

Preparation of Au-BiVO₄ Heterogeneous Nanostructures as Highly Efficient Visible-Light Photocatalysts

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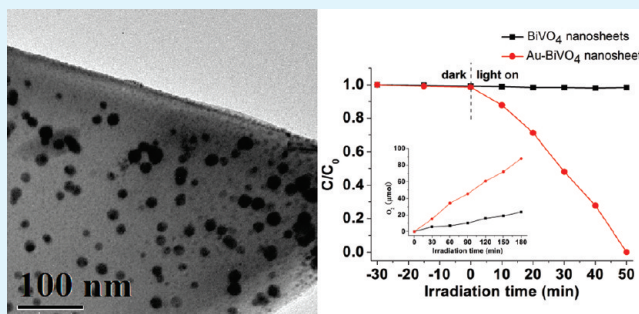
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S Supporting Information

ABSTRACT: Au-BiVO₄ heterogeneous nanostructures have been successfully prepared through in situ growth of gold nanoparticles on BiVO₄ microtubes and nanosheets via a cysteine-linking strategy. The experimental results reveal that these Au-BiVO₄ heterogeneous nanostructures exhibit much higher visible-light photocatalytic activities than the individual BiVO₄ microtubes and nanosheets for both dye degradation and water oxidation. The enhanced photocatalytic efficiencies are attributed to the charge transfer from BiVO₄ to the attached gold nanoparticles as well as their surface plasmon resonance (SPR) absorption. These new heteronanostructures are expected to show considerable potential applications in solar-driven wastewater treatment and water splitting.

KEYWORDS: electron transfer, heterojunction, photocatalyst, water splitting, surface plasmon resonance



INTRODUCTION

The increasing environmental problems and deficiencies of sustainable energy sources have driven considerable research efforts on photocatalytic pollutant degradation and water splitting by using visible light that is abundant in the solar spectrum. Many metal oxide semiconductors such as BiVO₄,^{1,2} Bi₂O₃,^{3,4} WO₃,^{5,6} Fe₂O₃,^{7,8} and Cu₂O^{9,10} have been developed as photocatalysts with visible-light activities. Among them, m-BiVO₄ with a band gap of $E_g \approx 2.40$ eV has been recognized as a potentially suitable visible-light photocatalyst for pollutant decomposition and water oxidation.¹¹ Therefore, m-BiVO₄ with various morphologies, such as hierarchical nanostructures,¹² quantum tubes,¹³ nanosheets,¹⁴ nanoparticles,¹⁵ microtubes,¹⁶ and hollow structures,¹⁷ have been synthesized by different methods and explored for photocatalytic reactions. These reported results indicate that the photocatalytic efficiencies of m-BiVO₄ are strongly dependent on its morphology and crystal phase. In addition, researchers have realized that the photocatalytic activity of BiVO₄ is usually not satisfied because the photogenerated active electrons and holes tend to rapidly decay through recombination,¹⁸ which significantly restricted the practical applications of BiVO₄ in photocatalysis.

It has been reported that semiconductor photocatalysts loaded with noble metals, such as gold and silver, can effectively promote their photocatalytic performance because the charge

transfer between the semiconductor and metal substantially improves the electron–hole separation, and the surface plasmon resonance (SPR) of the loaded metal nanoparticles provide additional visible-light absorption, which can also contribute to the overall photocatalytic activities.^{19–28} Herein we report the preparation of Au-BiVO₄ heterogeneous nanostructures by growing gold nanoparticles on presynthesized BiVO₄ microtubes and nanosheets through a cysteine-linking strategy. Significantly, these Au-BiVO₄ heterogeneous nanostructures exhibit much higher visible-light photocatalytic activities than the individual microtubes and nanosheets for both dye degradation and water oxidation. Furthermore, we have investigated the roles of gold nanoparticles and have discussed the photoinduced electronic interaction between gold and BiVO₄, in order to have in-depth understanding on the enhanced photocatalytic performance.

EXPERIMENTAL SECTION

Synthesis of BiVO₄ Microtubes and Nanosheets. The protocol is modified from a previously reported method for preparing BiVO₄ nanoplates.¹¹ Briefly, while stirring, 158 mg of BiCl₃ was initially

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dissolved in 50 mL of ultrapure water to form a white suspension, followed by the addition of 59 mg of NH_4VO_3 . Different amounts of 1 M aqueous ethanolamine solution (2.5 mL for microtubes, 0.3 mL for nanosheets) was then added into the suspension. The resultant mixture was sealed in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to and maintained at 160 °C for 12 h, and allowed to cool to room temperature. A yellow powder was collected after centrifugation, washed with water repeatedly, and then dried in a vacuum oven.

