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Surface-sulfurized Ag₂O nanoparticles with stable full-solar-spectrum photocatalytic activity

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ABSTRACT

Ag₂O has attracted much recent attention, because of its high photocatalytic activity in the ultraviolet (UV)-visible region. However, there have been few reports on the near-infrared (NIR) photocatalytic activity of Ag₂O. This paper reports the high NIR photocatalytic activity of Ag₂O nanoparticles. Ag₂O is unsuitable for application in full-solar-spectrum photocatalysis, because it is unstable under UV irradiation. A surface sulfurization process was carried out to address this issue. Specifically, a layer of Ag₂S₂O₇ nanoparticles was grown on the surface of the Ag₂O nanoparticles, to improve the stability of the Ag₂O photocatalyst and enhance its photocatalytic activity in the UV, visible and NIR regions. The Ag₂O/Ag₂S₂O₇ heterostructure is a stable and efficient full-solar-spectrum photocatalyst. It has potential application in the photodegradation of organic pollutants, and more generally in environmental engineering where full utilization of the solar spectrum is required.

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1. Introduction

Photocatalysts can convert sunlight into chemical energy, for use in the remediation of environmental pollutants and in the production of solar fuels. Photocatalysts therefore offer a “green” technology applicable to environmental and energy-related problems [1–7]. Semiconductors are commonly used as photocatalysts, because solar irradiation can generate free electrons and holes in semiconductors to degrade organic pollutants. The wide bandgaps of photocatalytic semiconductors such as TiO₂, ZnO and ZnS limit their excitation windows to the

ultraviolet (UV) or near UV regions, which therefore limits their efficient use of solar energy.[1,3,4,7–13]. UV wavelengths account for approximately 5% of the solar spectrum, compared with approximately 48% and 54% for visible (Vis) and near-infrared (NIR) (~54%) wavelengths, respectively [2,14–22].

Much research attention has been given to visible-light-active photocatalysts. Studies on visible-light-active photocatalysts have largely focused on broadening the photocatalytic activity of TiO₂ from the UV to Vis regions. This has been achieved by doping cations or anions into TiO₂

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[4,9,13,23–25], integrating semiconductors with narrow bandgaps into TiO_2 [2,6,14,15,20,26–31], and assembling visible-light-active semiconductor nanoparticles onto TiO_2 nanostructures [2,3,12,32–40].

Photocatalysts with NIR activity have also been intensely studied, in attempt to more efficiently utilize the solar spectrum [2,14–19,21,22,41]. Semiconductor nanomaterials with narrow bandgaps or hybrid semiconductor nanostructures with NIR, Vis-NIR and UV-Vis-NIR activity have been reported. Five design principles have generally been followed in attempts to prepare efficient photocatalysts with UV-Vis-NIR activity covering the full solar spectrum: (1) light conversion based on up-conversion luminescence of rare earth materials [17,19,22] or carbon quantum dots [15,42,43], to convert NIR to Vis and UV wavelengths, and subsequently transfer this energy to UV- and Vis-light-active photocatalysts; (2) designing heterostructures with quantum dot-semiconductor hybrid nanostructures to achieve appropriate band alignment [18,21]; (3) modifying the electronic structures of traditional UV-Vis-driven photocatalysts to achieve NIR-active photocatalysts [2,14,16,41]; (4) designing surface plasmonic nanoparticles which effectively separate electron-hole pairs at the interface, as a consequence of their intimate contact with the bulk semiconductor [44–46]; (5) investigating semiconductors with narrow bandgaps and UV-Vis-NIR broad-spectrum activity [14,20]. The last principle is based on the intrinsic NIR photocatalytic activity of semiconductors, and will likely be beneficial in the design and construction of full-solar-spectrum photocatalysts.

