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Article

Ag nanoparticles deposited on oxygen-vacancy-containing BiVO₄ for enhanced near-infrared photocatalytic activity

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ABSTRACT

This study investigates the photodegradation of the organic dye rhodamine B by Ag-nanoparticle-containing BiVO₄ catalysts under different irradiation conditions. The catalysts consist of Ag nanoparticles deposited on oxygen-vacancy-containing BiVO₄. The morphology of the BiVO₄ is olive shaped, and it has a uniform size distribution. The BiVO₄ possesses a high oxygen vacancy density, and the resulting Ag nanoparticle-BiVO₄ catalyst exhibits higher photocatalytic activity than BiVO₄. The RhB degradation by the Ag nanoparticle-BiVO₄ catalyst is 99% after 100 min of simulated solar irradiation. BiVO₄ containing oxygen vacancies as a rationally designed support extends the catalyst response into the near-infrared region, and facilitates the trapping and transfer of plasmonic hot electrons. The enhanced photocatalytic efficiency is attributed to charge transfer from the BiVO₄ to Ag nanoparticles, and surface plasmon resonance of the Ag nanoparticles. These insights into electron-hole separation and charge transfer may arouse interest in solar-driven wastewater treatment and water splitting.

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1. Introduction

Continuously increasing energy demands and environmental problems have drawn widespread global attention [1–8]. These problems have arisen from rapid population growth and developments in manufacturing and industry. This has led to a recent surge in sustainable and environmentally friendly energy technologies. Among these technologies, metal oxide semiconductors are efficient catalysts for photocatalytic pollutant degradation and water splitting. However, solar wavelengths are not efficiently utilized by most photocatalysts for solar-electricity conversion, which only efficiently absorb ultraviolet-visible (UV-Vis) wavelengths [9–16]. An example is BiVO₄ which is an environmentally friendly, low-cost, and high-performance photocatalyst [17–21], but has no response to near-infrared (NIR) wavelengths. Another challenge is the weak

interaction of O₂ with the photocatalyst surface, especially with defect-free surfaces, which leads to inefficient photooxidation of pollutants. The participation of O₂, either directly as a reactant or indirectly as an electron acceptor, should be accompanied by interfacial electron transfer.

To overcome this challenge, BiVO₄ containing oxygen vacancies (OVs) has been prepared. It exhibits a photocatalytic response under NIR wavelengths, which leads to an increase in adsorbed O₂. The formation of OVs narrows the band gap of BiVO₄ [22]. OVs on the BiVO₄ surface also facilitate the trapping and transfer of photogenerated electrons. While NIR wavelengths can be harvested by the photocatalyst, its photocatalytic activity is suppressed by other factors. The application of BiVO₄ as an efficient photocatalyst is hindered by poor electron transmission and insufficient charge separation [23–25]. Obtaining reliable materials that exhibit efficient performance for

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solar-driven wastewater treatment and water splitting remains a challenge.

The last few years have seen a significant increase in the preparation of hybrid nanomaterials. Despite this, the tailored syntheses of photocatalytic heterostructures have been limited by structural incompatibility within hybrid materials. Facile and reliable strategies for synthesizing practical heterostructured semiconductors are therefore required. Au and Ag have been shown to be efficient agents for harvesting solar energy in chemical processes involving localized surface plasmon resonance (SPR) [26,27]. SPR refers to the collective oscillation of conduction band (CB) electrons that are in resonance with the oscillating electric field of incident light. The decay of SPR can generate hot electrons and holes, which in turn can initiate chemical reactions [27–29]. Of interest is the oxidizing ability of hot holes within Ag, which is thought to be much milder than that of holes in the valence band (VB) of most photocatalytic semiconductors. This offers the possibility for application in oxidative organic transformations [30–32]. Hot carriers also rapidly decay, so inorganic supports are often integrated with Ag to promote the separation of hot electrons and holes [33–35]. The surface properties of the support are therefore very important, because they determine the dynamics of plasmonic hot carriers and the interaction of the support surface with reactants.

In the current study, we have prepared and investigated a plasmonic catalyst consisting of Ag nanoparticles deposited on BiVO_4 containing OVs (hereafter referred to as $\text{BiVO}_4\text{-OV}$). The introduction of OVs enables synergistic action of the plasmonic hot electrons and holes, and provides a new reaction pathway. Charge transfer from $\text{BiVO}_4\text{-OV}$ to the attached Ag nanoparticles, as well as the SPR absorption of the Ag nanoparticles, further enhances the photocatalytic efficiency [36].