Synthesis of Au-BiVO₄ Heterogeneous Nanostructures. Gold nanoparticles were grown on the BiVO₄ microtubes and nanosheets according to a modified literature method on preparing Fe₃O₄/Au hybrid spheres.²⁹ Briefly, 60 mg of the as-prepared BiVO₄ powder was suspended in 20 mL ultrapure water followed by the addition of 5 mL of an aqueous solution of 0.01 M L-cysteine. The mixture was subjected to sonication for 30 min followed by the addition of 5 mL of an aqueous solution of 3 mM HAuCl₄. After the solution was vigorously stirred for another 30 min, 10 mL of aqueous solution of 0.05 M L-ascorbic acid was quickly added into the solution. The reaction was allowed for rapid stirring for 3 h. The products were separated via centrifugation, washed with water repeatedly, and dried in a vacuum oven. Subsequently, UV/ozone cleaning was used to treat the powders to remove cysteine bound on the product surface.

Characterization. X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu K α source) at a scan rate of 1°/min with the 2 θ range from 15 to 60°. The field emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM-6340F scanning electron microscope. Energy dispersive X-ray spectra (EDX) were taken with a JEOL JSM-7600F scanning electron microscope equipped with energy-dispersive X-ray analysis system. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. UV-vis absorption spectra and diffuse reflectance spectra (DRS) were recorded on a Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA).

Photocatalytic Degradation of Methyl Orange. Methyl orange (MO) was used as a convenient photostable organic molecule to assay photochemical activity of Au-BiVO₄. The prepared Au-BiVO₄ heterogeneous nanostructures (10 mg) were dispersed into an aqueous solution (10 mL) of methyl orange (5 mg L⁻¹). The suspension was sonicated for 15 min followed by stirring in dark for 15 min to ensure an adsorption-desorption equilibrium prior to irradiation. The suspension was then irradiated while stirring by using a 300-W Xe lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cutoff filter ($\lambda > 420$ nm). The initial and final reaction temperature for MO solution were measured as 28 and 32 °C, respectively. Samples for analysis were taken from the reaction suspension after different reaction time and centrifuged at 10 000 rpm for 5 min to remove the particles. The MO concentration from the upper clear solution was analyzed according to the absorption intensity at 463 nm in the measured UV-vis spectra.

Photocatalytic Oxidation of Water for O₂ Generation. Typically, 5 mg of the prepared Au-BiVO₄ heterogeneous nanostructures were suspended in 15 mL aqueous solution of 5.33 mM Na₂S₂O₈. The suspension was purged with argon for 3 h to drive away the residual oxygen before sealed in a quartz flask. The photocatalytic water oxidation was carried out by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cutoff filter ($\lambda > 420$ nm). The initial and final reaction temperature for the reaction solution were measured as 28 and 34 °C, respectively. The gas product composition was analyzed every 30 min by an Agilent 7890A gas chromatograph (GC) with TCD detector.

RESULTS AND DISCUSSION

The prepared BiVO₄ samples are identified as monoclinic BiVO₄ through XRD analyses (JCPDS No. 83-1699) as shown in Figure 1. The SEM and TEM images (Figure 2) reveal that the sample prepared with 2.5 mL of a solution of ethanolamine

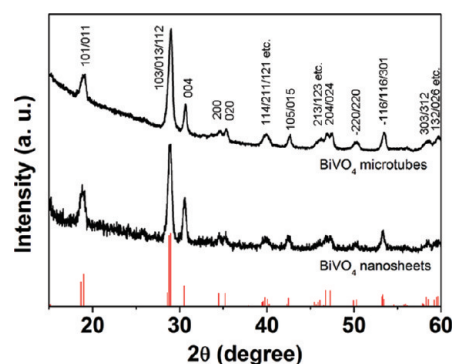


Figure 1. XRD patterns of BiVO₄ microtubes and nanosheets. The red lines stand for the standard data (JCPDS No. 83-1699) of monoclinic BiVO₄.

