Easy Synthesis of BiVO$_4$ for Photocatalytic Overall Water Splitting
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ABSTRACT: Developing a photocatalyst system to generate hydrogen from water is a topic of great interest for fundamental and practical importance. In this study, we develop a new Z-scheme photocatalytic system for overall water splitting that consists of Rh/$K_4Nb_6O_{17}$ for H$_2$ evolution, Pt/BiVO$_4$ for O$_2$ evolution, and $I^-/IO_3^-$ for an electron mediator under UV light irradiation. The oxygen evolution photocatalyst BiVO$_4$ was prepared by the microwave-assisted hydrothermal method. The method is fast and simple, as compared to conventional hydrothermal synthesis. The catalysts were characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and UV–visible spectroscopy. The photocatalytic water splitting is investigated in (i) aqueous AgNO$_3$ as sacrificial electron scavengers and (ii) a Z-scheme photocatalytic water splitting system. The BiVO$_4$ photocatalysts prepared by the microwave-assisted hydrothermal method not only showed a very high oxygen evolution rate (2622 μmol g$^{-1}$ h$^{-1}$) of water splitting reaction in an aqueous AgNO$_3$ solution but also achieved a high H$_2$ evolution rate (340 μmol g$^{-1}$ h$^{-1}$) and O$_2$ evolution rate (172 μmol g$^{-1}$ h$^{-1}$) in a Z-scheme overall water splitting system.

1. INTRODUCTION

Renewable hydrogen, which is an environmentally clean chemical fuel with high energy density, is attracting considerable attention for alternative nonfossil fuel energy. Electrochemical water splitting$^{1-4}$ and photocatalytic water splitting are two of the most widely studied topics in sustainable hydrogen production. Numerous studies have attempted to develop an active photocatalyst for splitting water into hydrogen and oxygen. In the water splitting reaction in standard conditions, it theoretically requires 237 kJ to decompose 1 mol of water into 1 mol of hydrogen and 1/2 mol of oxygen. To date, photocatalytic activity of water splitting on transition metal oxides such as NaTaO$_3$, K$_2$Nb$_2$O$_7$, and SrTiO$_3$ has been widely reported under UV light irradiation. Several excellent reviews on the developments of photocatalytic water splitting$^{9-11}$ are available.

The sun is the most important light source of our world, which contains about 8% UV radiation (200–400 nm) and about 50% visible radiation. A traditional photocatalyst with a large band gap mentioned above cannot be used under visible light irradiation. Therefore, the development of narrow band gap photocatalysts has attracted much attention.$^{12-14}$ However, a narrow band gap photocatalyst implies a lower (more positive) conduction band bottom or a higher (more negative) valance band potential, which lowers the driving force for the photocatalytic reduction and oxidation reactions. The electron–hole pairs generated by a narrow band gap semiconductor photocatalyst with sufficient redox potential for the water splitting reaction are very difficult to achieve.

The semiconductor-based Z-scheme system for overall water splitting has drawn much attention for the application of substantial hydrogen production.$^{15-17}$ The Z-scheme system is composed of a redox couple as an electron mediator and two different photocatalysts where photocatalytic H$_2$ evolution and O$_2$ evolution take place. Thus, the band edge potential of the photocatalysts only has to satisfy the stringent thermodynamics requirements to the half reactions for reduction and oxidation of water. As half reactions of the photocatalytic water splitting, the thermodynamic requirements are easier to satisfy.

In particular, a narrow band gap semiconductor BiVO$_4$ photocatalyst has high potential for photocatalytic applications due to its high stability and photocatalytic activity.$^{18,19}$ According to previous reports, BiVO$_4$ has three crystal systems of tetragonal scheelte (s-t), scheelite structure with monoclinic (s-m), and tetragonal zircon (z-t).$^{19,20}$ It is known that monoclinic BiVO$_4$ with a narrow band gap of 2.4 eV displays better photocatalytic performance than that of other crystal phases. The conduction band of the BiVO$_4$ photocatalyst is