2. Experimental

2.1. Syntheses of materials

Commercial chemicals were of analytical grade and used as received without further purification.

$\text{BiVO}_4\text{-OV}$ was prepared by a hydrothermal method. In a typical procedure, 0.4 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ powder was dissolved in 16 mL of glycerol under vigorous stirring for 1 h. 0.4 mmol of $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ was dissolved in 16 mL of deionized water under vigorous stirring for 0.5 h, until it became homogeneous and transparent under room temperature conditions. Then, the $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ solution was added dropwise to the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution under vigorous stirring for 0.5 h, to form a yellowish suspension. The resulting suspension was heated in a 50-mL polytetrafluoroethylene-lined stainless steel autoclave at 180 °C for 8 h. After cooling to room temperature, the precipitate was collected by centrifugation, thoroughly washed with distilled water and then absolute ethanol, and then dried in air at 60 °C for 4 h to yield $\text{BiVO}_4\text{-OV}$. The OVs would be expected to vanish through redox reaction, so the obtained $\text{BiVO}_4\text{-OV}$ powder was calcined in a muffle furnace at 300 °C for 5 h in air. The power was then removed from the

furnace, and stored at 20 °C in a hermetic bag. The sample is hereafter referred to as BiVO_4 .

$\text{BiVO}_4\text{-OV}$ (0.1 g) was dispersed in 50 mL of deionized water. A given amount of AgNO_3 was dissolved in 10 mL of deionized water, to provide Ag/ $\text{BiVO}_4\text{-OV}$ mass rates of 1.0, 2.0, 2.5, and 3.0Wt%. The AgNO_3 solution was then added to the $\text{BiVO}_4\text{-OV}$ dispersion under stirring. The resulting dispersion was subjected to UV treatment as described above, at room temperature under stirring. After 5 min of irradiation, the light grey product was collected by centrifugation, washed with water, and then dried in a vacuum oven. The product was then subjected to various characterizations and catalysis experiments. Samples are referred to as BiVO_4 , Ag- BiVO_4 (Ag2.5%- BiVO_4), $\text{BiVO}_4\text{-OV}$, Ag1.0%- $\text{BiVO}_4\text{-OV}$, Ag2.0%- $\text{BiVO}_4\text{-OV}$, Ag2.5%- $\text{BiVO}_4\text{-OV}$ (Ag- $\text{BiVO}_4\text{-OV}$), and Ag3.0%- $\text{BiVO}_4\text{-OV}$. The Ag loading content could be easily tuned by varying the AgNO_3 solution concentration.

2.2. Photocatalytic activity

The light source for the photocatalytic reactions was a 300-W Xe lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd., China). The photocatalytic activities of the samples were determined by measuring the degradation rate of rhodamine B (RhB) dye under different irradiation conditions. NIR irradiation was obtained from simulated solar irradiation by using a cut-off filter with that omitted wavelengths of <800 nm. 20 mg of sample was dispersed in 50 mL of RhB solution (10 mg/L), by sonication for 10 min. For comparison, the degradation of phenol solution (10 mg/L) was also measured with 20 mg of Ag- $\text{BiVO}_4\text{-OV}$ under the same conditions. Then, the solution was stirred for 30 min in the dark to establish adsorption-desorption equilibrium. The reaction solution was then irradiated with different sources for the degradation of RhB. At 20 min intervals, 4 mL aliquots of suspension were removed, and the catalyst was separated by centrifugation. The degradation of RhB was monitored by measuring the absorbance of the aliquot supernatant at a wavelength of 554 nm, using a UV-Vis spectrophotometer. The RhB concentration after irradiation for a certain duration is indicated by C , while C_0 is the RhB concentration at adsorption-desorption equilibrium prior to irradiation [37].

