Strain Adjustment Realizes the Photocatalytic Overall Water Splitting on Tetragonal Zircon BiVO$_4$

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Overall water splitting to generate $\text{H}_2$ and $\text{O}_2$ is vital in solving energy problem. It is still a great challenge to seek efficient visible light photocatalyst to realize overall water splitting. In this work, the tetragonal zircon BiVO$_4$ is prepared by epitaxial growth on FTO substrate and its overall water splitting reaction is studied. Under the influence of epitaxial strain, the conduction band position shifts negatively and beyond $\text{H}^+/\text{H}_2$ reduction potential (0 V vs NHE), which enables it to possess the photocatalytic hydrogen evolution activity. After loading cocatalysts, the overall water splitting ($\lambda > 400$ nm) is realized ($\text{H}_2$: $\approx 65.7$ μmol·g$^{-1}$·h$^{-1}$, $\text{O}_2$: $\approx 32.6$ μmol·g$^{-1}$·h$^{-1}$), and the value of solar hydrogen conversion efficiency is 0.012%. The single-particle photoluminescence (PL) spectra and PL decay kinetics tests demonstrate the cocatalysts are beneficial to the separation and transfer of carriers. The new strategy of adjusting the band structure by strain is provided.

1. Introduction

In recent years, solar-driven water splitting to produce clean hydrogen has been considered as a promising approach to solve energy and environmental issues. Since Honda and Fujishima used TiO$_2$ to produce hydrogen and oxygen in 1972, photocatalytic water splitting has been one of the research hotspots.[1–9] Recently, Domen’s group used Al-doped SrTiO$_3$ to achieve a 96% external quantum efficiency of ultraviolet light from 350 to 360 nm,[10] which led the development of photocatalysis, and ignited the hope of light-driven water splitting. Although recent research on overall water splitting makes great progress,[10–12] developing the efficient photocatalysts which have suitable band structure, visible light response, and high charge separation efficiency is still a great challenge.

BiVO$_4$ as a chemically stable and visible-light responsive photocatalyst have drawn much attention. It has three main crystal structures containing monoclinic scheelite (s-m), tetragonal zircon (z-t), and tetragonal scheelite (s-t). Although the z-t BiVO$_4$ shows lower oxygen evolution activity than s-m BiVO$_4$, it does not prevent scientists from further exploring it. Our group has previously reported that z-t BiVO$_4$ can be used as photocathode to construct a bias-free PEC cell.[13,14] In addition, no matter which crystal phase of BiVO$_4$, as the conduction band minimum (CBM) is more positive than $\text{H}^+/\text{H}_2$ reduction potential, it has basic limitation of releasing $\text{H}_2$. The current research on BiVO$_4$ overall water splitting is mainly focused on constructing Z-scheme systems and phase transition-induced band edge engineering.[15,16] However, overall water splitting on pure z-t BiVO$_4$ still has not come true.

As we all know, the different lattice parameters of substrate and epitaxial layer may cause lattice mismatch, which leads to epitaxial growth with strain accumulation. The mismatch strain at interface will adjust its physical and chemical properties.[17–21] Zheng et al. have reported the textured substrate accumulating strain locally greatly enhances the light absorption and surface reaction of the BiVO$_4$ photoanode, reducing the total amount of light absorber required.[22] Minseok Choi theoretically reported the tensile strain makes the CBM energy in s-m BiVO$_4$ very close to $\text{H}^+/\text{H}_2$ level, while the CBM energy in z-t BiVO$_4$ shifts upward or even higher than this level.[23] However, there is still lack of general understanding of how epitaxial strain experimentally affects photocatalytic property of BiVO$_4$. Here, we take z-t BiVO$_4$ as the research object, using unstrained BiVO$_4$ powder and epitaxially strained BiVO$_4$ to study the effect of strain on the band structure and overall water splitting.