is composed of tubular microstructures (Figure 2a, b), whereas using 0.3 mL of a solution of ethanolamine leads to nanosheet formation (Figure 2c, d). Both SAED patterns of a single microtube (Figure 2b) and a single nanosheet (Figure 2d) reveal the single crystalline nature of these structures. The corresponding diffraction spots can be indexed as 200, 020, and 220 reflections, indicating the preferred (001) surface orientation of both microtubes and nanosheets. The growth of Au on the BiVO₄ surface is facilitated in the presence of L-cysteine, which can bind to the BiVO₄ surface through its carboxylate group. When the gold salt precursor (HAuCl₄) is subsequently added and reduced, the produced gold atoms can be captured by the L-cysteine on the BiVO₄ surfaces through Au-S bonding.³⁰ These gold atoms then serve as the nucleation sites for further in situ growth on BiVO₄ surfaces. The original morphologies of microtube and nanosheet are retained during the gold nanoparticle growth process, as shown in Figure 3b and d. The high-magnification TEM images (see Figure S1a-c in the Supporting Information) reveal that many small gold nanoparticles with an average size of 7.2 (± 1.3) nm are sticking on the surfaces of BiVO₄ microtubes and nanosheets. In comparison, the surfaces of the pure BiVO₄ microtubes and nanosheets are very smooth, as shown in images a and c in Figure 3. The EDX analysis (Figure 3e and f) further confirms the presence of gold on the nanostructures with an estimated gold content of 3.71 and 3.50 wt % for Au-BiVO₄ microtubes and nanosheets, respectively. Indeed, this cysteine-linking strategy is superior for preparing Au-BiVO₄ heterogeneous nanostructures as compared with simply mixing presynthesized gold nanoparticles (see Figure S2 in the Supporting Information) with cysteine-modified BiVO₄ nanostructures. The latter did not result in the formation of heterogeneous Au-BiVO₄ structures (see Figure S3 in the Supporting Information).

The diffuse reflectance spectra of the prepared BiVO₄ and Au-BiVO₄ samples are shown in Figure 4. The band gaps estimated by extrapolating the linear region of a plot of the absorbance squared vs energy³¹ are 2.52, 2.51, 2.55, and 2.54 eV for BiVO₄ microtubes, Au-BiVO₄ microtubes, BiVO₄ nanosheets, and Au-BiVO₄ nanosheets, respectively. Thus these samples have almost no difference in the bandgap energy. Note the SPR band of gold nanoparticles does not appear in the spectra, though the TEM images clearly indicate their existence on the BiVO₄ surfaces. Such a gold SPR band has been numerous observed in Au-TiO₂ heterostructures,³²⁻³⁵ whereas in the heterogeneous Au-BiVO₄ structure

