrons of Ru/SrTiO₃:Rh. The C=O content of PRGO/SrTiO₃:Rh was found to be only 10% after illumination by the X-ray photoelectron spectra (XPS) analysis, which indicates that RGO can be used as a stable electron transport medium. However, the dispersion of the photocatalyst in water was found to be extremely low due to the strong hydrophobicity of RGO produced by photoinduction on Ru/SrTiO₃:Rh. Therefore, it is crucial to obtain a balance between the degree of GO reduction and the hydrophilicity of the composite photocatalytic material. As shown in Figure 10d, the presence of PRGO can facilitate the cascade electron transfer from BiVO₄ to Ru/SrTiO₃:Rh for the photocatalytic OWS process.

It is important to achieve efficient electron transfer from the O₂-producing photocatalyst to the H₂-producing photocatalyst and suppress inverse reactions that consume photogenerated electrons and holes in the Z-scheme photocatalyst suspension system. For this purpose, photocatalyst plates coated by photocatalyst particles have been designed by embedding hydrogen-producing and oxygen-producing photocatalysts into the conductive layer.[79,80] The first photocatalyst plate was formed using particles of the hydrogen-producing photocatalyst La,Rh: SrTiO₃ and the oxygen-producing photocatalyst Mo:BiVO₄ homogeneously embedded in the Au layer by the particle transfer method, followed by particle transfer to form the photocatalyst plate (Figure 11).[81] This photocatalyst plate achieved an STH conversion efficiency of 1.1% and an AQY of 33% at 420 nm, and the plate exhibited an OWS activity under visible light irradiation at 520 nm, which represents the highest photocatalytic performance of the Z-scheme monolithic photocatalyst OWS system to date. For this Z-OWS system, the existing HEP and OEP need to be replaced with narrow-bandgap photocatalysts to extend the use of visible light and thus improve the STH conversion efficiency.

4. Conclusion

Benefiting from the superflexibility and inclusiveness of perovskite structures, various kinds of electronic engineering strategies have been exploited to induce the visible light response of perovskite oxides, including cation doping, anion substitution, and construction of the solid solution. Moreover, photocatalysts based on these perovskite structure semiconductors have achieved a series of appealing photocatalytic OWS performances, and the STH of the particulate sheet contains La,Rh-SrTiO₃[Au] BiVO₄ that also reached a breakthrough value of 1.1%.[82] In addition, a large group of perovskite-structure oxynitrides with low bandgap and suitable band edges were successfully constructed as photocatalysts. A big group of visible light-responsive semiconductors with controllable bandgaps was fabricated through constructing solid solutions comprising a perovskite oxynitride and a perovskite oxide. These visible light-responsive photocatalysts with perovskite structure hold promise for photocatalytic water splitting, and there are some outlooks for the extension and promotion of the photocatalysts based on the ABO₃ perovskite structure.

Due to the extreme flexibility of the structure and the composition of perovskite materials, there are an unlimited number of multimetal composite perovskite structure semiconductors that may be efficient visible light-responsive photocatalysts. The discovery of perovskite structure semiconductors that have high carrier mobility and can respond to visible light is an upstream strategy that could lead to breakthroughs in photocatalytic efficiency. The use of high-throughput computing and machine learning can reveal the intrinsic connections between the structure, composition, and physical properties of the materials.[82,83] Machine learning may help to accelerate the discovery of promising perovskite structure semiconductors for efficient photocatalytic water splitting. To establish an effective machine learning route, it is of great significance to establish the correlation functions between the structural parameters (including bandgap, band-edge positions, carrier concentration, conductivity, lattice distortion, etc.) and the photocatalytic performance of perovskite structure photocatalysts. The elemental compositions of the perovskite semiconductors determine their structural parameters, and it is expected to establish a channel for analyzing the photocatalytic performance of perovskite semiconductors of various compositions through combining with the theoretically calculated structural parameters, so as to screen out efficient photocatalytic materials.

Attention has recently been drawn to the construction of multiple-coupled OWS systems. Z-scheme photocatalytic plates consisting of photocatalyst particles are promising and innovative systems that have the potential to be scaled up in the field of OWS. Even so, the charge transfer kinetics for the Z-scheme system still leaves much to be explored deeply, including the detection of the electron transfer direction, the matching of the amount of electron transfer in the medium, and the optimal regulation of the photocatalyst composition ratio. In addition, not only the electrical properties of the
electron transfer media have to be investigated, but also their working functions and the control of their interface with the coupling semiconductor.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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