2. Results and Discussion

2.1. Fabrication and Characterization of Tetragonal BiVO$_4$

When BiVO$_4$ grows on another crystalline material, due to the different lattice parameters of two materials, strain will generate...
Figure 1. a) The band structure change induced by tensile strain on tetragonal BiVO$_4$ based on DFT. b) Detailed preparation process for BiVO$_4$-FTO film and crystal structure of tetragonal BiVO$_4$. c) XRD patterns of BiVO$_4$-FTO film and BiVO$_4$ powder. d) UV–vis DRS spectrum and e) the energy level difference between the $E_{\text{VB}}$ and Fermi level of BiVO$_4$-FTO sample. f) The band structure diagram of BiVO$_4$-FTO sample and BiVO$_4$ powder.

during the growth process. Specifically, when epitaxially growing on a substrate with larger lattice parameters, the BiVO$_4$ unit cell ($a = b = 0.730$ nm) will suffer in-plane tensile strain. The greater the lattice mismatch is, the larger the in-plane tensile strain, leading to the change of each BiVO$_4$ unit cell’s lattice parameters ($a = b$). Based on the density functional theory (DFT), the influence of tensile strain on energy band structure of tetragonal BiVO$_4$ is calculated. As shown in Figure 1a, under tensile strain, the energy band of BiVO$_4$ undergoes a certain degree of negative shift, in which the valence band (VB) moves to a small extent (inset of Figure 1a), and the conduction band (CB) moves significantly. So here we can envisage that under the effect of strain, the CB position of BiVO$_4$ can be optimized, and stride the H$^+$/H$_2$ reduction potential. Combining with its intrinsic oxygen evolution activity, the z-t BiVO$_4$ has promise to achieve photocatalytic overall water splitting. Accordingly, the FTO glass consisting of tetragonal fluorine-doped SnO$_2$ ($a = b = 0.476$ nm) is chosen as a substrate (Figure S1, Supporting Information) which could subject the tetragonal BiVO$_4$ film to the mismatch strain. The uniform BiVO$_4$ film is epitaxially growing on FTO substrate, and the detailed scheme of preparing process is depicted in Figure 1b. As shown, the tetragonal zircon BiVO$_4$ unit cell consists of a regular VO$_4$ tetrahedron (V–O bond length is 1.7062 Å) and a slightly twisted BiO$_6$ dodecahedron (one Bi–O bond length is 2.4142 Å and another is 2.5489 Å, respectively). To make convenience for characterization and testing, the BiVO$_4$ film grown on FTO
substrate is scraped for collection, which is denoted as BiVO₄-FTO sample. In contrast, the naturally nucleated BiVO₄ is prepared by coprecipitation method, hereinafter referred to BiVO₄ powder. As shown in Figure 1c, all diffraction peaks are consistent with z-t BiVO₄ (space group I41/amd, JCPDS: 14-133). Due to the same symmetry with the [101] direction of SnO₂, the epitaxially grown BiVO₄ shows strong crystallinity along the [101] orientation. The Raman and X-ray photoelectron spectroscopy (XPS) spectra further show the z-t BiVO₄ is synthesized (Figures S2 and S3, Supporting Information). According to the diffuse reflectance spectrum (DRS) of BiVO₄ (Figure 1d), the bandgap of BiVO₄-FTO is 2.86 eV. As seen from the ultraviolet photoelectron spectroscopy (UPS) spectra (Figure 1e and Figure S4a, Supporting Information), it can be determined that the E₉ and E₈ of BiVO₄-FTO sample are 2.47 and −0.39 eV, respectively. The E₉ is more negative than H⁺ to H₂ reduction potential (0 V vs NHE), and E₈ is more positive than H₂O to O₂ oxidation potential (1.23 V vs NHE), indicating the BiVO₄-FTO sample has the possibility of photocatalytic overall water splitting. The specific calculation process and band position analysis of BiVO₄ powder were depicted in the DRS and UPS spectra in Figure S4 (Supporting Information). Further, as shown in Figure 1f, there is a great difference between BiVO₄-FTO sample and BiVO₄ powder at the edge of energy bands. The band arrangement of BiVO₄ explains why the BiVO₄-FTO sample and BiVO₄ powder exhibit significantly different photocatalytic activities.