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composed of mainly V 3d states with small contributions from O 2p and Bi 6p, and the valence band of the BiVO 4 consists of Bi 6s and O 2p. This characteristic band structure of monoclinic BiVO 4 originates from the distortion of Bi-O dodecahedra (BiO8).19 It is well known that crystallinity is an important factor to influence photocatalytic activity. Several routes were taken to prepare the BiVO4 photocatalyst via the wet chemical route, including the sol–gel synthesis, and hydrothermal synthesis.21-23 Morphology control of the BiVO4 photocatalyst, such as nanotubes,24 nanoribbons,25 nanorods,26 nanofibers, and nanoplates,27 is extensively studied and indicates that the morphology of the BiVO4 photocatalyst is a crucial factor for characteristic properties of BiVO4. Particularly, the hydrothermal method had been used to synthesize structure-controlled and highly crystalline nanomaterials. It was reported that a variety of BiVO4 nanoparticles with specific morphologies such as flowerlike structures, needle-like structures, and hierarchical sphere structures can be fabricated via the hydrothermal method.29,30 These reports demonstrated the photocatalytic activity of BiVO4 in reduction of commonly used organic dyes such as methylene blue (MB) and rhodamine B (RhB). BiVO4 also functions as O2 evolution photocatalysts in a Z-scheme system for water splitting. Furthermore, Kudo and co-workers15 reported that BiVO4 can be used as an O2 evolution photocatalyst for the Z-scheme overall water splitting system under visible light irradiation byRu-SrTiO3:Rh and tris(2,2′-bipyridine)cobalt(II)/tris(2,2′-bipyridine)cobalt(III) were used as the H2 evolution photocatalyst and electron redox shuttles.

In this paper, we present a simple method for preparing BiVO4 photocatalysts by the microwave-assisted hydrothermal method. During the hydrothermal reaction under microwave irradiation, heat can be generated from the inside of BiVO4 due to its dielectric properties, and a faster and more efficient synthesis process can be achieved.31 Different from the previously reported MW-assisted synthesis of BiVO4 by using ammonium metavanadate (NH4VO3) and bismuth nitrate (Bi(NO3)3) as precursors, vanadium pentoxide (V2O5) and bismuth oxide (Bi2O3), which were less toxic chemicals, were used as vanadium and bismuth precursors. Our results show that various shapes of high-crystallinity monoclinic scheelite BiVO4 photocatalysts can be synthesized in 1 h at a low temperature. The effects of preparation conditions on the particle structure of BiVO4 photocatalysts and the photocatalytic activity of photocatalytic O2 evolution in AgNO3 solution, NaIO3 solution, and a Z-scheme overall water splitting reaction using Rh/K4Nb6O17 for H2 evolution and the BiVO4 photocatalyst for O2 evolution were investigated.

2. EXPERIMENTAL SECTION

2.1. Synthesis of BiVO4 for O2 Evolution. Typically, the BiVO4 photocatalysts were synthesized as follows: Bi2O3 and V2O5 in a molar ratio of 1:1 were added to 30 mL of 0.5, 0.75, and 1 M HNO3 solution (denoted as S, M, and L, respectively, in the sample name) under vigorous stirring for 20 min at room temperature. The reagents were directly used as purchased without further pretreatment. Then, the starting materials were transferred to a 100 cm3 Teflon reaction vessel, and the microwave hydrothermal process was performed at the desired reaction temperature (T = 160 and 180 °C, denoted as 17 and 18 in the sample name) for 60 to 120 min (denoted as A and B in the end of sample name). The microwave-assisted hydrothermal synthesis was performed in a commercial microwave digestion system (StartD, Milestone). After microwave-assisted hydrothermal reactions, the product was washed by distilled H2O and dried at 60 °C overnight. The BiVO4 photocatalysts showed a vivid orange-yellow color. The preparation conditions of the BiVO4 photocatalysts are labeled as listed in Table 1.

For Pt-modified BiVO4 photocatalysts, an aqueous solution of H2PtCl6·6H2O (0.5 wt % Pt for complete loading) was added to a BiVO4 photocatalyst by impregnation. The Pt nanoparticles were simultaneously deposited on the surface of BiVO4 during the photocatalytic water splitting reaction, and no further treatment was required.