Silver oxide (Ag_2O) is a brown powder with a simple cubic crystalline lattice and a lattice parameter of 0.472 nm. Ag_2O has been widely applied in industry [30,47–49]. The bandgap energy of Ag_2O is reported to be 1.2 eV, and the energy level of the conduction band (CB) edge to be +0.2 eV versus the standard hydrogen electrode (SHE) [5,50,51]. Ag_2O is a photosensitive material, so is seldom used as a photocatalytic material, except as a co-catalyst [28,29,37,52–54]. NIR-active photocatalysts based on Ag_2O nanoparticles and $\text{Ag}_2\text{O}/\text{TiO}_2$ composites were recently reported [32, 55]. The narrow bandgap of Ag_2O makes it easily reduced by photo-induced electrons. Thus, these Ag_2O -based photocatalysts are unsuitable for UV wavelengths and thus full-solar-spectrum applications. We previously demonstrated that a $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelt heterostructure was an efficient UV-Vis photocatalyst, but had low stability because of the photosensitivity of Ag_2O [5,53]. Ag_2O can be transformed into $\text{Ag}_2\text{S}_2\text{O}_7$ through a sulfur doping process similar to vulcanization. The resulting $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7/\text{TiO}_2$ nanobelt heterostructure was stable and exhibited high photocatalytic activity under UV and Vis irradiation [53].

Ag_2O is a narrow-bandgap semiconductor, but has received little attention as a NIR photocatalyst [32,55]. In the current study, Ag_2O nanoparticles are shown to have high NIR photocatalytic activity and good UV and Vis photocatalytic activity. Under UV and Vis irradiation, Ag_2O nanoparticles can lose their photocatalytic activity due to the photo-reduction of Ag_2O . To overcome this problem, a surface sulfurization process is used to grow a layer of $\text{Ag}_2\text{S}_2\text{O}_7$ on the surface of Ag_2O nanoparticles, to form heterostructured nanoparticles. The heterojunction

between $\text{Ag}_2\text{S}_2\text{O}_7$ and Ag_2O promotes the UV-Vis-NIR photocatalytic activity of the resulting hybrid photocatalyst, and improves its stability compared with that of Ag_2O . The resulting stable full-solar-spectrum photocatalyst has potential in the photodegradation of organic pollutants in wastewater treatment [32,55].

2. Experimental

2.1. Materials

Sodium hydroxide (NaOH), silver nitrate (AgNO_3) and sodium sulfide (Na_2S) were purchased from China National Medicines Corporation Ltd. All chemicals were used as received without further purification. Deionized water was used throughout all experiments.

2.2. Synthesis of Ag_2O and S-doped Ag_2O nanoparticles

In a typical procedure, 0.29 g of AgNO_3 was dissolved in 100 mL of deionized water, which was stirred magnetically for 30 min. 0.2 mol·L⁻¹ of NaOH solution was added dropwise to the above solution under magnetic stirring until the pH reached 14. The resulting suspension was incubated in the dark for 12 h. The brown-black product was separated by centrifugation, and subsequently washed several times with deionized water. Drying at 50 °C in an oven for 12 h yielded the Ag_2O nanoparticles.

0.1 g of Ag_2O nanoparticles was dispersed in 50 mL of distilled water, which was stirred magnetically for 30 min. 10.77 mL or 43.10 mL of aqueous Na_2S solution (0.01 mol·L⁻¹) was slowly added to the above Ag_2O suspension, to give oxygen: sulfur molar ratios of 1:4 or 1:1, respectively. The resulting mixture was stirred magnetically for 2 h. The S-doped Ag_2O nanoparticles were then separated by centrifugation, washed several times with deionized water, and dried at 50 °C in an oven for 12 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns of the Ag_2O and S-doped Ag_2O samples were recorded using a Bruker D8 Advance powder X-ray diffractometer, using $\text{Cu K}\alpha$ radiation with a wavelength (λ) of 0.15406 nm. A Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) was used to characterize the morphology and particle size of the Ag_2O and S-doped Ag_2O samples. Chemical compositions were investigated using energy-dispersive X-ray spectroscopy (EDS) attached to a transmission electron microscope (TEM). High-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) images were acquired using a JOEL JEM 2100 microscope. UV-Vis-NIR diffuse reflectance spectra (DRS) were recorded using a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu), with an integrating sphere attachment and BaSO_4 as a reflectance standard. Photoluminescence (PL) spectra were recorded using a FLS920 fluorescence spectrometer, at an excitation wavelength of 380 nm. X-ray photoelectron (XPS) spectra were recorded using an ESCALAB

250 instrument.

