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Article

Sonochemical fabrication, characterization and enhanced photocatalytic performance of $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrods

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ABSTRACT

$\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrods, with lengths of 0.2–1 μm and diameters of 20–30 nm, were fabricated by a facile sonochemical route. The as-synthesized products were intensively investigated by a series of physicochemical characterizations, such as N_2 physical adsorption, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, photoluminescence spectroscopy and photocurrent response measurements. Ultrasonic irradiation yields an obvious improvement in the photocatalyst texture, for example, an increase in crystallinity and surface area. Moreover, sonochemically fabricated $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ microrods display strong visible light absorption and a high transient photocurrent response. The produced intimate $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ interface between Ag_2S and Ag_2WO_4 crystal phases largely promotes the separation of photogenerated holes and electrons. High photocatalytic activity and stability were obtained over $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrods. The dye degradation rate constant of $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ was 4.7 times and 29.8 times higher than that of bare Ag_2WO_4 and Ag_2S , respectively.

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1. Introduction

The optimal way to deal with the organic pollutants in wastewater is an important issue for environmental protection. Semiconductor photocatalytic technology displays promising applications in the decomposition of organic compounds in polluted water [1–4]. The photocatalyst TiO_2 has been widely used in the degradation of various pollutants. However, the wide band gap energy (~ 3.2 eV) of TiO_2 leads to its low application efficiency of solar light because TiO_2 can only absorb the

small ultraviolet light fraction of solar light (about 2%–3%) [5–8]. Therefore, many studies have focused on developing visible light response semiconductor photocatalysts with a narrow band gap [9–11].

Among the numerous narrow band gap photocatalysts, although pure Ag_2S displays poor photocatalytic performance in the degradation of pollutants, as a narrow band gap and stable direct semiconductor, Ag_2S exhibits excellent performance in accelerating the electron transfer [12]. The formation of a heterojunction can highlight this effect [13–16]. For example, the

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heterojunctions of $\text{Ag}_2\text{Mo}_3\text{O}_{10}$ - Ag_2S [14], TiO_2 - Ag_2S [18], ZnS - Ag_2S [19] and NiO - Ag_2S [20] display superior photocatalytic performance. As a novel and stable semiconductor material, Ag_2WO_4 has been widely used in catalysis, sensing, and antibacterial and photoluminescence (PL) applications [21–24]. However, as a photocatalyst, Ag_2WO_4 can only absorb UV light owing to its large band gap (~ 3.5 eV). Additionally, Ag_2WO_4 exhibits poor stability because photocorrosion readily takes place over Ag-based semiconductors with light illumination, if no sacrificial reagent is present [25].

Selecting a suitable synthetic route is the key to a successful photocatalyst because the textural properties and photocatalytic performance are determined by how they are prepared. A nanostructure/microstructure is highly desirable in photocatalyst synthesis. Recently, the application of high-intensity ultrasound or sonochemistry has provided a green and effective synthetic strategy for nanostructured photocatalyst that is often unavailable with the traditional methods. In the sonochemical synthesis, the acoustic cavitation effect is able to generate extraordinary physicochemical conditions, for example, high local temperatures (5000 °C), high pressures (100 MPa), and rapid cooling and heating rates ($> 10^{10}$ °C/s). These unusual physicochemical conditions could greatly benefit the fabrication of photocatalysts with novel nanostructures [26–30].

In the present work, $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrods were fabricated by a facile sonochemical route and exhibited excellent photocatalytic activity and stability.

2. Experimental

2.1. Synthesis of Ag_2S , Ag_2WO_4 and $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$

All chemicals were of analytical grade obtained from the Shanghai Chemical Company and were used without further purification. For the sonochemical fabrication of $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ (denoted as U- $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$), 10 mmol AgNO_3 was dissolved in 20 mL of deionized (DI) water under stirring, to obtain solution A. Next, 2.5 mmol Na_2S was dissolved in 20 mL of DI water, and the resulting solution was added dropwise to solution A. After stirring for 3 h, 20 mL Na_2WO_4 solution (2.5 mmol) was added dropwise to the Ag_2S liquid suspension. Then, a VOSHIN 10-501D ultrasonic generator connected by a $\Phi 10$ luffing rod (selected ultrasonic power was 10%, each ultrasonication was 5 s, with a rest period of 2 s) was used to irradiate the mixture for 1 h. After the irradiation, the suspensions were further stirred for 3 h. The resulting powder was collected by filtration, and washed with DI water and ethanol for several times. Finally, U- $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ products were obtained after drying at 70 °C for 4 h. U- Ag_2S and U- Ag_2WO_4 were fabricated by the same method.