2.2. Synthesis of K4Nb6O17 with the Rh Cocatalyst for H2 Evolution. The prepared K4Nb6O17 catalysts were synthesized by a two-step solid-state reaction using K2CO3 and Nb2O5 with 99.99% purity (molar ratio, 2:1:3). The mixed precursor was first calcined in air at 1073 K for 5 h, cooled to room temperature, ground into fine powders, and then calcined in air at 1273 K for 5 h. The Rh/K4Nb6O17 catalyst was prepared by loading 1.5 wt % rhodium on the surface of K4Nb6O17 powders using aqueous Na4RhCl6 solution. After the impregnation process, the Rh/K4Nb6O17 catalyst was dried at 60 °C overnight. The Rh nanoparticles were formed by photoreduction of Na4RhCl6 during the photocatalytic reaction, and no further heat treatment was required. Characterization of the Rh/K4Nb6O17 catalyst was described in detail in our previous work.31

2.3. Characterization and Photocatalytic Reactions. The photocatalysts were characterized by using powder X-ray diffraction (XRD, Rigaku X-ray diffractometer, MAX-2500 V) analysis using Cu Kα radiation (λ = 1.54178 Å). The UV−vis
diffuse reflectance spectra of samples were measured by a Varian UV–vis spectrophotometer. The morphologies of BiVO₄ samples and the Pt nanoparticle cocatalyst were examined by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F) and transmission electron microscopy (TEM, JEOL JEM-2000FX).

The photocatalytic reaction was carried out in a reactor equipped with an inner irradiation quartz cell with a cooling water jacket under stirring at 43 °C. A 400 W medium-pressure halide lamp (Phillips HPA400, λ_{max} = 360 nm, irradiation of 150 mW/cm²) was mounted inside the quartz cell. The reactor contains a suspension of photocatalyst (0.2 g) in (i) 550 mL of 0.5 M AgNO₃ solution and (ii) 0.5 mM NaIO₃ for photocatalytic sacrificial water splitting for O₂ evolution. The photocatalytic Z-scheme overall water splitting was performed in 550 mL of 5 mM NaI solution containing 0.2 g of H₂ evolution and O₂ evolution photocatalysts. The gas product was analyzed by gas chromatography (China Gas Chromatography 9800) with a packed column (MS-5A, 3.5 m in length) and thermal conductivity detector.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Microwave-Assisted Synthesized BiVO₄ Photocatalyst. Figure 1 shows the

![Figure 1. XRD patterns of (a) MW-S17A, (b) MW-M17A, (c) MW-S17B, (d) MW-M17B, (e) MW-S18A, (f) MW-M18A, and (g) MW-L18A.](https://dx.doi.org/10.1021/acsomega.0c00699)

XRD patterns of BiVO₄ prepared by microwave-assisted hydrothermal synthesis. The preparation conditions are listed in Table 1. The diffraction peaks observed in all XRD patterns can be indexed as (110), (011), (121), (040), (200), (002), (141), (211), (150), (132), (240), (042), (202), (161), (251), (321), and (123) planes, which are identical to those of fully crystallized single-phase monoclinic BiVO₄ (JCPDS 14-0688, corresponding to the I2/a space group) without any impurity phases such as Bi₂O₃, V₂O₅, and tetragonal BiVO₄ (JCPDS 14-133). The presented diffraction peaks of high-index facets such as (002), (321), (132), and (121) indicate that the BiVO₄ samples are enclosed by multi-high-index crystal facets. The average crystallite sizes of the BiVO₄ samples prepared by the microwave-assisted hydrothermal method are determined from the Scherrer equation and listed in Table 1. Typically, the long hydrothermal reaction time (6–48 h) in the conventional hydrothermal process is required to synthesize single-phase monoclinic BiVO₄ nanocrystals. Our results show that high-crustallinity single-phase BiVO₄ was synthesized fast and efficiently and no post-treatment at a high temperature is required.

It is clear that the higher nitric acid concentration favors the formation of BiVO₄ with a larger crystallite size. Furthermore, it can be seen that the BiVO₄ samples show an increase in crystallinity with increasing synthesis time and temperature. The crystallite size of MW-S17A was 25.3 nm and became 27.9 nm when the synthesis time was prolonged from 60 to 120 min. The results also indicated that the crystallite size of BiVO₄ was changed more sensitively due to the increasing synthesis temperature than the synthesis time by comparing the crystallite size of MW-S17B (27.9 nm) with that of the MW-S18A catalyst (28.3 nm). Synthesis of BiVO₄ through the hydrothermal reaction in nitric solution was based on a series of dissolution–precipitation steps. V₂O₅ and Bi₂O₃ can be dissolved in acid solution and converted to soluble Bi³⁺ and VO₄⁻. In the dissolution–precipitation mechanism, the solute concentration strongly affects the nucleation and particle growth of BiVO₄. To obtain information on their size and morphology, the photocatalysts were subjected to SEM analysis. The field-emission SEM results show that, although all these BiVO₄ samples have a high crystalline structure, their morphology was significant different. Figure 2 depicts the SEM images of BiVO₄ photocatalysts prepared from different nitric concentrations, reaction times, and reaction temperatures.