X-ray diffraction method was used to prove the existence of residual strain. The residual stress can be calculated from the strain which is measured by XRD diffraction. According to the material parameters (Table S1, Supporting Information), the residual stress is 390.29 ± 47.44 MPa, as shown in Supporting Information 2. Although scratching will cause some stress loss, the increase in cell parameters caused by strain is irreversible, which also can be proved by XRD refinement. Through XRD data refinement (Figure 2a-c), all the diffraction peaks of BiVO₄-FTO film and BiVO₄-FTO sample as well as BiVO₄ powder are consistent with the Bragg position (represented by the blue-green vertical line) of tetragonal zircon BiVO₄ with space group I41/amd (PDF: 14-133). It is worth noting that compared with the naturally nucleated BiVO₄ powder, the main peak of BiVO₄-FTO sample shifts toward lower angle (Figure 2d), which corresponds to the larger lattice parameters after tensile strain. The detailed crystal structures and unit cell parameters are further established (see Table S2, Supporting Information). As known, when BiVO₄ grows on the substrate with larger lattice parameters, it will suffer in-plane tensile strain and lattice parameters will change. Compared with BiVO₄ powder (a = b = 7.3007 Å), the BiVO₄-FTO film and BiVO₄-FTO sample collected from the substrate have the same in-plane lattice parameters (a = b = 7.3044 ± 7.3047 Å), which is larger than that of naturally nucleated BiVO₄ powder.

Figure 3 depicts cross-sectional FIB-TEM images of BiVO₄-FTO. As shown in Figure 3a, continuous BiVO₄ film grows on
the surface of FTO, which can completely bridge the gap at the interface. Figure 3b is the enlarged view of selected area of Figure 3a. The yellow dotted line is the interface between FTO substrate and BiVO₄ growth layer, and the contact interface is the region where a large number of lattice distortion occur. Therefore, the FIB-HRTEM image in Figure 3c reveals the defect details of the selected white area in Figure 3b. The interplanar spacings of 0.367 and 0.267 nm are ascribed to (200) plane of BiVO₄ and (101) plane of SnO₂. Due to the incomplete matching of the interplanar spacing between SnO₂ and BiVO₄ in the [101] direction, BiVO₄ bears strain from interface and shows deformation near the contact interface between them. The BiVO₄ sample growing on FTO substrate was carefully scraped off and analyzed by HRTEM. After fast Fourier transform, it is found that there are still lattice distortions in the region near the FTO substrate (white square in the inset), which is consistent with the refined XRD results, indicating the interface strain exist between substrate and film during epitaxial growth progress (Figure 3d).

The scanning electron microscope (SEM) image of BiVO₄-FTO film nanocrystals is shown in Figure 4a which presents the uniformly distributed cuboid with the width about 810 nm and thickness about 420 nm. More detailed structure of collected BiVO₄-FTO sample was further studied by HRTEM (Figure 4b). The crystalline lattice spacing of d = 0.489 and 0.367 nm can be attributed to the (101) and (200) planes of tetragonal BiVO₄, and the included angle of 48.5° is consistent with the theoretical value of the angle between (101) and (200) planes. In contrast, according to the XRD (Figure 1c) and SEM (Figure S5, Supporting Information), no obvious orientation of the naturally nucleated BiVO₄ powder was found. Due to different crystal planes have different redox ability, the inherent charge separation characteristics of BiVO₄-FTO photocatalyst were studied by photochemical deposition method. Through SEM imaging, the different migration of photogenerated carriers can be proven. The detailed results are shown in Figure 4c,d. Metals (Ag, Rh) are selectively deposited on the (101) planes, where the photogenerated electrons accumulate and reduce the metal ions (Ag⁺, Rh³⁺) to metals. Due to the metal (Ag, Rh) particles are small in Figure 4c,d, detailed SEM images of BiVO₄-FTO photocatalyst loaded with Ag or Rh are provided in Figure S6 (Supporting Information). Similarly, metal oxides (MnOₓ, PbO₂) are selectively deposited on the (200) planes under light irradiation where photogenerated holes accumulate and oxidize metal ions (Mn²⁺, Pb²⁺) to metal oxides. The relative position of energy levels of different crystal planes can be evaluated by the density functional theory (DFT) calculation.[31–33] According to the results in Figure 4e, compared with (200) crystal plane, the (101) crystal plane of BiVO₄ shows the higher CBM and valence band maximum (VBM) position, and the VBM of (101) crystal plane is closer to the CBM of (200) crystal plane. This relative energy level position has a positive effect on the formation Z-type arrangement. Reasonably, the SEM results of photodeposition can be further explained by the electron flow pattern in Figure 4f, where (101) planes tend to be electron enriched and (200) planes tend to be hole enriched.
2.2. Photocatalytic Activity of BiVO₄