To evaluate the effects of ultrasonic irradiation, the corresponding Ag_2S and Ag_2WO_4 samples were fabricated by a common precipitation method, and $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composites were fabricated by the successive precipitation method. For example, for the synthesis of the $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite, 10 mmol AgNO_3 was dissolved in 20 mL of DI water under stirring, to obtain solution A. Na_2S (2.5 mmol) was dissolved in 20 mL of

DI water, and the resulting solution was added dropwise to solution A. After stirring for 3 h, 20 mL Na_2WO_4 solution (2.5 mmol Na_2WO_4) was added dropwise to the Ag_2S liquid suspension and was further stirred for 3 h. The resulting powder was collected by filtration and washed several times with DI water and ethanol. Finally, $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ products were obtained after drying at 70 °C for 4 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded at a scanning rate of $0.05^\circ/\text{s}$ using a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA with a $\text{Cu } K_\alpha$ radiation source ($\lambda = 0.15418$ nm). The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was measured on a Micromeritics ASAP2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 120 °C for 1 h before nitrogen adsorption measurement. The S_{BET} was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. Scanning electron microscopy (SEM) images were collected using an MLA650F scanning electron microscope and were used to investigate the sample morphologies. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected using a TECNAI G2F20 microscope. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded using a UV-vis spectrophotometer (UV-2550, Shimadzu). PL emission spectra were obtained with excitation at 325 nm using an F-4600 spectrometer. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 XPS system with a monochromatic $\text{Al } K_\alpha$ source and a charge neutralizer. Photocurrent measurements were performed on a CHI 660E electrochemical work station (Chenhua Instrument, China) in a conventional three electrode configuration with a Pt foil as the counter electrode and a Ag/AgCl (saturated KCl) as the reference electrode. A 500-W Xe lamp served as a light source. 0.1 mol/L Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 10 mg of the as-prepared photocatalyst and 0.5 mL Nafion dispersing reagent were added in 5 mL absolute ethanol and sonicated for 30 min. The slurry was then spread on a $1.0\text{-cm} \times 1.0\text{-cm}$ indium-tin oxide (ITO) glass substrate and dried in air. The photoresponse of the samples, as light on and light off, was measured at 0.0 V.

2.3. Photocatalytic activity

The photocatalytic activities of the as-prepared samples were determined by the degradation of methylene blue (MB) and methyl orange (MO) dyes in aqueous solution. The photocatalytic reaction was carried out in a photochemical reactor (XPA, Xujiang Electromechanical Plant, Nangjing). The light source was a 400-W metal halide lamp. In each test, 30 mg of the as-prepared samples were added into 60 mL of 20 mg/L MB or MO aqueous solution. Then, the suspension was stirred in the dark for 40 min to achieve the adsorption-desorption equilibrium prior to visible light irradiation. During the degra-

dation process, the reaction temperature was maintained at 20 °C by the circulation of water. After fixed irradiation intervals, ~2-mL aliquots of suspension were sampled, and the solids were removed by centrifugation. The MB and MO concentration of the clear upper layer was determined by UV-vis spectrophotometry.