2.4. Assessment of photocatalytic degradation activity under UV, Vis and NIR irradiation

Methyl orange (MO, 20 mg·L⁻¹) was used as a model dye, to evaluate the activities of the photocatalysts. In a typical experiment, 20 mL of aqueous MO solution and 20 mg of photocatalyst powder were added to a 50 mL beaker. Prior to irradiation, suspensions were magnetically stirred in the dark for 30 min under ambient conditions, to establish adsorption-desorption equilibrium between the dye and catalyst. During photocatalysis experiments, a medium pressure mercury lamp with a maximum emission at 365 nm, a xenon arc lamp with a UV cut-off filter, and an infrared light-emitting diode (LED) lamp with a maximum emission at 850 nm were used as the UV, Vis and NIR light sources, respectively. These light sources provided irradiation powers of 30.4, 25.4 and 56.0 mW·cm⁻², respectively. Aliquots of reaction solution were removed at different irradiation intervals. The aliquots were centrifuged to remove the catalyst, and the MO concentration of the supernatant was determined by monitoring its absorbance with an UV-Vis spectrophotometer (UV-2102PC). Photocatalyst samples were then subjected to six consecutive photodegradation reactions under the same experimental conditions, to investigate their photocatalytic stabilities.

2.5. Photocurrent measurements

To fabricate the photocatalytic electrodes, 1 mL of terpineol suspension of the as-prepared photocatalyst powder (20 mg) was drop-cast on indium tin oxide (ITO) glass, with a coverage of 1 cm². The coated ITO glass was allowed to dry under ambient conditions. The photocurrent was measured using an electrochemical workstation (CHI 750E, CH Instruments Inc., Shanghai, China), using a three-electrode cell configuration with aqueous 1 mol·L⁻¹ Na₂SO₄ as the electrolyte. The reference and counter electrodes were a Ag-AgCl electrode (saturated KCl) and platinum wire, respectively. The photocatalytic working electrode was the anode. An infrared LED lamp with a central emission at 850 nm was used as the NIR light source, and had an intensity of 125.0 mW·cm⁻².

3. Results and discussion

The crystal structures of Ag₂O, Ag₂S, the Ag₂O/Ag₂S₂O₇ heterostructure (degree of doping approximately 25%), and the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure (degree of doping approximately 50%) were investigated by XRD, as shown in Fig. 1. The diffraction peaks at $2\theta = 32.8^\circ, 38.1^\circ, 55.0^\circ$ and 65.6° (Fig. 1(a)) can be assigned to cubic Ag₂O (PDF file No. 75-1532). Pure Ag₂S is obtained after complete sulfur doping (Fig. 1(d)), as indicated by the diffraction peaks at $2\theta = 29^\circ, 31.5^\circ, 33.6^\circ, 34.4^\circ, 34.7^\circ, 36.5^\circ, 36.8^\circ, 37.1^\circ, 37.7^\circ, 40.7^\circ$ and 43.4° (PDF file No. 11-0688). When the Ag₂O nanoparticles react with a lesser amount of Na₂S solution (S: O molar ratio of 1: 4), the resulting solid is a mixture of Ag₂S₂O₇ and Ag₂O nanoparticles. This is

Fig. 1. XRD patterns of Ag₂O (a), Ag₂O/Ag₂S₂O₇ heterostructure (degree of doping = 25%) (b), Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure (degree of doping = 50%) (c), and Ag₂S (d).