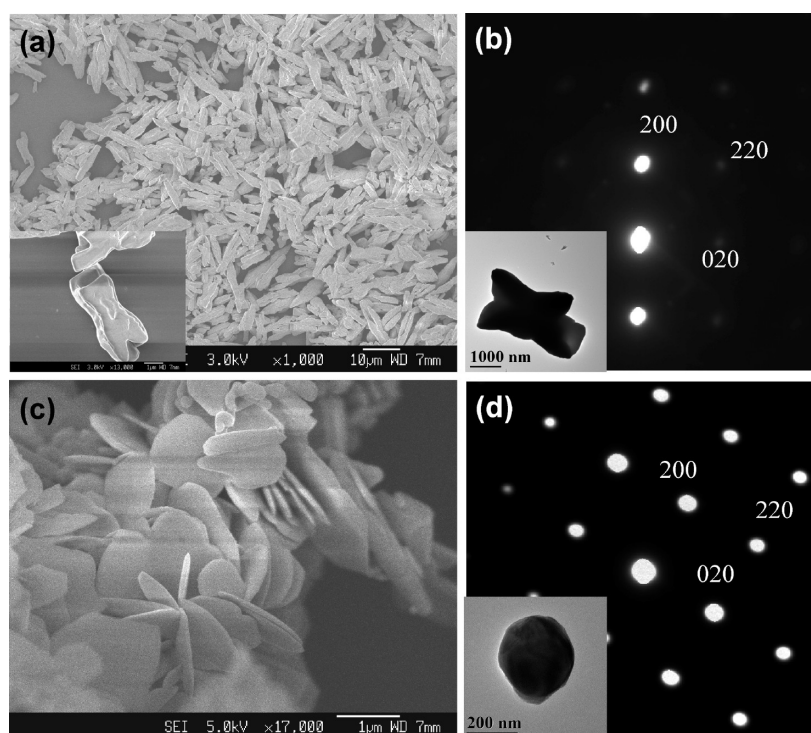


Figure 2. (a) SEM image of BiVO₄ microtubes, inset is the zoom-in view of a representative microtube; (b) SAED pattern of a single BiVO₄ microtube, inset shows its TEM image; (c) SEM image of BiVO₄ nanosheets; (d) SAED pattern of a single BiVO₄ nanosheet, inset shows its TEM image.

presented here, the absence of Au SPR band may be due to the low concentration of gold nanoparticles, thus the spectrum feature of Au SPR may be overwhelmed by the absorption of BiVO₄, which also exhibits considerable absorption in the same spectral region.

The photocatalytic activities of the Au-BiVO₄ heterogeneous nanostructures were evaluated through MO degradation under visible-light ($\lambda > 420$ nm) irradiation. As an example, Figure 5a shows the absorption spectra of MO solution in the presence of Au-BiVO₄ nanosheets as a function of illumination time. The absorption peak at 463 nm decreases significantly over a period of tens of minutes, indicating a relatively fast degradation of MO molecules in solution. For comparison, pure BiVO₄ microtubes and nanosheets were also used for photocatalytic MO degradation under the same conditions. Figure 5b shows that after 50 min visible-light irradiation, the degradation percentage of MO in the presence of Au-BiVO₄ microtubes and nanosheets are 36% and nearly 100%, respectively. The corresponding MO degradation rates are normalized per gram photocatalyst as 3.6 and 10 mg L⁻¹ min⁻¹ for Au-BiVO₄ microtubes and nanosheets, respectively. However, the pure BiVO₄ microtubes and nanosheets exhibit almost no activities for MO degradation even though they have some absorption in the visible region, which excludes the MO self-degradation originated from dye-sensitization effect. The lower efficiency of Au-BiVO₄ microtubes than Au-BiVO₄ nanosheets might be partially due to the smaller light absorption cross-section of microtubes arising from the curved surface. Another reason could be because the absorption of gold nanoparticles attached on the inner surface of BiVO₄ microtubes is blocked by the tube wall so that these gold particles can not be excited to contribute SPR-enhancement. In contrast, the gold particles on the two sides of BiVO₄ nanosheets have equal opportunities to

receive excitation. Nevertheless, our results still demonstrate that the deposited gold nanoparticles endow greatly enhanced visible-light photocatalytic efficiency.

We further compare the visible light ($\lambda > 420$ nm) activities of the Au-BiVO₄ heterogeneous nanosheets with pure BiVO₄ nanosheets for photocatalytic water oxidation in the presence of sacrificial electron acceptor S₂O₈²⁻. As shown in Figure 6, the light induced O₂ evolution rate for Au-BiVO₄ nanosheets (5862 $\mu\text{mol h}^{-1} \text{g}^{-1}$) is more than three times higher than that of pure BiVO₄ nanosheets (1579 $\mu\text{mol h}^{-1} \text{g}^{-1}$). This further confirms the high visible-light photocatalytic efficiency of the Au-BiVO₄ heterogeneous nanostructures caused by the in situ grown gold nanoparticles.

The gold-enhanced photocatalytic efficiencies are attributed to two aspects. First, the conjugated gold nanoparticles on BiVO₄ surfaces may act as electron sinks to retard the recombination of the photogenerated electrons and holes in BiVO₄ so as to improve the charge separation on its surfaces. It is known that the Fermi level of gold is 0.5 V (versus NHE),²⁸ which is lower than the conduction band (CB) edge of BiVO₄ (0 V versus NHE).³⁶ At the Au-BiVO₄ heterojunction, the interactions between Au and BiVO₄ establish an interfacial charge equilibrium. When the BiVO₄ is excited by visible light with photon energy larger than its band gap, electrons in the valence band (VB) are excited to the CB with simultaneous generation of holes in the VB. At the interface of Au and BiVO₄, the photogenerated electrons are distributed, and some of them transfer into the Au nanoparticle until new interfacial charge equilibrium is attained. The electron accumulation on Au increases the Fermi level (E_f) of the gold nanoparticle to more negative potentials (E_f^*), which is closer to the BiVO₄ conduction band. This energy alignment for the Au-BiVO₄ junction is shown in Figure 7. Such a charge transfer process