When the nitric acid concentration was increased, the BiVO₄ photocatalysts (MW-x17A, x = S, M, L) formed irregular aggregates at low nitric acid concentration and transformed to ball-like aggregates without the addition of any direction agent. At a longer hydrothermal time, the ball-like aggregates with primary particles ranging from 200 to 400 nm seemed to collapse, forming an irregular structure assembled by rhombus-like BiVO₄ primary particles (MW-S17B), indicating the preferential orientation growth of (040) facets. This result is consistent with the XRD result of MW-S17B with the increase in the (040) diffraction peak (2θ = 30.5°). For the MW-x18A (x = S, M, L) samples, the increased primary particle size within the aggregates of BiVO₄ with increased nitric acid concentration is also seen. On the other hand, the same trends are not seen on the BiVO₄ photocatalysts prepared at a higher hydrothermal temperature (MW-x18A, x = S, M, L) where significant morphological changes of BiVO₄ aggregates were not observed with the increasing nitric concentration. The results also indicate that the morphology of BiVO₄ photocatalysts was changed sensitively with the increasing synthesis temperature. As shown in Figure 1a,b, while XRD will reveal a larger crystallite size of the MW-S18A samples, the morphologies of MW-S17A and MW-S18A samples were similar, where the BiVO₄ aggregates are composed of different polyhedral-shaped primary particles with sizes less than 1 μm. This suggests that
the dissolution-recrystallization cycles during the crystallization process were improved by the increasing hydrothermal temperature.

Figure 3 shows the UV–vis diffuse reflectance spectra of the BiVO₄ photocatalysts prepared by different synthesis parameters. These BiVO₄ photocatalysts had a vivid yellow color and gave similar spectra. As compared to MW-x17A (x = S, M, L) samples prepared at 170 °C, the absorption edges of MW-x18A (x = S, M, L) samples shifted to the short-wavelength region with increased synthesis temperature. On the other hand, no significant difference was found in the UV–vis spectra of these BiVO₄ photocatalysts with increasing nitric acid concentration.

Compared to all BiVO₄ samples in Figure 3, a small absorption shoulder at 550–650 nm can be observed in the UV–vis spectra of MW-S17B and MW-M17B samples. The absorption extension of the longer-wavelength region was ascribed to the formation of crystal defects during the crystal growth of monoclinic BiVO₄. Similar results were also obtained by Shi et al., where the surface oxygen vacancies induced defect states on BiVO₄ and lead to absorption bands in the long-wavelength region. Generally, the band gap of a semiconductor can be determined by the Tauc plot in which the absorption coefficient (α) as a function of photon energy (hv) obeys the power law

\[(hvα)^m = A(hv - E_g)\]  

where \(E_g\) is the optical band gap, and \(m\) is 1/2 and 2 for indirect and direct allowed transition, respectively. Since BiVO₄ is a direct band gap semiconductor, \(m = 2\) is used for these samples. The band gaps of BiVO₄ photocatalysts were about 2.4 eV, estimated from the UV–vis spectra (see Table 1). Apparently, the band gap values of the microwave-assisted hydrothermally synthesized BiVO₄ samples are similar to those of BiVO₄ materials reported in the literature that are prepared by the conventional hydrothermal method.