The light absorption of FTO was tested, which appears at about 350 nm (Figure S8, Supporting Information). To exclude its contribution to H₂ production, the photocatalytic activities of tetragonal BiVO₄ with and without epitaxial strain were tested under visible light irradiation (λ > 400 nm). As indicated in Figure S9 (Supporting Information), bare BiVO₄ powder cannot release H₂, while bare BiVO₄-FTO sample releases small amount of H₂. Therefore, to ensure the reaction gas release smoothly, the dual cocatalysts Rh/Cr₂O₃ and MnOₓ[10,34] were loaded by photodeposition method. The loading of cocatalysts is proved by SEM, XPS, and EDS analysis (Figures S10–S12, Supporting Information). SEM images (Figure S10, Supporting Information) demonstrate the deposition of cocatalysts on specific crystal facets, which is consistent with SEM observations (Figure 4). Moreover, XPS and EDS results (Figures S11 and S12, Supporting Information) further confirm that the cocatalysts are successfully deposited on the surface of BiVO₄. The LSV analysis of tetragonal BiVO₄ before and after loading cocatalysts is shown in Figure S13 (Supporting Information). After loading dual cocatalysts, BiVO₄-Rh/Cr₂O₃/MnOₓ yields higher photocurrent than pure BiVO₄ and single cocatalyst BiVO₄-Rh/Cr₂O₃, which proves that more photogenerated carriers accumulate on the surface of BiVO₄-Rh/Cr₂O₃/MnOₓ to participate in surface reactions. The half-reaction of hydrogen evolution (HER) and oxygen evolution (OER) in the presence of sacrificial agents have been operated (Figure S14, Supporting Information). Compared with BiVO₄ powder, BiVO₄-FTO sample shows higher photocatalytic HER and OER activity, which is caused by improved reduction ability and carriers' separation efficiency. Further, because s-m phase BiVO₄ is usually used for photocatalytic water oxidation among the BiVO₄ polymorphs, the photocatalytic property of s-m BiVO₄ is also studied for comparison (Figure S15, Supporting Information).
Information). Although s-m BiVO₄ has higher oxygen evolution activity in the presence of sacrificial agent, it cannot evolve H₂ due to insufficient reduction ability. In addition, s-m BiVO₄ cannot epitaxial grow on FTO substrate because of the different crystal structure and too large lattice mismatch between s-m BiVO₄ and SnO₂. As shown in Figure 5a, under visible light irradiation (λ > 400 nm), the simultaneous release of hydrogen and oxygen is achieved on BiVO₄-FTO sample with cocatalysts, and the solar hydrogen conversion efficiency (STH) is 0.012%. Other single-step overall water splitting photocatalysts are shown in Table S3 (Supporting Information). It can be clearly seen from Figure 5b that the water splitting activity of the photocatalyst gradually decreases during the 12 h irradiation period. The origin of this phenomenon was further studied. The XRD patterns before and after the reaction didn’t change significantly, indicating the BiVO₄-FTO sample still retains the crystal structure (Figure S16, Supporting Information). However, the ICP-OES measurement prove that vanadium ions are dissolved as the photocatalytic reaction proceeds (Figure S17, Supporting Information), indicating the decrease in stability is mainly due to the photoinduced dissolution of V⁵⁺ ions, leading to the severe photocorrosion, which is consistent with the previously report.¹³⁵,¹³⁶ The stability of BiVO₄ has been a hot and challenging issue for a long time, further exploration of strategies to improve the photostability of tetragonal BiVO₄ is the focus of our follow-up research. The wavelength-dependent apparent quantum efficiency (AQE) of BiVO₄-FTO sample is depicted in Figure 5c. The AQE values match well with the diffuse reflectance spectrum, demonstrating that the overall water splitting is caused by the absorption of incident light. To determine the oxygen source of the reaction product, gas chromatography-mass spectrometer (GC-MS) test was applied to detect ¹⁶O₂ and ¹⁸O₂. As shown in Figure 5d, the retention time of ¹⁶O₂ and ¹⁸O₂ from H₂¹⁶O are earlier than that of ¹⁸O₂ from H₂¹⁸O. GC-MS analysis (shown in the inset of Figure 5d) further shows that the main product with H₂¹⁶O as the oxygen source is ¹⁶O₂ (m/z = 32), while the main product with H₂¹⁸O as the oxygen source is ¹⁸O₂ (m/z = 36). Therefore, it is clear that the photocatalytic reaction product originates from the H₂O splitting. To verify the effect of the crystal planes on photocatalytic hydrogen production, strong alkali was used to treat BiVO₄-FTO film. It can be seen from Figure S18 (Supporting Information) that the etched BiVO₄-FTO retain the crystal structure and chemical composition basically but the original smooth crystal planes are corroded (Figure S19, Supporting Information). The etched sample are collected for photocatalytic hydrogen test and the activity is greatly reduced (Figure S20, Supporting Information), revealing that crystal planes are beneficial to the separation of carriers. Moreover, the tetragonal BiVO₄-FTO film with different redox crystal facets exposure ratio are provided in Figure S21 (Supporting Information), which are obtained by adjusting the pH of precursor. By comparing the water splitting activity in Figure S22 (Supporting Information), it is found that under the same loading of cocatalysts, the activity of BiVO₄-FTO (pH = 2) is higher than those of BiVO₄-FTO (pH = 1.6) and
BiVO₄-FTO (pH = 3), indicating that the properly exposed redox crystal facets are beneficial to the photocatalytic water splitting reaction. Surface photovoltage (SPV) measurements (Figure S23, Supporting Information) indicate that BiVO₄-FTO sample has higher photovoltage than BiVO₄ powder, confirming the effective separation and transportation of photogenerated carriers in BiVO₄-FTO sample. In addition, BiVO₄-FTO film with different thicknesses can be obtained by adjusting the hydrothermal time (Figures S24 and S25, Supporting Information). It can be seen that as the synthesis time increases from 3 to 24 h, the hydrogen evolution rate gradually decreases (Figure S26a, Supporting Information), which is associated with the reduction of lattice strain. In addition, after further loading the cocatalysts, the gas evolution rates are significantly increased (Figure S26b, Supporting Information), and the best gas release rate is achieved at the synthesis time of 12 h. Furthermore, to prevent the presence of incompletely consumed organic reactants in the product from affecting the source of hydrogen, infrared analysis is carried out, and no obvious organic peaks of reactant is detected (Figure S27a, Supporting Information). Moreover, it can be seen from the TG analysis (Figure S27b, Supporting Information) that from ambient temperature to 600 °C, the BiVO₄-FTO sample shows basically no change when heated in air atmosphere. The slight weight loss of BiVO₄ powder can be attributed to the evaporation of adsorbed water on the surface. The above results indicate that the tetragonal BiVO₄ has good thermodynamic stability.