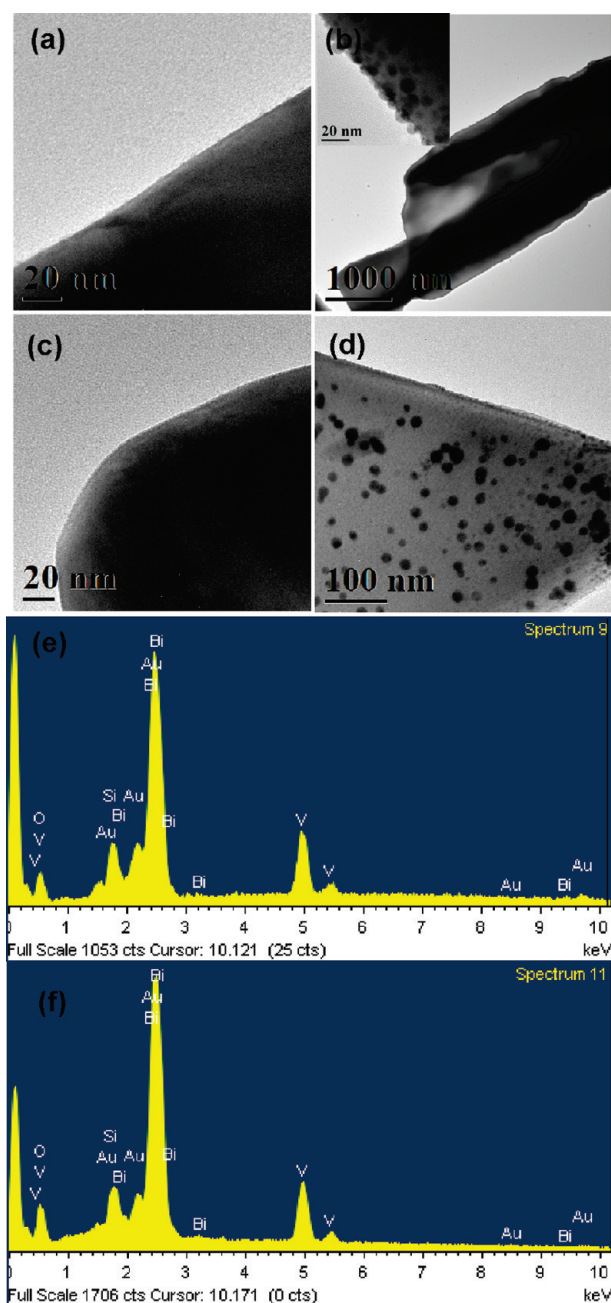


Figure 3. TEM images of the samples: (a) BiVO_4 microtubes, (b) Au-BiVO_4 microtubes, inset is the edge of a single Au-BiVO_4 microtube, (c) BiVO_4 nanosheets, and (d) Au-BiVO_4 nanosheets. EDX spectra of the samples: (e) Au-BiVO_4 microtubes, and (f) Au-BiVO_4 nanosheets. The Si peak comes from the silicon substrate.

enhances the separation of photogenerated electrons and holes and thereby increases their lifetime.^{28,37} This is particularly important for photocatalytic water oxidation because it is slow as multielectron processes with kinetic restraints.³⁸ As illustrated in Figure 7, when the photogenerated electrons transfer to the gold nanoparticle and reduce the adsorbed $\text{S}_2\text{O}_8^{2-}$ to SO_4^{2-} on the Au surface, the holes remain on BiVO_4 surface will have relatively longer lifetime to carry out the four-electron process of H_2O oxidation to O_2 .

Second, the SPR of gold nanoparticles attached on BiVO_4 surfaces can also enhance the visible light photocatalytic efficiency. Although the spectra (Figure 4) did not show

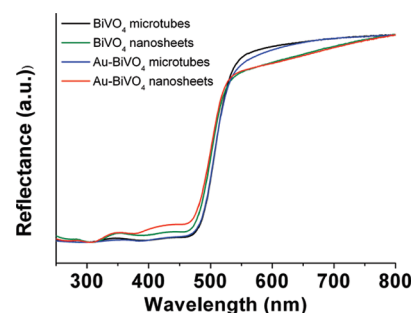


Figure 4. Diffuse reflectance spectra of BiVO_4 and Au-BiVO_4 structures.