3.2. Photocatalytic Activity of Microwave-Assisted Hydrothermally Synthesized BiVO₄ Photocatalysts.

Figure 4 shows the time course of the sacrificial O₂ evolution of photocatalytic water splitting on the BiVO₄ photocatalysts in aqueous AgNO₃ solution where the silver ion acted as an efficient electron scavenger and inhibited the charge recombination during the water splitting reaction. The O₂ evolution data are summarized in Table 1, which shows that the microwave-assisted hydrothermally synthesized BiVO₄ samples exhibited a higher O₂ evolution rate than the conventionally synthesized samples. This is attributed to the improved crystallinity and enhanced light absorption of the microwave-assisted samples.
production stopped when the light was turned off, and the O₂ evolution rate was decreased with reaction time due to the consumption of the sacrificial agent and the deposition of Ag. As shown clearly in Figure 4, the formation rates of O₂ were increased in the following order: MW-L17A < MW-M17B < MW-M17A < MW-L18A < MW-S17A < MW-M18A < MW-S18A. The initial production rates of oxygen are listed in Table 1. As shown in the above results, MW-M18A and MW-S18A samples exhibited a much higher oxygen production rate as compared with the BiVO₄ photocatalysts synthesized at a lower temperature. Comparing the BiVO₄ photocatalysts synthesized in a lower nitric acid concentration, the MW-L17A and MW-L18A showed a much lower and rather low photocatalytic activity. It is known that the crystallite size, crystal structure, particle morphology, and exposed facets are important factors influencing the photocatalytic performance of BiVO₄ photocatalysts. The high crystallinity but low photocatalytic activities of MW-L17A and MW-L18A samples indicated that other factors might be the impact of the photocatalytic activity of BiVO₄. The low photocatalytic activities of MW-L17A and MW-M17B samples suggest that the photocatalytic activity of O₂ evolution was hindered by the aggregates of the ball-like morphology. Kudo et al. reported that photocatalytic reduction and oxidation occurred on different facets of BiVO₄, where reduction located more at the exposed (010) plane and the exposed (110) and (011) planes for an oxidation site. Therefore, the higher percentage of exposed (040) facets might be one reason for the low activity of MW-S18B. Our results also showed that the photocatalytic activity of microwave-assisted hydrothermally synthesized BiVO₄ photocatalysts is significantly affected by the synthesis conditions. The MW-S18A sample exhibited the highest oxygen evolution rate, with a rate of initial O₂ production of 2622 μmol g⁻¹ h⁻¹ under UV light irradiation. However, pure BiVO₄ usually exhibits limited photocatalytic activity without an efficient electron scavenger because of its electron–hole recombination rate. The photogenerated carrier recombination on semiconductor photocatalysts can be suppressed by loading cocatalysts such as Pt, Au, Ag, etc. It is reported that metallic nanoparticles can be selectively deposited on the electron-rich (010) facet on BiVO₄ by the photodeposition process. In the present study, the overall photocatalytic water splitting into H₂ and O₂ was carried out on two different photocatalysts and an iodate/iodide (IO₃⁻/I⁻) shuttle redox mediator. The time courses of the O₂ evolution of photocatalytic water splitting on the BiVO₄ and Pt-modified BiVO₄ photocatalysts in aqueous NaIO₃ (IO₃⁻ as the electron acceptor) solution are shown in Figure 5. It can be seen that the activity of water splitting was improved by loading platinum cocatalysts where the Pt/MW-S18A photocatalyst increased to 127 μmol h⁻¹ g⁻¹, which was approximately 1.6 times greater than MW-S18A. Figure 6 shows the TEM images of Pt/MW-S18A photocatalyst. According to Li et al., the reduced Pt cocatalysts were preferentially deposited on the electron-rich (010) facets of BiVO₄ by a photoreduction deposition method. As shown in Figure 6, it is clearly revealed that about 5–10 nm Pt nanoparticles were selectively formed on the surface of BiVO₄.

Figure 7 shows the H₂ and O₂ evolution time courses of the Z-scheme overall water splitting system performed on Rh/K₄Nb₆O₁₇–Pt/MW–BiVO₄ for 8 h. As shown in Figure 7, continuous H₂ and O₂ were produced in a theoretical stoichiometric ratio without noticeable deactivation. These results verified that the Z-scheme overall water splitting on Rh/K₄Nb₆O₁₇–Pt/MW–BiVO₄ possessed good photocatalytic activity and photostability. The Z-scheme water splitting is based on a two-step photoexcitation process. The photogenerated holes on Pt/MW–BiVO₄ oxidized water to O₂, while the electrons reduced the redox mediator IO₃⁻ to I⁻. Meanwhile, the photoexcited electrons on Rh/K₄Nb₆O₁₇ reduced water to H₂, and the photoexcited holes oxidized the redox mediator I⁻ to IO₃⁻. Hence, steady H₂ evolution by photocatalytic water reduction and O₂ evolution by photocatalytic oxidation can be achieved. The related reactions of Z-
respectively. It should be noted that the O2 evolution rate in the absence of the hydrogen evolution catalyst, O2 evolution was readily terminated by the competing reaction of I− oxidation, which can consume the photoexcited holes in the valance band of Rh/K4Nb6O17. On the other hand, O2 evolution proceeded with a higher electron separation on Rh/K4Nb6O17 and showed superior and stable hydrogen evolution. To our knowledge, this is the first Z-scheme overall water splitting on Rh/K4Nb6O17–Pt/BiVO4 photocatalysts. These results show that the microwave-assisted hydrothermal method has distinct advantages in the synthesis of high-crystallinity BiVO4 photocatalysts.