2.3. Characterization

The crystallinities and purities of samples were characterized by powder X-ray diffraction (XRD) using a Shimadzu XRD-6100 diffractometer, operated at 40 kV and 40 mA with $\text{Cu } K_\alpha$ radiation. Scanning electron microscopy (SEM) images were collected using a field-emission scanning electron microscope (JSM-7800F, JEOL). Transmission electron microscopy (TEM) images were collected using a JEOL JEM-2100F transmission electron microscope. The absorption properties were evaluated using a UV-Vis diffuse reflectance (UV-Vis DRS) spectrometer (CARY 100&300, VARIAN), with BaSO_4 as a reflectance standard. Raman spectra were recorded using a LabRam-1B Raman spectroscopy, with He-Ne laser excitation

at 532 nm. Data were recorded at a scan rate of 0.07 s^{-1} in the 2θ range of 10° – 70° . X-ray photoelectron spectra (XPS) were recorded using a Thermo VG ESCALAB-250 system with Al $K\alpha$ and Mg $K\alpha$ sources operated at 15 kV. Photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer.

2.4. Photoelectrochemical tests

A CHI660E electrochemical workstation (Shanghai Chenhua, China) with a three-electrode configuration was used for carrying out photoelectrochemical measurements, with the sample acting as the working electrode, Pt wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and 0.5 mol/L sodium sulfate as the electrolyte. The working electrode was prepared by dip-coating. Specifically, 5 mg of sample was suspended in 0.15 mL of ultrapure water. The mixture was then ultrasonicated for 20 min to form a homogeneous solution. From this solution, 10 μL was used to dip-coat a glass carbon electrode, which was then dried at room temperature. The light source was a 300-W Xe lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd., China). The photocurrent response was measured using a potentiostatic (current vs. time, I - t) under intermittent irradiation at a bias of 0.3 V vs. SCE. Electrochemical impedance spectra (EIS) were recorded using an alternating current signal (10 mV) in the frequency range of 0.1–105 Hz at open circuit potential (OCP).

3. Results and discussion

3.1. Characterization of photocatalysts

In this study, oxygen-deficient BiVO_4 was used as a model inorganic support for Ag nanoparticles. BiVO_4 is a typical visible-light-responsive semiconductor, and is a promising photocatalyst due to its defect-related reactivity. OV provides sites for O_2 adsorption and activation. Surface OVs affect the CB and can act as traps for photogenerated electrons, which promotes charge carrier separation and charge transfer to adsorbates. Thus, oxygen-deficient BiVO_4 was considered to be an appropriate support for this study. The crystal structures of the sam-

Fig. 2. SEM images of BiVO_4 -OV (a) and Ag-BiVO_4 -OV (b). TEM images of BiVO_4 -OV (c) and Ag-BiVO_4 -OV (d). Inset in (c) shows a TEM image of BiVO_4 -OV.

ples are all consistent with monoclinic BiVO_4 . All diffraction peaks of the phases can be characterized by XRD (JCPDS No. 83-1699 and 01-1167). In Fig. 1(a) and (b), the diffraction at $2\theta = 38^\circ$ can be indexed to the Ag (111), and its intensity increases with increasing Ag nanoparticle content. The intensities of the peaks decrease and they shift with the presence of OVs. The XRD results show that BiVO_4 -OV and Ag-BiVO_4 -OV were prepared without impurities.

SEM images show that the morphologies of BiVO_4 , BiVO_4 -OV, and Ag-BiVO_4 -OV are olive shaped, and that they have uniform size distributions. The morphology does not significantly differ between BiVO_4 -OV and Ag-BiVO_4 -OV, as shown in Fig. 2(a) and (b), respectively. The microstructures of the samples were investigated by TEM. Fig. 2(c) and (d) shows that BiVO_4 -OV and Ag-BiVO_4 -OV have differing microstructures. Ag-BiVO_4 -OV contains small nanoparticles (Fig. 2(d) marked with red circles). BiVO_4 -OV (Fig. 2(c)) does not show the pres-

Fig. 1. XRD patterns of the samples.

ence of such nanoparticles. A disordered layer and lack of a well-defined lattice indicate the presence of OV in the inset in Fig. 2(c) [38]. The TEM results indicate that Ag-loaded BiVO₄-OV had been synthesized.