Here, the single-particle photoluminescence (PL) spectra and PL decay kinetics tests were used to explore the role of cocatalysts in photocatalytic overall water splitting reaction. Compared with the ordinary photoluminescence spectra, the single particle photoluminescence has less noise and interference from other molecules or particles, so the role of cocatalyst can be studied from the perspective of single particle. PL images of single BiVO₄-FTO sample and BiVO₄-FTO sample with cocatalysts are

Figure 6. PL images of single a) BiVO₄-FTO sample and b) BiVO₄-FTO sample with cocatalysts. c) PL intensities and d) PL decay spectra of single BiVO₄-FTO sample with and without cocatalysts. e) Schematic diagram of photocatalytic overall water splitting on tetragonal zircon BiVO₄ loaded with Rh/Cr₂O₃/MnOₓ cocatalysts.
depicted in Figure 6a,b. Compared with Figure 6a, the blue area in the center of Figure 6b represents the shorter average lifetime, which means that after loading cocatalysts, the photogenerated carriers are quickly captured by the cocatalysts and participate in the water splitting reaction. As shown in Figure 6c, the significant decreased intensity of PL peak is observed, indicating the reduced recombination of photogenerated carriers on BiVO$_4$-FTO sample with cocatalysts. Further, according to the three-exponential fitting, it is determined that the lifetime of BiVO$_4$-FTO sample with cocatalysts is shorter than that of BiVO$_4$-FTO sample, demonstrating that the carriers are separated and transferred more quickly after loading cocatalysts. The schematic diagram of photocatalytic overall water splitting on tetragonal zircon BiVO$_4$ loaded with cocatalysts is shown in Figure 6e. Under the visible-light excitation, photogenerated electrons and holes are generated at the CBM and VBM of tetragonal BiVO$_4$, which then migrate to the H$_2$- and O$_2$-evolution cocatalyst Rh/Cr$_2$O$_3$ and MnO$_2$ to participate the surface redox reaction, respectively. This spatially separated structure is beneficial to inhibit the recombination of photogenerated carriers and promote photocatalytic overall water splitting reaction.