4. CONCLUSIONS

In this study, we demonstrated an easy method to prepare BiVO4 photocatalysts with high crystallinity by the microwave-assisted hydrothermal method. Our results showed that synthesis conditions of the microwave-assisted hydrothermal reaction may strongly affect the morphology and photocatalytic activities of BiVO4. The optimal condition of microwave-assisted hydrothermal synthesis for the best photocatalytic performance of BiVO4 was obtained at 180 °C in 0.5 M HNO3 for 1 h. The BiVO4 particles were of polyhedral shape with high crystallinity and did not form compact aggregates. The Rh/K4Nb6O17–Pt/BiVO4 Z-scheme system exhibited the highest photocatalytic activities with a H2 evolution rate of 340 μmol g−1 h−1 and O2 evolution rate of 172 μmol g−1 h−1 in 0.5 mM I−/IO3− solution under UV light irradiation.

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Notes

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■ REFERENCES

(1) Liu, Y.; Yong, X.; Liu, Z.; Chen, Z.; Kang, Z.; Lu, S. Unified Catalyst for Efficient and Stable Hydrogen Production by Both the Electrolysis of Water and the Hydrolysis of Ammonia Borane. Adv. Sustainable. 2019, 3, 1800161.
(2) Liu, Y.; Li, X.; Zhang, Q.; Li, W.; Xie, Y.; Liu, H.; Shang, L.; Liu, Z.; Chen, Z.; Gu, L.; Tang, Z.; Zhang, T.; Lu, S. A General Route to Prepare Low-Ruthenium-Content Bimetallic Electrocatalsysts for pH-Universal Hydrogen Evolution Reaction by Using Carbon Quantum Dots. Angew Chem Int., Ed. Engl. 2020, 59, 1718–1726.
(3) Li, W.; Liu, Y.; Wang, B.; Song, H.; Liu, Z.; Lu, S.; Yang, B. Kilogram-scale synthesis of carbon quantum dots for hydrogen evolution, sensing and bioimaging. Chin. Chem. Lett. 2019, 30, 2323–2327.
(4) Li, W.; Wei, Z.; Wang, B.; Liu, Y.; Song, H.; Tang, Z.; Yang, B.; Lu, S. Carbon quantum dots enhanced the activity for the hydrogen evolution reaction in ruthenium-based electrocatalsysts. Mater. Chem. Front. 2020, 4, 277–284.
(5) Kato, H.; Asakura, K.; Kudo, A. Highly Efficient water splitting into H2 and O2 over lanthanum-doped NaTaO3 photocatalysts with high crystallinity and surface nanostructure. J. Am. Chem. Soc. 2003, 125, 3082–3089.
(6) Lin, H. Y.; Lee, T. H.; Sie, C. Y. Photocatalytic hydrogen production with nickel oxide intercalated K4Nb6O17 under visible light irradiation. Int. J. Hydrogen Energy 2008, 33, 4055–4063.
(7) Yu, K.; Zhang, C.; Chang, Y.; Feng, Y.; Yang, Z.; Yang, T.; Lou, L.-L.; Liu, S. Novel three-dimensionally ordered macroporous SrTiO3 photocatalysts with remarkably enhanced hydrogen production performance. Appl. Catal., B 2017, 200, 514–520.
(8) Chen, W.; Liu, H.; Li, X.; Liu, S.; Gao, L.; Mao, L.; Fan, Z.; Shangguan, W.; Fang, W.; Liu, Y. Polymerizable complex synthesis of SrTiO₃:Cr(Ta) photocatalysts to improve photocatalytic water splitting activity under visible light. Appl. Catal., B 2016, 192, 145–151.

(9) Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering heterogeneous semiconductors for solar water splitting. J. Mater. Chem. A 2015, 3, 2485–2534.

(10) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chem. Soc. Rev. 2009, 38, 253–278.

(11) Wang, W.; Tadé, M. O.; Shao, Z. Research progress of perovskite materials in photocatalysis- and photovoltaics-related energy conversion and environmental treatment. Chem. Soc. Rev. 2015, 44, S371–S400.

(12) Hisatomi, T.; Kubota, J.; Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem. Soc. Rev. 2014, 43, 7520–7535.