To confirm the existence of Ag, areas in SEM images containing nanoparticles were investigated by energy-dispersive X-ray (EDX) microanalysis. Fig. 3(a) shows an SEM image of Ag-BiVO₄-OV, and Fig. 3(b)–(d) shows corresponding Ag, Bi, and V mapping images. The EDX images suggest that the nanoparticles uniformly dispersed on the BiVO₄ surface consist of silver. The chemical state of Ag in Ag-BiVO₄-OV was analyzed by XPS. The XPS survey spectrum in Fig. 4(a) shows the presence of Bi, V, O, and Ag throughout the material. Fig. 4(b) shows a high-resolution spectrum of the Ag 3d region, which contains two obvious peaks corresponding to the Ag 3d_{5/2} and Ag 3d_{3/2} binding energies. The two Ag 3d peaks at 367.8 and 373.8 eV originate from metallic Ag⁰ species [39]. The high-resolution spectrum of the O 1s region is shown in Fig. 4(c). The two peaks at binding energies of 530.0 and 532.1 eV correspond to lattice oxygen and adsorbed oxygen, respectively. The presence of OV means that adsorbed oxygen is readily observed in the XPS spectrum of BiVO₄-OV [40]. The presence of Ag in Ag-BiVO₄-OV results in a decrease in the intensity of the XPS peak of adsorbed oxygen. This indicates that OV contribute to the deposition of Ag nanoparticles on the BiVO₄-OV surface. Fig. 4(d) shows the high-resolution spectrum of the Bi 4f region, in which the Bi 4f_{7/2} and Bi 4f_{5/2} states of Bi³⁺ occur at 159.3 and 164.6 eV, respectively. The Bi 4f peaks in the spectra of BiVO₄-OV and Ag-BiVO₄-OV show shifts to lower binding ener-

Fig. 3. SEM image of Ag-BiVO₄-OV (a) and corresponding Ag (b), Bi (c), and V (d) mapping images.

gies, compared with the spectrum of BiVO₄. These results further support the presence of OV on the sample surfaces due to oxygen adsorption and the presence of Bi³⁺ [41,42]. Fig. 4(b) shows that Ag⁺ is readily reduced to Ag⁰ on BiVO₄-OV by photoreduction [43,44].

Raman spectroscopy was used to investigate the structure and bonding in the samples. Fig. 5(a) shows the Raman spectra of the samples, in which peaks are located at 200–1000 cm⁻¹. Peaks at around 127, 211, 329, 367, 713, and 820 cm⁻¹ are consistent with the characteristic Raman bands of monoclinic Bi-

Fig. 4. XPS spectra of Ag-BiVO₄-OV. (a) Survey spectrum; (b) Ag 3d; (c) O 1s; (d) Bi 4f.

Fig. 5. Raman spectra of BiVO₄, Ag-BiVO₄, BiVO₄-OV, and Ag-BiVO₄-OV.

VO₄ [45,46]. The symmetric and symmetric V–O stretching modes occur at around 823 and 713 cm^{−1} (Fig. 5(b)), which appear as a peak and weak shoulder, respectively. Peaks in the spectrum of BiVO₄ at 329 and 367 cm^{−1} are attributed to the asymmetric and symmetric bending vibrations of two adverse types of VO₄ band (Fig. 5(c)). The external mode (rotation/translation) occurs at 211 cm^{−1}, as shown in Fig. 5(d) [47]. Fig. 5(a)–(d) shows that the typical peaks of Ag-BiVO₄, BiVO₄-OV, and Ag-BiVO₄-OV are weaker than those of BiVO₄. The peaks also shift to lower frequency compared to that of BiVO₄ (823 cm^{−1}). These results indicate that OVs [38,48,49] and Ag nanoparticles had been introduced into BiVO₄ [50].

Electron spin resonance (ESR) spectroscopy is useful for investigating unpaired electrons in materials, and can potentially provide evidence for the presence of OVs. The ESR spectrum of BiVO₄-OV exhibits a fingerprint signal at about $g = 2.0$ (Fig. 6(a)), which could be ascribed to electrons trapped in OVs [51]. This is consistent with the formation of OVs on the BiVO₄ surface. Compared to the spectrum of BiVO₄-OV, no obvious signal is observed in the ESR spectrum of BiVO₄. This suggests that OVs were removed during the high temperature annealing process.