confirmed by the diffraction peaks at $2\theta = 24.0^\circ, 28.4^\circ, 30.4^\circ, 40.2^\circ, 44.6^\circ$ and 46.0° in Fig. 1(b), which correspond to Ag₂S₂O₇ (PDF file No. 21-1343). Further sulfur doping (S:O molar ratio of 1:2) yields a mixture of Ag₂S, Ag₂S₂O₇ and Ag₂O nanoparticles, as confirmed by a series of diffraction peaks (the XRD pattern of the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure is shown in Fig. 1(c)). It has previously been shown that Ag₂S₂O₇ is the metastable interphase between Ag₂O and Ag₂S [53].

The morphologies and microstructures of Ag₂O, Ag₂S and the Ag₂O/Ag₂S₂O₇ heterostructure were investigated by SEM, STEM and HRTEM. Fig. 2(a) and (b) show SEM images of Ag₂O nanoparticles obtained through a precipitation method, with particle sizes of 100–500 nm. These Ag₂O nanoparticles were used as a precursor for synthesizing the Ag₂O/Ag₂S₂O₇ heterostructure. During the initial stages of sulfur doping, O atoms on the surface of the Ag₂O nanoparticles are partially substituted by S atoms, forming a Ag₂S₂O₇ layer on the surface of the Ag₂O nanoparticles. The thickness of the Ag₂S₂O₇ layer increases as the reaction proceeds. After the Ag₂S₂O₇ layer grows on the surface of the Ag₂O nanoparticles, the composite nanoparticles retain the morphology of the initial Ag₂O nanoparticles, but with slightly rougher surfaces, as shown in Fig. 2(c) and (d). The increasing thickness of the Ag₂S₂O₇ layer causes it to eventually migrate from the surface of the Ag₂O nanoparticles, because of the stress associated with the lattice mismatch between Ag₂S₂O₇ and Ag₂O (see below). Completely substituting O for S yields single-phase porous Ag₂S nanoparticle aggregates with diameters of 5–10 nm. Their morphology (Fig. 2(e) and (f)) is significantly different from that of the initial Ag₂O nanoparticles. EDS analysis indicates that the Ag₂O nanoparticles consist only of Ag and O, and that the S and O contents increase and decrease during sulfur doping, respectively (Fig. 2(g)–(i)). No O is detected in the Ag₂S nanoparticles.

HRTEM images of the Ag₂O/Ag₂S₂O₇ nanoparticles are con-

Fig. 2. SEM images of Ag₂O (a, b), Ag₂O/Ag₂S₂O₇ heterostructure (c, d) and Ag₂S nanoparticles (e, f) at different magnifications, and corresponding EDS spectra (g, h and i).

sistent with the formation of the Ag₂O/Ag₂S₂O₇ heterostructure (Fig. 3(a)–(c)). Adding a certain amount of aqueous Na₂S to the Ag₂O nanoparticle suspensions causes Ag₂S₂O₇ nanoparticles of

10–30 nm in diameter to grow on the surfaces of the Ag₂O nanoparticles, yielding a Ag₂O/Ag₂S₂O₇ heterostructure. The interplanar distances are 0.236 and 0.260 nm, corresponding to the (200) plane of Ag₂O and the (212) plane of Ag₂S₂O₇, respectively. These results suggest that each nanoparticle is a well-crystallized heterostructure composed of a large Ag₂O nanoparticle and a Ag₂S₂O₇ domain. STEM images and EDS maps also indicate that the Ag₂O/Ag₂S₂O₇ heterostructure is composed of O, Ag and S (Fig. 3(d)).