(13) Suzuki, T. M.; Iwase, A.; Tanaka, H.; Sato, S.; Kudo, A.; Morikawa, T. Z-scheme water splitting under visible light irradiation over powdered metal-complex/semiconductor hybrid photocatalysts mediated by reduced graphene oxide. J. Mater. Chem. A 2015, 3, 13383–13390.

(14) Lin, H. Y.; Shih, C. Y. Efficient one-pot microwave-assisted hydrothermal synthesis of M (M=Cr, Ni, Cu, Nb) and nitrogen co-doped TiO2 for hydrogen production by photocatalytic water splitting. J. Mol. Catal. A: Chem. 2016, 411, 128–137.

(15) Sasaki, Y.; Kato, H.; Kudo, A. [Co(bpy)3]3+/2+ and [Co(phen)3]3+/2+ Electron Mediators for Overall Water Splitting under Sunlight Irradiation Using Z-Scheme Photocatalyst System. J. Am. Chem. Soc. 2013, 135, S541–S549.

(16) Maeda, K.; Lu, D.; Domen, K. Solar-Driven Z-scheme Water Splitting Using Modified BaZrO3-BaTaO2N Solid Solutions as Photocatalysts. ACS Catal. 2013, 3, 1026–1033.

(17) Wang, Q.; Li, Y.; Hisatomi, T.; Nakabayashi, M.; Shibata, N.; Kubota, J.; Domen, K. Z-scheme water splitting using particulate semiconductors immobilized onto metal layers for efficient electron relay. J. Catal. 2015, 328, 308–315.

(18) Yang, M.; He, H.; Liao, A.; Huang, J.; Tang, Y.; Wang, J.; Ke, G.; Dong, F.; Yang, L.; Bian, L.; Zhou, Y. Boosted Water Oxidation Activity and Kinetics on BiVO4 Photoanodes with Multihigh-Index Crystal Facets. Inorg. Chem. 2018, 57, 15280–15288.

(19) Kim, J. H.; Lee, J. S. BiVO₄-Based Heterostructured Photocatalysts for Solar Water Splitting: A Review. Energy Environ. Focus 2014, 3, 339–353.

(20) Iwase, A.; Kudo, A. Photoelectrochemical water splitting using visible-light-responsive BiVO₄ fine particles prepared in an aqueous acetic acid solution. J. Mater. Chem. 2010, 20, 7536–7542.

(21) Ren, L.; Jin, L.; Wang, J. B.; Yang, F.; Qu, M. Q.; Yu, Y. Template-free synthesis of BiVO₄ nanostructures: I. Nanotubes with hexagonal cross sections by oriented attachment and their photocatalytic activity for water splitting under visible light. Nano-technology 2009, 20, 115603.

(22) Chen, L.; Wang, J.; Meng, D.; Xing, Y.; Tian, X.; Yu, X.; Xu, K.; Wu, X. Effects of citric acid and urea on the structural and morphological characteristics of BiVO₄ synthesized by the sol–gel combustion method. J. Sol-Gel Sci. Technol. 2015, 76, 562–571.

(23) Gabadiya, T. S.; Selvarasu, P.; Murugan, A. V. Tetragonal to Monoclinic Crystalline Phases Change of BiVO₄ via Microwave-Hydrothermal Reaction: In Correlation with Visible-Light-Driven Photocatalytic Performance. Inorg. Chem. 2019, 58, 5096–5110.

(24) Lv, C.; Sun, J.; Chen, G.; Zhou, Y.; Li, D.; Wang, Z.; Zhao, B. Organic salt induced electrosprining gradient efficiency for enhanced Photocatalytic BiVO4 nanotubes with promoted photocatalytic performance. Appl. Catal., B 2017, 208, 14–21.

(25) Wang, F.; Shao, M.; Cheng, L.; Hua, J.; Wei, X. The synthesis of monolonic bismuth vanadate nanoribbons and studies of photocatalytic, photoresponse, and photocatalytic properties. Mater. Res. Bull. 2009, 44, 1687–1691.

(26) Hou, L.; Yang, L.; Li, J.; Tan, J.; Yuan, C. Efficient Sunlight-Induced Methylene Blue Removal over One-Dimensional Mesoporous Monolonic BiVO4 Nanorods. J. Anal. Methods Chem. 2012, 345247.

(27) Yu, M.; Shang, C.; Ma, G.; Meng, Q.; Chen, Z.; Jin, M.; Shui, L.; Zhang, Y.; Zhang, Z.; Yuan, M.; Wang, X.; Zhou, G. Synthesis and characterization of mesoporous BiVO4 nanoparticles with enhanced photocatalytic water oxidation performance. Appl. Surf. Sci. 2019, 481, 255–261.