PL spectra were recorded to investigate the dynamics of photo-generated electron-hole pairs. Measurements of PL emission can reveal the efficiency of charge carrier trapping, migration, transfer, and separation [52]. The PL spectrum of Ag-BiVO₄-OV in Fig. 6(b) shows a prominent band at 500 nm. The PL emission arises from the recombination of free carriers, so the lower intensity of this peak is ascribed to a decrease in the recombination of photo-generated electrons and holes. In

support of this, we present a detailed diagram. These emission bands originate from the radiative recombination of electron-hole pairs via several major pathways, upon photoexcitation by energy higher than the band gap [53–55]. The photocatalysts are excited by incident light, which could lead to charge separation and thus electrons and holes forming in the conduction and valence bands, respectively. These electron-hole pairs can then recombine radiatively or non-radiatively, and the dominant pathway contributes to band edge emission. OVs and Ag⁰ are electron acceptors, so Ag-BiVO₄-OV exhibits the lowest recombination of electrons and holes among the four samples.

UV-Vis DRS was used to investigate the optical absorption characteristics of the samples. The UV-Vis DRS spectrum of Ag-BiVO₄-OV is red-shifted compared to that of BiVO₄-OV. Fig. 6(c) shows that Ag-BiVO₄-OV exhibits a photoresponse from UV through the visible and into NIR wavelengths, which is due to the introduction of OVs [55,56]. The prominent absorption is attributed to the SPR effect of the Ag nanoparticles, which may contribute to the photocatalytic activity of BiVO₄.

The energy band structure of a semiconductor determines its photocatalytic activity. The band gaps of the samples can be estimated from:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where α , h , ν , and E_g are the absorption coefficient, Planck's constant, incident light frequency, and band gap energy, respectively. Values for n of 1 or 4 indicate a direct or indirect band gap material, respectively. The optical transition of BiVO₄ is direct and the value of n is thus 1. From Fig. 6(d), the band gaps of BiVO₄, Ag-BiVO₄, BiVO₄-OV, and Ag-BiVO₄-OV are esti-

Fig. 6. (a) ESR spectra of BiVO₄ and BiVO₄-OV; (b) PL spectra of the samples; (c) UV-Vis DRS spectra of the samples; (d) $(\alpha h\nu)^2$ versus $h\nu$ plots for the samples; (e) Nyquist plots of the samples; (f) I - t curves for Ag-BiVO₄-OV (1), BiVO₄-OV (2), Ag-BiVO₄ (3), and BiVO₄ (4).

estimated to be 2.33, 2.27, 2.16, and 2.08 eV, respectively. The results indicate that the OVs and Ag nanoparticles provide a synergistic enhancement in absorption, both enhancing the absorption ability and broadening the absorption window. This in turn promotes the energy coupling between photons and excitons [57,58].

EIS provided further evidence for the suppression of surface charge recombination through the electron capture effects of the OVs and Ag NPs. EIS can provide information about the photogenerated charge transfer resistance and separation efficiency. Fig. 6(e) shows Nyquist plots of the samples, reflecting the charge transfer process occurring at the electrode-electrolyte interface. A smaller radius indicates a lower charge transfer resistance, so Ag-BiVO₄-OV has a lower charge transfer resistance than the other samples. Photocurrent-time (I - t) curves were also measured to investigate the charge carrier separation capacities of the photocatalysts. A larger photocurrent indicates better electron-hole separation [59]. Fig. 6(f) shows I - t curves of the samples, in which Ag-BiVO₄-OV exhibits the highest photoelectric conversion under simulated solar irradiation. The photocurrent is reproducible and exhibits a steady state during repeated on-off irradiation cycling. The photocurrent of Ag-BiVO₄-OV reaches a maximum of about 17 μA , which is higher than that of the other samples. This demonstrates that the electron-hole separation efficiency and light utilization of Ag-BiVO₄-OV are better than those of the other samples. It is inferred that introducing Ag nanoparticles on the BiVO₄-OV surface inhibits the recombination of electrons and holes, and thus improves the photocatalytic activity.

3.2. RhB degradation by samples under various irradiation conditions

We investigated the photocatalytic properties of the samples. The photocatalytic performances of Ag-BiVO₄ containing different Ag contents were determined by comparing their RhB degradation efficiencies. As shown in Fig. 7(a), increasing Ag content promoted the RhB degradation rate of Ag-BiVO₄ under simulated solar irradiation. More Ag on the BiVO₄-OV surface restrains the photocatalytic conversion, and Ag-BiVO₄-OV exhibits the highest RhB degradation ability. For comparison, BiVO₄, Ag-BiVO₄, BiVO₄-OV, and Ag-BiVO₄-OV were also tested for photocatalytic RhB degradation under the same conditions, as shown in Fig. 7(c). The RhB degradation percentages in the presence of BiVO₄, Ag-BiVO₄, BiVO₄-OV, and Ag-BiVO₄-OV after 100 min of solar of irradiation are 21%, 38%, 88%, and nearly 100%, respectively. The presence of OVs in BiVO₄ extends the photocatalytic response from the UV to NIR region. Fig. 7(e) shows that Ag-BiVO₄-OV has excellent photocatalytic properties. The rate constant for the photodegradation of RhB is usually described by pseudo-first-order kinetics, in terms of the Langmuir-Hinshelwood model equation [60]:

$$\ln(C/C_0) = -kt \quad (2)$$

where C_0 , C , and k are the initial RhB concentration, RhB concentration at time t , and pseudo first-order rate constant, respectively [61]. Kinetic plots of the samples under different conditions are shown in Fig. 7(d) and (f). The high photocatalytic activity of Ag-BiVO₄-OV is attributed to the synergistic effect of plasmonic hot electrons and the OVs. To investigate the stability of the Ag-BiVO₄-OV photocatalyst, cycling experiments were carried out for RhB photodegradation under simulated solar irradiation (Fig. 8(a)). The RhB degradation rate remains stable after four consecutive cycles, indicating that Ag-BiVO₄-OV is stable in the photocatalytic process. The degradation of phenol was also carried out, as shown in Fig. 8(b).

Fig. 7. RhB degradation curves over samples under simulated solar (a, c) and NIR irradiation (e) and $\ln(C/C_0)$ curves of RhB degradation under simulated solar (b, d) and NIR irradiation (f).

Fig. 8. (a) Cycling runs for the photocatalytic degradation of RhB over Ag-BiVO₄-OV under simulated solar irradiation; (b) Photocatalytic degradation of phenol over Ag-BiVO₄-OV under simulated solar irradiation.

This result verifies that Ag-BiVO₄-OV can degrade organic pollutants in the absence of dye sensitization.

3.3. Effects of scavengers and reaction mechanism

Various scavengers were tested to investigate the active species responsible for the degradation of RhB over Ag-BiVO₄-OV. Isopropanol for tested for the presence of $\cdot\text{OH}$, p-benzoquinone for superoxide radical anions ($\cdot\text{O}_2^-$), and EDTA for positive holes (h^+). Fig. 9(a) shows that RhB degradation is significantly lower when a scavenger is added. This indicates that $\cdot\text{O}_2^-$, h^+ , e^+ , and $\cdot\text{OH}$ are generated over the semiconductor under simulated solar irradiation. These active species are considered to act as bridges during the RhB photodegradation.

A reaction mechanism for the RhB degradation is shown in Fig. 9(b). Ag-BiVO₄-OV absorbs UV-Vis-NIR wavelengths. The direct excitation-initiated photocatalytic reaction typically involves: (1) electrons (e^-) in the VB excited to the CB, with the generation of the same number of h^+ ; (2) photogenerated e^-

and h^+ diffuse to the bulk and surface, respectively; (3) surface oxidation mediated by h^+ and/or derivative active species [62]. The photogenerated electrons transfer to the Ag nanoparticles, and adsorbed O_2 is converted to $\cdot\text{O}_2^-$ on the Ag surface [63–66]. $\cdot\text{O}_2^-$ forms via the reaction of adsorbed O_2 and SPR-excited electrons on the Ag nanoparticle surface. Holes generated on the BiVO₄ surface cannot react with $\text{OH}^-/\text{H}_2\text{O}$ to form $\cdot\text{OH}$. This is because the oxidation ability of h^+ in the VB of Bi-containing oxides is weaker than the redox potential of $\cdot\text{OH}$ radicals [$\text{Bi}_2\text{O}_4/\text{BiO}^+$ (+1.00 eV) vs. SHE; $\cdot\text{OH}/\text{H}_2\text{O}$ (+2.27 eV) vs. SHE]. This implies that $\cdot\text{OH}$ is generated by $\cdot\text{O}_2^-$ reacting with H_2O . Thus, h^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$ oxidize RhB adsorbed on the active sites of Ag-BiVO₄-OV [67,68].