The photocatalytic degradation of aqueous MO in the presence of Ag₂O, Ag₂S, the Ag₂O/Ag₂S₂O₇ heterostructure, and the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure was investigated under UV, Vis and NIR irradiation, as a function of irradiation time (Fig. 4(a)–(c)). The photocatalytic activities of Ag₂O, Ag₂S, the Ag₂O/Ag₂S₂O₇ heterostructure, and the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure under UV irradiation are discussed first (Fig. 4(a)). After 25 min of UV irradiation, the amounts of MO degraded in the presence of Ag₂O, Ag₂S, the Ag₂O/Ag₂S₂O₇ heterostructure, and the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure are 32.9%, 27.9%, 88.1% and 72.4%, respectively. The Ag₂O/Ag₂S₂O₇ heterostructure exhibits much higher photocatalytic activity than those of Ag₂O, Ag₂S and the Ag₂O/Ag₂S₂O₇/Ag₂S heterostructure, for MO degradation under UV irradiation. This is because the photocatalytic stability of the Ag₂O/Ag₂S₂O₇ heterostructure under UV irradiation is enhanced by the sulfur doping [53]. We previously demonstrated that the UV photocatalytic activity of a Ag₂O/TiO₂ heterostructure decreased to 60% after four consecutive 96 min photodegradation experiments [5]. This was because Ag₂O was readily degraded to metallic Ag and O₂ under UV irradiation. Fig. 4(d) shows that after six consecutive 25 min photodegradation experiments, the photocatalytic degradation rate for MO by the Ag₂O/Ag₂S₂O₇ heterostructure decreases by only 10%. The

Fig. 3. (a, b) TEM images of the Ag₂O/Ag₂S₂O₇ heterostructure at different magnifications; (c) HRTEM image of the Ag₂O/Ag₂S₂O₇ heterostructure; (d) STEM image and EDS elemental maps of the Ag₂O/Ag₂S₂O₇ heterostructure.

Fig. 4. Photocatalytic degradation of MO in the presence of Ag_2O , Ag_2S and the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure under UV (a), Vis (b) and NIR (c) irradiation. Irradiation-time dependence of photocatalytic degradation of aqueous MO in the presence of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure, during consecutive photocatalytic experiments under UV (d), Vis (e) and NIR (f) irradiation.

$\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure therefore exhibits stable and efficient photocatalytic performance.

The photocatalytic activities of Ag_2O , Ag_2S , the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure, and the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7/\text{Ag}_2\text{S}$ heterostructure under Vis irradiation are discussed next (Fig. 4(b)). After 140 min of Vis irradiation, the amounts of MO degraded in the presence of Ag_2O , Ag_2S , the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure, and the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7/\text{Ag}_2\text{S}$ heterostructure are 79.3%, 26.5%, 92.0%, and 57.5%, respectively. The $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure exhibits much higher photocatalytic activity than Ag_2O , similar to the result under UV irradiation. Ag_2O -based photocatalysts exhibit high photocatalytic activity under Vis irradiation. However, their structure and photocatalytic activity under Vis irradiation can only be maintained after a partial metallic Ag layer forms on their surface during the photodegradation of organic molecules [51]. This results in decreasing photocatalytic activity of Ag_2O nanoparticles under Vis irradiation. In contrast, assembling $\text{Ag}_2\text{S}_2\text{O}_7$ on the Ag_2O surface greatly improves the Vis photocatalytic performance of the resulting $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure (Fig. 4(b)). The photocatalytic performance of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure under Vis irradiation decreases by <5% after six consecutive 25 min photodegradation experiments (Fig. 4(e)). Thus, the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure exhibits good photocatalytic activity and stability under Vis irradiation.