3. Results and discussion

3.1. Texture analysis

The phase composition and crystal properties of the samples were analyzed by XRD. Fig. 1(a) shows the XRD patterns of the as-prepared Ag₂S, Ag₂WO₄ and Ag₂S/Ag₂WO₄ samples. The Ag₂S sample corresponded to the monoclinic phase of Ag₂S (JCPDS 14-0072). The main characteristic peaks of Ag₂WO₄ at 16.7°, 30.2°, 31.5°, 32.9°, 45.2°, 54.5° and 58.1° can be indexed to the (011), (002), (231), (400), (060), (233) and (262) crystal planes of Ag₂WO₄ (JCPDS 70-1719) with orthorhombic phase. The observed main diffraction peaks of Ag₂S/Ag₂WO₄ are the diffraction peaks of Ag₂WO₄. Additionally, a series of weak diffraction peaks at $2\theta = 20^\circ$ – 30° and 35° – 45° for Ag₂S are observed. Fig. 1(b) shows the XRD patterns of the ultrasonically prepared U-Ag₂S, U-Ag₂WO₄ and U-Ag₂S/Ag₂WO₄ samples. Careful observation shows that ultrasonic irradiation exerts an obvious influence on the crystal structure. For U-Ag₂S, after ultrasonic irradiation, the diffraction peaks at 21.2°, 24.6°, 27.6°, 30.3°, 32.8°, 35.1°, 37.3°, 39.5°, 43.4°, 45.3° and 50.6° can be indexed to the (102), (112), (210), (202), (212), (004), (300), (222), (204), (214) and (400) crystal planes of Ag₈S₄(O₄) (JCPDS 032-1023) with tetragonal phase. The unique physico-chemical conditions generated by the acoustic cavitation effect could cause the O to enter the Ag₂S lattice. On the whole, the U-Ag₂S/Ag₂WO₄ maintained the Ag₂WO₄ crystal phase structure. However, the intensity of the characteristic peaks at 30.3°, 32.9° and 45.2° was obviously increased with respect to Ag₂S/Ag₂WO₄. This could arise from the ultrasonic irradiation resulting in an increase in crystallinity.

The average crystallite size of the as-prepared samples was

Table 1

The average crystallite sizes and specific surface areas of the samples.

Sample	Specific surface area (m ² /g)	Crystal size (nm)
Ag ₂ S	2.7	36.6
U-Ag ₂ S	4.3	23.4
Ag ₂ WO ₄	3.9	38.7
U-Ag ₂ WO ₄	5.7	13.2
Ag ₂ S/Ag ₂ WO ₄	3.5	53.3
U-Ag ₂ S/Ag ₂ WO ₄	5.6	47.1

estimated using the Scherrer equation. The strongest diffraction peaks, ~39.5° for U-Ag₂S and ~31.5° for the other samples, were used in this calculation. Table 1 shows that ultrasonic irradiation obviously decreased the average crystallite size of the samples. The surface area of the fabricated samples was determined by nitrogen physical adsorption and the obtained results are shown in Table 1. Obviously, ultrasonic irradiation has a distinct influence on the surface area. A slight increase in surface area after ultrasonic irradiation was observed, which could arise from the ultrasonic irradiation, improved the dispersion and decreased the crystallite sizes.

3.2. Morphology analysis

The morphologies of the prepared samples were characterized by SEM and the results were shown in Fig. 2. The inset photographs in the corresponding images display the color of the samples. Fig. 2(a) shows that pure Ag₂WO₄ exhibits micro-rod morphology with lengths of 0.2–1 μm and diameters of 20–30 nm. After ultrasonic irradiation, some cracks were observed in the U-Ag₂WO₄ microrods (Fig. 2(b)). Fig. 2(c) suggests that pure Ag₂S shows no special morphology. The Ag₂S sample was composed of small irregular particles. Compared with Ag₂S, U-Ag₂S (Fig. 2(d)) has a rounder and smoother surface, and the connections among particles become closer. Fig. 2(e) and (f) show the SEM images of Ag₂S/Ag₂WO₄ and U-Ag₂S/Ag₂WO₄, respectively. Over Ag₂S/Ag₂WO₄, many segregated nanoparticles (NPs) were attached on the surface of a micro-

Fig. 1. XRD patterns of the as-prepared samples.

Fig. 2. The SEM images of the as-prepared samples. (a) Ag_2WO_4 ; (b) $\text{U-Ag}_2\text{WO}_4$; (c) Ag_2S ; (d) $\text{U-Ag}_2\text{S}$; (e) $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$; (f) $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$.

rod. As for $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$, the attached NPs fused into fluffy particles. The inset photographs indicate that the colors of Ag_2WO_4 , Ag_2S and $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$ are white, black and light brown, respectively. Ultrasonic irradiation slightly changed the color of samples. The colors for Ag_2WO_4 , Ag_2S and $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$ changed to light brown, deep brown and brown, respectively. Ultrasonic irradiation changed the texture and color, which will certainly result in variations in the surface area and light absorption.