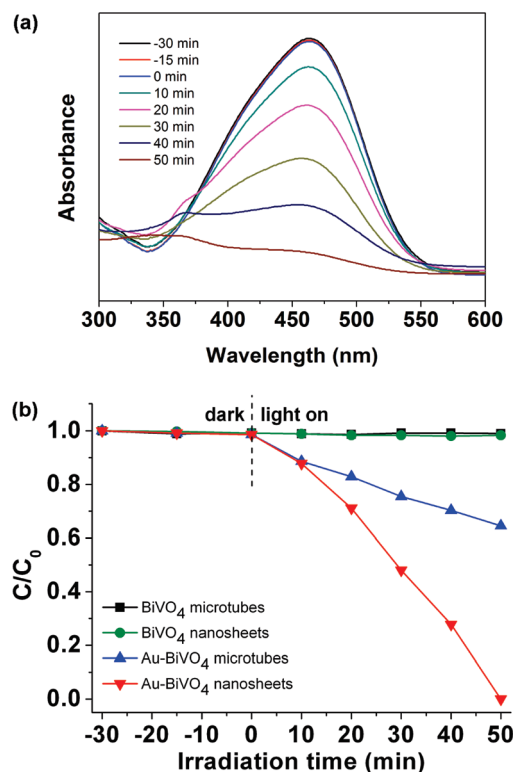


Figure 5. (a) Time-dependent UV-vis absorption spectra of the MO solution in the presence of Au-BiVO_4 nanosheets; (b) photocatalytic degradation ratio of MO versus visible light ($\lambda > 420$ nm) irradiation time by using various photocatalysts.

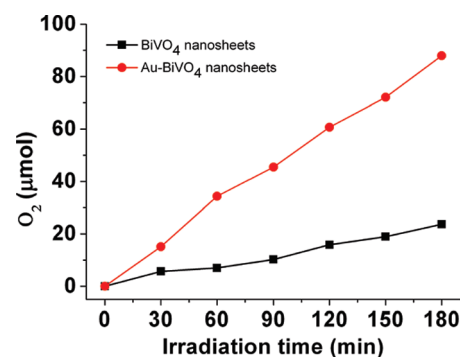


Figure 6. The amount of oxygen evolution versus visible light ($\lambda > 420$ nm) time through photocatalytic water oxidation by using BiVO_4 and Au-BiVO_4 nanosheets.

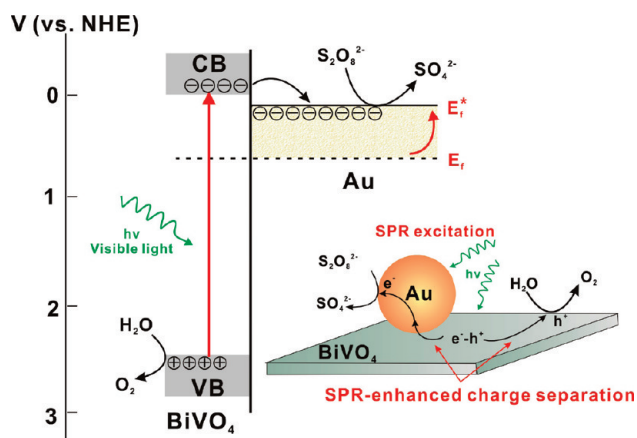


Figure 7. Schematic illustration of the detailed energy alignment in the Au-BiVO₄ heterogeneous structure and the proposed mechanism of photocatalytic water oxidation by Au-BiVO₄ nanosheets in the presence of sacrificial agent S₂O₈²⁻. The Fermi level (E_f) of Au shifts to more negative potentials (E_f^*) because of the transfer of photogenerated electrons from BiVO₄ to Au. The SPR excitation of the gold nanoparticle is believed to enhance electron–hole separation near the Au-BiVO₄ heterojunction.

observable SPR peak of gold nanoparticles because of the low concentration of gold nanoparticles on BiVO₄ surface, the effect of SPR-driven enhancement may still contribute to the photocatalytic reaction. To clarify the possible involvement of gold SPR in the enhanced photocatalytic activity of Au-BiVO₄ structures, we prepared Pt-BiVO₄ nanosheets (see Figure S4a,b in the Supporting Information) through the same strategy (Pt content as 3.78 wt %, see the Supporting Information for details) to compare their photocatalytic efficiency with Au-BiVO₄ nanosheets for MO degradation under light irradiation at 500 ± 20 nm. This wavelength range is accordance with the SPR band of normal gold nanoparticles, while Pt nanoparticles have no absorption within this range.