The photocatalytic activities of Ag_2O , Ag_2S , the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure, and the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7/\text{Ag}_2\text{S}$ heterostructure under NIR irradiation are finally discussed. Ag_2O exhibits good NIR photocatalytic activity, with 100% MO degradation after 120 min (Fig. 4(c)). After complete sulfur doping, Ag_2S exhibits very low NIR photocatalytic activity

(23.9%). This may be due to the poor crystallinity of Ag_2S , despite its low bandgap energy (0.9–1.05 eV) [56–58]. The low crystallinity of Ag_2S also results in the low MO degradation efficiency of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7/\text{Ag}_2\text{S}$ heterostructure. Fig. 4 shows that the photocatalytic activity of the $\text{Ag}_2\text{O}(\text{S})$ heterostructure decreases dramatically with increasing S doping. MO is completely degraded by the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure within 140 min under NIR irradiation, which is slightly longer than that for Ag_2O (120 min) (Fig. 4(c)). Fig. 4(f) shows that the NIR photodegradation of MO by the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure is very stable, with no decrease in photocatalytic activity observed after six consecutive 25 min photodegradation experiments. The good photocatalytic performance may be attributed to the favorable band alignment of Ag_2O and $\text{Ag}_2\text{S}_2\text{O}_7$. This could enhance the separation of photoinduced carriers, and enhance the band structure of Ag_2O and $\text{Ag}_2\text{S}_2\text{O}_7$. A control experiment for NIR activity was carried out using colorless 2,4-dichlorophenol. The intensity of all 2,4-dichlorophenol peaks decreases with increasing NIR irradiation time. The absence of any new peaks indicates that the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure degrades 2,4-dichlorophenol without forming any by-products. The NIR photon energy is insufficient to photo-reduce Ag_2O . Thus, no XRD peaks of Ag are observed after NIR irradiation in the presence of Ag_2O after six consecutive photocatalytic experiments.

The above results suggest that the stable efficient UV-Vis-NIR photocatalytic activity of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure results from three factors: (1) the broad-spectrum photocatalytic activity originating from the narrow bandgap of Ag_2O ; (2) the high photocatalytic activity of the heterostructure contributes to the efficient formation of photo-induced carriers,

Fig. 5. UV-Vis-NIR absorption spectra (a) and time-dependent photocurrent responses (b) (0.06 V bias voltage, 125.0 mW·cm⁻² NIR LED source) of Ag₂O, Ag₂S, and the Ag₂O/Ag₂S₂O₇ heterostructure. (c) Schematic of photo-induced charge transfer and separation at the interface of the Ag₂O/Ag₂S₂O₇ heterostructure.

because of the favorable band alignment of Ag₂O and Ag₂S₂O₇; (3) the chemical stability of the Ag₂O/Ag₂S₂O₇ nanoparticles results from the stable Ag₂S₂O₇ layer on the Ag₂O nanoparticle surface.

The UV-Vis-NIR absorption spectrum of the Ag₂O/Ag₂S₂O₇ heterostructure was derived from its diffuse reflectance spectrum, and was used to compare its absorption characteristics. Fig. 5(a) shows the absorption spectra of Ag₂O, Ag₂S, and the Ag₂O/Ag₂S₂O₇ heterostructure. The brown Ag₂O powder absorbs strongly in the UV-Vis-NIR range (200–1000 nm). This absorption is the intrinsic absorption band derived from its small bandgap (1.2 eV). The optical bandgap of the Ag₂O nanoparticles can be estimated from the UV-Vis-NIR absorption spectrum [5,51,59]. After sulfur doping, the black Ag₂O/Ag₂S₂O₇ heterostructure exhibits slightly stronger absorption. These results confirm that Ag₂O and the Ag₂O/Ag₂S₂O₇ heterostructure both have broad absorption from the UV to NIR regions. This indicates that Ag₂O may act as an efficient UV-Vis-NIR sensitizer, leading to the favorable photocatalytic activity of the Ag₂O/Ag₂S₂O₇ heterostructure. After complete sulfur doping, the absorption edge of Ag₂S red-shifts to approximately 1350 nm. This illustrates that Ag₂S nanoparticles strongly absorb in the NIR region. Previous studies have shown that Ag₂S absorbs NIR wavelengths to generate heat [60–63], so the NIR photocatalytic activity of Ag₂S is very low.