4. Conclusions

Ag-deposited BiVO₄ containing oxygen defects was prepared using a simple photocatalytic reduction process. Ag-BiVO₄-OV exhibits efficient light-driven photocatalytic ac-

Fig. 9. (a) RhB degradation by Ag-BiVO₄-OV in the presence of various scavengers under simulated solar irradiation; (b) Proposed RhB degradation mechanism and associated energy levels.

tivity for RhB degradation, which is higher than that of BiVO₄. The improved photocatalytic activity is attributed to: (1) the Ag nanoparticles enhancing photogenerated charge separation, allowing photogenerated electrons and holes sufficient time to participate the photocatalytic reaction; (2) the SPR of Ag nanoparticles in Ag-BiVO₄-OV contributing to its visible light photocatalytic activity; (3) the presence of OV in Ag-BiVO₄-OV widening the absorption into NIR wavelengths; (4) OVs facilitating the trapping and transfer of plasmonic hot electrons to adsorbed O₂, producing $\cdot O_2^-$, while hot holes remaining on the Ag surface oxidize RhB. These findings provide insights into the efficient solar utilization of photocatalysts.

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Graphical Abstract

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Ag nanoparticles deposited on oxygen-vacancy-containing BiVO₄ for enhanced near-infrared photocatalytic activity

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Ag nanoparticles are deposited on BiVO₄ containing oxygen vacancies, which increases the photocatalytic efficiency of the resulting composite compared to the corresponding single component samples. Oxygen vacancies and surface plasmon resonance collectively contribute to electron-hole separation and charge transfer, enhancing the photocatalytic performance.

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银纳米粒子沉积含有氧空位的钒酸铋能够提高其近红外光催化性能

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摘要: 钒酸铋因其独有的廉价、低毒性、热稳定性和高氧化性能等特性而备受瞩目, 是利用太阳能降解污染物、水分解等应用方面最优选择的半导体纳米材料之一。选择表面粗糙多孔尺寸均匀的橄榄状钒酸铋有助于吸附更多的电子受体参与到半导体表面的氧化还原反应当中, 从而提高其光催化活性。另外, 太阳能谱中紫外光占不到5%, 可见光占45%, 与传统的

半导体 TiO_2 材料相比, 钒酸铋禁带宽度在2.4 eV左右, 能较好地吸收太阳光能实现光能转化. 但是太阳光中近一半的光能属于近红外, 不能被传统的纯相钒酸铋所利用. 为了更好地利用太阳能, 可将氧空位缺陷引入到钒酸铋晶体中, 以实现近红外光能的转化利用. 氧空位缺陷在半导体材料中不仅能够吸收近红外光, 在低于导带的位置形成电子传输的桥梁, 而且能够吸附更多的氧分子转化成活性物种. 另一方面, 氧空位缺陷态的引入使半导体钒酸铋材料暴露更多的活性位点, 参与到溶液的氧化还原反应中. 由于钒酸铋光激发的载流子浓度有限, 并且光生电子-空穴容易复合, 本文采用银纳米粒子负载在钒酸铋表面, 利用其等离子共振效应产生的热电子与氧空位缺陷的协同作用, 能够提高其载流子传输速率, 抑制光生电子-空穴复合, 达到更优的光能到化学能转化的目的. 基于此, 本文采用电子自旋共振光谱(ESR), X射线光电子能谱(XPS)和紫外可见光谱(UV-Vis)等手段研究了氧空位缺陷引入到钒酸铋以及Ag纳米粒子负载于橄榄状半导体材料上对光催化降解罗丹明B染料中太阳能驱动活性的影响.

ESR结果证明, 在测试过程中橄榄状钒酸铋材料吸收了更多的电子, 表明存在很多氧空位缺陷. XPS结果表明出现高浓度的吸收氧峰意味着钒酸铋材料上存在大量氧空位缺陷; 银纳米粒子成功负载在具有氧空位缺陷的钒酸铋材料上. UV-Vis结果表明该材料光吸收范围扩展到近红外光范围, 其禁带宽度比传统纯相钒酸铋减小, Ag-BiVO₄-OV样品的导价带位置发生明显变化. 因此, 由于氧空位和银纳米粒子存在于橄榄状钒酸铋主体中, 其光催化降解罗丹明B的效率远远高于纯相钒酸铋样品. 由此可见氧空位缺陷和银纳米粒子的引入使得半导体光催化材料光学性能正效应增加.

关键词: 钒酸铋; 氧空位; 银纳米粒子; 表面等离子共振; 太阳能驱动

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