As shown in Figure 8, the Au-BiVO₄ nanosheets are quite active for photocatalytic MO degradation, while the pure

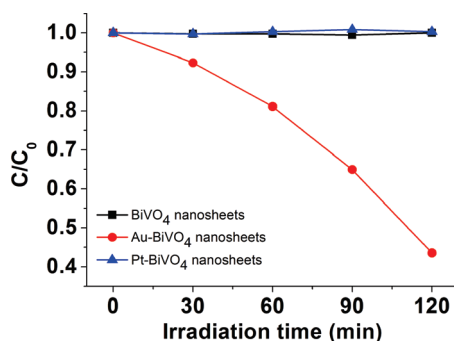


Figure 8. Photocatalytic degradation ratio of MO versus time under irradiation of 500 ± 20 nm light by using Au-BiVO₄ nanosheets (red), Pt-BiVO₄ nanosheets (blue), and pure BiVO₄ nanosheets (black), respectively.

BiVO₄ nanosheets and Pt-BiVO₄ nanosheets show no activity for MO degradation under irradiation at the same wavelength range. This indicates that the relatively weak absorption of BiVO₄ at 500 ± 20 nm does not induce obvious photocatalytic activity even with Pt as electron sink. This might be due to the very inefficient excitation by the photons with energy close to

the band gap so that the recombination of photogenerated electrons and holes dominate.³⁹ However, the gold nanoparticles deposited on BiVO₄ nanosheets exhibit strong SPR at 500 ± 20 nm. It has been extensively demonstrated that the plasmon-exciton coupling can result in significant enhancement of charge separation.⁴⁰ Therefore, we believe that the gold SPR can enhance the electron–hole separation near the Au-BiVO₄ heterojunction, and thus improve the photocatalytic efficiency of the Au-BiVO₄ heterogeneous nanostructures, which is also supported by our observations.

Indeed if we use fully visible light ($\lambda > 420$ nm) irradiation, the Pt-BiVO₄ nanosheets still exhibit certain photocatalytic activity for MO degradation (see Figure S4c in the Supporting Information) even though pure BiVO₄ nanosheets show no activity (Figure 5). This means that the deposited metal nanoparticles as “electron sink” do contribute to the improved charge separation and photocatalytic activity. Because the Au-BiVO₄ nanosheets still show much higher activity than the Pt-BiVO₄ by comparing Figure 5 and Figure S4c in the Supporting Information, it indicates that the SPR excitation of Au nanoparticles would provide stronger enhancement on charge separation than the effect only from “electron sink”, especially when the excitation photon energy is low (visible light) and closely above the bandgap of BiVO₄.

CONCLUSIONS

In summary, Au-BiVO₄ heterogeneous nanostructures have been successfully prepared through in situ growth of gold nanoparticles on BiVO₄ microtubes and nanosheets by using a cysteine-linking strategy. These Au-BiVO₄ heterogeneous nanostructures exhibit highly efficient visible-light-driven photocatalytic activities for dye degradation and water oxidation as compared to pure BiVO₄ microtubes and nanosheets. The improved photocatalytic efficiencies are attributed to the enhanced charge separation by the contacting gold nanoparticles, allowing the photogenerated electrons and holes to have sufficient time to participate the overall photocatalytic reactions. Further comparison with Pt-BiVO₄ indicates that the SPR absorption of gold nanoparticles on the Au-BiVO₄ nanostructures also has significant contribution to the visible light photocatalytic activities. We believe that our strategy of the heterostructure synthesis involving tethered Au nanoparticles on a semiconductor surface and exploiting their SPR for enhancing photocatalytic activities can have considerable impact on the future development of highly efficient visible-light photocatalysts for organic pollutant degradation and water splitting.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for compared samples, and additional HRTEM images for Au-BiVO₄ microtubes and nanosheets. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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