The photo-induced charge transfer properties of Ag₂O, Ag₂S, and the Ag₂O/Ag₂S₂O₇ heterostructure were then studied under NIR irradiation (Fig. 5(b)). The NIR excitation of Ag₂O and the Ag₂O/Ag₂S₂O₇ heterostructure produces electron-hole pairs (because of their narrow bandgaps of 1.2 and 2.24 eV, respectively), and thus NIR photocatalytic activity. Ag₂O and Ag₂O/Ag₂S₂O₇ generate photocurrents with reproducible responses to on-off cycles under NIR irradiation, indicating effective charge transfer and electron collection at the electrode. Ag₂O generates the highest photocurrent density, which is consistent with its highest NIR photocatalytic activity among the four tested photocatalysts. Hydroxyl radicals (•OH) are a key active species in the photodegradation of organic pollutants. The degradation of •OH under NIR irradiation in presence of

the Ag₂O/Ag₂S₂O₇ heterostructure is shown in Fig. 6. The PL emission peak of 2-hydroxyterephthalic acid (HTA) is observed upon NIR irradiation, and its intensity increases with increasing irradiation time. This indicates that •OH are produced under NIR irradiation, and that their concentration increases with increasing irradiation time. Thus, the Ag₂O/Ag₂S₂O₇ heterostructure exhibits stable and efficient UV-Vis-NIR photocatalytic activity.

A mechanism for the stable efficient photocatalytic activity of the Ag₂O/Ag₂S₂O₇ heterostructure is proposed, as shown in Fig. 5(c). The Ag₂O nanoparticle is excited to produce holes (h⁺) and electrons (e⁻) under irradiation. The band positions of Ag₂S₂O₇ and Ag₂O result in photogenerated electrons in the CB of Ag₂O being injected into the CB of Ag₂S₂O₇, while photogenerated holes in the valence band (VB) of Ag₂S₂O₇ are injected into the VB of Ag₂O. The Ag₂S₂O₇ nanoparticles on the surface of the Ag₂O nanoparticles efficiently capture electrons, preventing electron-hole recombination and the reduction of Ag₂O to Ag.

4. Conclusions

The full-solar-spectrum photocatalytic activities of Ag₂O

Fig. 6. •OH trapping PL spectra of Ag₂O/Ag₂S₂O₇ in 2-hydroxyterephthalic acid solution under NIR irradiation.

nanoparticles and a $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure are demonstrated. The Ag_2O nanoparticles effectively harness UV, Vis, and NIR wavelengths, because of their narrow bandgap. Sulfur doping of Ag_2O results in the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure, which retains the NIR, UV and Vis photocatalytic activity of the Ag_2O . The stability of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure is dramatically improved compared with that of Ag_2O . The stability and photocatalytic activity of the $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure results from the favorable band alignment between Ag_2O and $\text{Ag}_2\text{S}_2\text{O}_7$, and the excellent chemical stability of $\text{Ag}_2\text{S}_2\text{O}_7$ under UV and Vis irradiation. The $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure therefore has potential in photodegradation and solar-cell applications, where full utilization of the solar spectrum is required.

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Graphical Abstract

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Surface-sulfurized Ag_2O nanoparticles with stable full-solar-spectrum photocatalytic activity

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The full-solar-spectrum photocatalytic activity of $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructure is demonstrated. $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructures can not only keep NIR photocatalytic activity, but also enhance UV and Vis photocatalytic activity of Ag_2O . Most importantly, the stability of $\text{Ag}_2\text{O}/\text{Ag}_2\text{S}_2\text{O}_7$ heterostructures is dramatically improved.