3. Conclusion

In summary, tetragonal BiVO$_4$ on FTO substrate was prepared and overall water splitting under visible light irradiation was evaluated. The BiVO$_4$ grown on substrate has better catalytic performance than the naturally nucleated BiVO$_4$. By introducing strain, the energy band position could be effectively adjusted, so that conduction band position shifts up and exceeds the hydrogen evolution potential. The common exposure of oxidizing crystal planes and reducing crystal planes increase the separation efficiency of photogenerated carriers and promote photocatalytic reaction. Considering the s-m BiVO$_4$ has better light absorption and oxygen generation kinetics, the works on monoclinic BiVO$_4$ and other substrate are in procedure. The new initiative is put forward to adjust the band structure of photocatalyst for overall water splitting under visible light irradiation.

4. Experimental Section

Preparation of BiVO$_4$-FTO Film

All chemicals are of analytical grade and do not require further purification when used. The BiVO$_4$-FTO film was grown by hydrothermal method. Typically, the precursor Bi(NO$_3$)$_2$·5H$_2$O (1 mmol) was dissolved in HNO$_3$ solution (20 mL, 2 mol), and C$_{10}$H$_{14}$N$_2$Na$_2$O$_4$ (1 mmol) was added and stirred for 30 min to obtain solution A. At the same time, NH$_4$VO$_3$ (1 mmol) was dissolved in NaOH solution (40 mL, 1 mol), and then C$_{10}$H$_{14}$N$_2$Na$_2$O$_4$ (1 mmol) was added and stirred for 30 min to obtain solution B. Then A solution was slowly poured into the B solution and the solution became a yellow solution. After adjusting the pH to 2, continue to stir the solution for another 30 min and transfer to 100 mL Teflon-lined autoclave. The FTO glass was sonicated sequentially in acetone, ethanol, and isopropanol for 30 min. Then, put the cleaned FTO glass (3 cm × 4 cm) into 100 mL Teflon-lined autoclave at an angle, with the conductive surface facing down. After sealing the autoclave, the hydrothermal reaction was carried out at 160 °C for 12 h. The autoclave was naturally cooled to room temperature, and then the FTO glass was taken out, rinsed with deionized water several times, and dried at room temperature. The obtained product was called BiVO$_4$-FTO film. To make the test convenience, the scraped sample was called BiVO$_4$-FTO sample.

Surface Selective Photodeposition

To perform photooxidation deposition, the BiVO$_4$-FTO film was immersed in an aqueous solution containing 0.2 × 10$^{-3}$ m KIO$_3$ (100 mL), 0.1 × 10$^{-3}$ m Mn(NO$_3$)$_2$ for MnO$_x$ deposition, and 0.1 × 10$^{-3}$ m Pb(NO$_3$)$_2$ for PbO$_2$ deposition, respectively. The reaction system was irradiated under a 300 W Xe lamp (full arc) for 10 min. After irradiation, the BiVO$_4$-FTO film was washed with deionized water and ethanol and dried. For photo-reduction deposition, the steps were almost the same, except that the deposition aqueous solution was composed of 10% (volume ratio) methanol, 0.1 × 10$^{-3}$ m AgNO$_3$ for Ag deposition and 2 mg mL$^{-1}$ RhCl$_3$·3H$_2$O for Rh deposition, respectively.

Preparation of BiVO$_4$ Powder

BiVO$_4$ powder was synthesized by coprecipitation method. Typically, Bi(NO$_3$)$_2$·3H$_2$O (2 mmol) and NH$_4$VO$_3$ (2 mmol) were simultaneously dissolved in 60 mL of deionized water and stirred vigorously for 2 h. The reaction product was filtered, washed with deionized water and ethanol, and dried in an oven at 100 °C for 5 h. The obtained product was called BiVO$_4$ powder.