(28) Gao, B.; Wang, T.; Fan, X.; Gong, H.; Meng, X.; Li, P.; Feng, Y.; Huang, X.; He, J.; Ye, J. Selective Deposition of Ag, PO4 on Specific Facet of BiVO4 Nanoplate for Enhanced Photoelectrochemical Performance. Solar RRL 2018, 2, 1800102.

(29) Obregon, S.; Caballero, A.; Colon, G. Hydrothermal synthesis of BiVO4: Structural and morphological influence on the photocatalytic activity. Appl. Catal., B 2012, 117–118, 59–66.

(30) Wei, W.; Yue, X.; Cui, H.; Liu, X.; Xie, J. Hydrothermal synthesis and properties of BiVO4 photocatalysts. J. Mater. Res. 2013, 28, 3408–3416.

(31) Lin, H. Y.; Lin, Y. C. Photocatalytic Water Splitting on Rh/K2NbO4: Nanosheets. J. Nanosci. Nanotechnol. 2020, 20, 1224–1231.

(32) Li, P.; Chen, X.; He, H.; Zhou, X.; Zhou, Y.; Zou, Z. Polyhedral 30-Faceted BiVO4 Microcrystals Predominantly Enclosed by High-Index Planes Promoting Photocatalytic Water-Splitting Activity. Adv. Mater. 2018, 30, 1703119.

(33) Yu, J.; Kudo, A. Effects of structural variation on the photocatalytic performance of hydrothermally synthesized BiVO₄. Adv. Funct. Mater. 2006, 16, 2163.

(34) Zhang, A.; Zhang, J. Synthesis and characterization of Ag/BiVO₄ composite photocatalyst. Appl. Surf. Sci. 2010, 256, 3224–3227.

(35) Huang, Z.-F.; Pan, L.; Zou, J.-J.; Zhang, X.; Wang, L. Nanostructured bismuth vanadate-based materials for solar-energy-driven water oxidation: a review on recent progress. Nanoscale 2014, 6, 14044–14063.

(36) Shi, C.; Dong, X.; Wang, J.; Wang, X.; Ma, H.; Zhang, X. Interfacial defect engineering over fusiform bismuth vanadate photocatalysts constructed by rational assembly of dual-cocatalysts separately on different facets of BiVO₄. J. Hazard. Mater. 2012, 217–218, 92–99.

(37) Pankove, J. I. Optical Processes In Semiconductors. Dover Publications: New York, 1971.

(38) Walsh, A.; Yan, Y.; Huda, M. N.; Al-Jassim, M. M.; Wei, S. H. Band Edge Electronic Structure of BiVO4: Elucidating the Role of the Bi s and V d Orbitals. J. Anal. Methods Chem. 2016, 5408, 7535–7541.

(39) Jiang, H.; Meng, X.; Dai, H.; Deng, J.; Liu, Y.; Zhang, L.; Zhao, Z.; Zhang, R. High-performance porous spherical or octapod-like single-crystalline BiVO4 photocatalysts for the removal of phenol and methylene blue under visible-light illumination. J. Hazard. Mater. 2012, 217–218, 92–99.

(40) Soma, K.; Iwase, A.; Kudo, A. Enhanced Activity of BiVO4 Powdered Photocatalyst Under Visible Light Irradiation by Preparing Microwave-Assisted Aqueous Solution Methods. Catal. Lett. 2014, 144, 1962–1967.

(41) Wang, X.; Liao, D.; Yu, H.; Yu, J. Highly efficient BiVO4 single-crystal photocatalyst with selective Ag, O–Ag modification: orientation transport, rapid interfacial transfer and catalytic reaction. Dalton Trans. 2018, 47, 6570–6577.

(42) Li, R.; Han, H.; Zhang, F.; Wang, D.; Li, C. Highly efficient photocatalysts constructed by rational assembly of dual-cocatalysts separately on different facets of BiVO4. Energy Environ. Sci. 2014, 7, 1369–1376.

(43) Abe, R.; Sayama, K.; Sugihara, H. Development of new photocatalytic water splitting into H-2 and O-2 using two different semiconductor photocatalysts and a shuttle redox mediator I03 (–)/I. J. Phys. Chem. B 2005, 109, 16052–16061.