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Ag₂S₂O₇/Ag₂O纳米颗粒异质结构的制备及其太阳光全光谱光催化降解应用

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摘要: Ag₂O是优良的感光材料, 很少作为光催化材料, 而常被用作光催化材料的共催化剂. 此外, 由于Ag₂O禁带宽度窄, 且可有效吸收近红外光, 因而不能用于全太阳光谱的光催化应用中. 同时很少被用作NIR催化剂. 本文中不仅研究了纳米Ag₂O颗粒的UV-Vis光催化性能, 而且还系统探究了其NIR光催化活性. 由于在紫外线和可见光的照射下, Ag₂O纳米颗粒易发生光还原失活, 因而对Ag₂O表面硫化处理, 使其表面上生长Ag₂S₂O₇层以形成Ag₂S₂O₇/Ag₂O异质结, 探究了该异质结UV-Vis光催化活性及其光催化循环稳定性; 同时, 考察了其近红外光催化及其重复使用性能.

利用沉淀法成功制备了Ag₂O纳米颗粒, 并通过在其表面部分硫化处理得到Ag₂S₂O₇, 成功构筑Ag₂S₂O₇/Ag₂O异质结构, 并研究了该Ag₂S₂O₇/Ag₂O异质结构UV-Vis-NIR光催化降解有机污染物性能. 研究表明, Ag₂O纳米颗粒在光子能量较低的NIR照射条件下具有较强的光催化活性, 但UV-Vis照射下, 虽然Ag₂O具有光催化活性, 但易发生光还原生成单质银, 降低其光催化稳定性; Ag₂S₂O₇/Ag₂O纳米异质结, 虽然在UV-Vis-NIR范围内光催化活性略低于Ag₂O, 但稳定性显著提高, 总体来看, Ag₂S₂O₇/Ag₂O异质结构在全光谱催化方面更具优势. 这主要是由于Ag₂O表面部分硫化得到的Ag₂S₂O₇纳米颗粒, 且二者之间能带匹配促进了光生载流子分离, 同时Ag₂O表面的Ag₂S₂O₇颗粒直接吸收能量较高的UV-Vis, 进而保护内部Ag₂O, 抑制了其自身还原, 可显著提高Ag₂S₂O₇/Ag₂O异质结在UV-Vis-NIR催化活性及稳定性.

实验结果分析表明, Ag₂S₂O₇/Ag₂O异质结纳米颗粒在UV-Vis-NIR条件下均具有稳定且高效的光催化活性, 其主要原因为: (1)具有窄带隙的Ag₂O可有效拓宽该异质结的光谱吸收; (2)Ag₂S₂O₇/Ag₂O异质结能带匹配可有效促使光生载流子分离; (3)Ag₂O颗粒表面的Ag₂S₂O₇纳米颗粒可有效提高Ag₂S₂O₇/Ag₂O异质结纳米颗粒的光化学稳定性, 尤其是在UV-Vis条件下的化学稳定性. Ag₂O纳米颗粒受到光照(UV-Vis-NIR)激发后产生电子-空穴对, 由于Ag₂S₂O₇与Ag₂O能带位置的匹配,

Ag₂O导带的光生电子注入Ag₂S₂O₇的导带; 而Ag₂S₂O₇价带的光生空穴注入Ag₂O的价带. Ag₂O表面的Ag₂S₂O₇颗粒可有效捕捉电子, 从而阻止Ag₂O产生的电子-空穴对复合, 进而提高光催化活性; 同时当光子能量较高(UV以及部分短波长的Vis)时, Ag₂O表面的Ag₂S₂O₇颗粒直接吸收该部分光能, 进而保护内部Ag₂O发生自身还原, 因此, Ag₂S₂O₇/Ag₂O异质结纳米颗粒在UV, Vis及NIR条件下均具有稳定且高效的光催化活性, 在高效利用全光谱光催化降解有机污染物方面具有较大的潜力.

关键词: 全光谱太阳光; Ag₂O纳米颗粒; Ag₂O/Ag₂S₂O₇; 异质结; 光催化

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