Computational Details

All the calculations were performed by using the Vienna Ab Initio Simulation Package (VASP). The ion–electron interactions were described by projector augmented wave (PAW) method. The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerh (PBE) with a cutoff energy of 500 eV for exchange–correlation interactions were adopted. A Monkhorst–Pack 7 × 7 × 1 k-point grid was adopted for all the calculations. The convergence criteria for the force and energy were set to be 0.01 eV Å$^{-1}$ and 10$^{-6}$ eV with a vacuum space larger than 20 Å in the z-direction to avoid interactions between periodic units during the structure relaxation. The magnitude of strain is described by $\epsilon = a_0/a$, where $a_0$ and $a$ denote the lattice parameters of the unstrained and strained systems, respectively. As a result, 10% in-plane tensile strain is applied to (101) plane of BiVO$_4$.

Characterization

XRD patterns were conducted on a Bruker AXS D8 diffractometer equipped with Cu K$_\alpha$ radiation to reveal the crystal structure. Morphologies were investigated by SEM (Hitachi S-4800) equipped with an EDS. The UV–vis DRS analyses were recorded by Shimadzu UV-2550 spectrophotometer using BaSO$_4$ as reflectance standard to explore the optical absorption. The TEM and HRTEM tests were performed with a JEOl JEM-2100F microscope to analyze the nanostructure and composition of the as-prepared BiVO$_4$ photocatalyst. The cross-sectional FIB-HRTEM samples were analyzed by focused ion beam (FIB) technology. UPS measurements of the as-prepared samples were performed with He I (21.2 eV) as monochromatic light source and a total instrumental energy resolution of 100 meV. XPS measurements were carried out on a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al-K$_\alpha$ source to explore the element composition and valence states on the surface, and the binding energies were calibrated by the C 1s peak (284.8 eV). Raman spectra were measured on a LabRAM HR800 with laser excitation of 532 nm. The reaction liquid used for gas measurement was analyzed by ICP-OES/AES: Varian (720-ES). The amounts of H$_2$ and O$_2$ evolution were analyzed using gas chromatography (GC-7920) equipped with a thermal conductivity detector (As carrier...
The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Typically, the area of the BiVO₄-FTO film is 12 cm², on which the mass is estimated to be ≈5 mg. Generally, 10 mg photocatalyst was immersed in 100 mL of reaction solution. The photocatalytic HER, OER, and overall water splitting reaction were carried out in 0.02 × 10⁻³ M H₂O₂, 0.02 M AgNO₃ and pure water, respectively. The theoretical loading amounts were 2, 2, and 0.5 wt% for Rh, Cr, and MnOₓ. For the overall water splitting reaction, after the catalyst was ultrasonically dissolved, the cocatalyst precursor was sequentially added to the reaction solution to carry out the photodeposition reaction. First, a specific amount of RhCl₃·3H₂O solution (2 mg mL⁻¹) was added to the reaction system, and irradiated for 10 min. Subsequently, the K₂CrO₄ (2 mg mL⁻¹) and Mn(NO₃)₂·6H₂O (0.1 × 10⁻³ M) solution were added to the suspension and irradiated for another 5 min, respectively. The system was evacuated for 30 min to ensure complete removal of air, and then illuminated from the top surface with a 300 W Xe lamp (PLS-SXE300D, Beijing PerfectLight Technology Co., Ltd.) equipped with a 400 nm cut-off filter (λ > 400 nm). A cooling water stream was used to maintain the reaction suspension at 288 K. The separated gas was analyzed by gas chromatography (GC-7290, TCD with Ar as a carrier gas). The photocatalytic stability test was performed every 4 h as a cycle. After each independent cycle, the photocatalyst was recycled by centrifugation and dispersed in new solution. The wavelength dependence of the AQE was tested under the same photocatalytic reaction conditions, through the 365, 420, 450, 500, 530, and 700 nm bandpass filters and the masked area of 1 cm². The photon flux of the incident light was determined using a PL-MW2000 spectrophotometer (PerfectLight, China). The AQE was calculated from the ratio of the number of electrons reacted to the number of incident photons during the water splitting process. The calculation formula is

\[ \text{AQE} = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\% \]  

(1)

The STH efficiency was measured under simulated sunlight (AM 1.5G, 1 cm² irradiation area). The calculation formula is

\[ \text{STH} = \frac{\text{output energy as H}_2}{\text{energy of incident solar light}} \]  

(2)

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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charge separation, overall water splitting, strain engineering, tetragonal zircon BiVO₄, visible light photocatalyst

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