Fig. 3 shows the TEM images for the $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$ composite. Fig. 3(a) clearly shows that the Ag_2S NPs were attached on the smooth surface of the Ag_2WO_4 microrod. We selected one of the attached nanoparticles to analyze with high resolution HRTEM, and the result is shown in Fig. 3(b). Three clear lattice spacings of approximately 0.297, 0.255 and 0.227 nm correspond to the (202), (004) and (222) planes of Ag_2S , respectively, which confirms the high crystallinity of the attached Ag_2S NPs. Fig. 3(c) shows the HRTEM image of one of the Ag_2WO_4 microrods. In this image, two lattice spacings of ap-

proximately 0.297 and 0.284 nm are clearly observed, which are attributed to the (002) and (231) planes of Ag_2WO_4 , respectively. Furthermore, an intimate interface between Ag_2S and Ag_2WO_4 was observed from the TEM images. The good interfacial contact in $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$ composite could promote the transfer of charge carriers between the Ag_2WO_4 host photocatalytic material and the Ag_2S co-catalyst, thus promoting the photocatalytic performance.

3.3. XPS analysis

The surface element composition and chemical state of $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$ were evaluated by XPS. As shown in Fig. 4(a), the XPS survey spectrum proves the co-existence of Ag, S, W and O elements. In the high resolution XPS spectrum of Ag 3d (Fig. 4(b)), the two separate peaks at 373.3 and 367.3 eV are assigned to the Ag^+ for Ag 3d_{3/2} and Ag 3d_{5/2} [17], respectively. Fig. 4(c) shows the high resolution spectrum of O 1s. The peaks at 530.6 and 529.7 eV correspond to the lattice oxygen in Ag_2WO_4 and absorbed oxygen [31], respectively. The peak at 531.8 eV is assigned to the chemisorbed oxygen in S–O [31]. The band energies of S 2p (Fig. 4(d)) at 168.2 and 167.1 eV arise from the S in Ag–S–O [32,33]. This suggests that an $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$ heterojunction could be formed between the Ag_2S NPs and Ag_2WO_4 microrods. The two peaks at 162.3 and 161.0 eV can be assigned to S 2p_{1/2} and S 2p_{3/2} [16], respectively. Fig. 4(e) shows the W 4f spectrum, and the two peaks at 36.6 and 34.4 eV are assigned to W 4f_{7/2} and W 4f_{5/2} for W⁶⁺ in Ag_2WO_4 , respectively.

3.4. Light absorption properties

UV-vis DRS was used to evaluate the light absorption behavior of the samples in the UV to visible light range ($\lambda = 250\text{--}800\text{ nm}$). Fig. 5(a) shows that the absorption edge of pure Ag_2WO_4 is at $\sim 380\text{ nm}$ and its light absorption is focused in the ultraviolet region. Ag_2S displays obvious ultraviolet and visible light absorption and its absorption is mainly at $\sim 450\text{ nm}$. After the introduction of Ag_2S , the absorption edge of $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$ samples shows a red-shift and an increase in the visible light absorption appears. Comparing the absorption spectrum of $\text{Ag}_2\text{S/Ag}_2\text{WO}_4$ with that of $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$, we can observe that the ultrasonic treatment obviously shifts the light absorption

Fig. 3. TEM (a) and HRTEM (b, c) images of the $\text{U-Ag}_2\text{S/Ag}_2\text{WO}_4$ sample.

Fig. 4. XPS spectra of the as-prepared U-Ag₂S/Ag₂WO₄. (a) Survey spectrum; (b) Ag 3d; (c) O 1s; (d) S 2p; (e) W 4f.

Fig. 5. (a) UV-vis diffuse reflectance spectra of the as-prepared samples; (b) $(\alpha h\nu)^2$ versus $h\nu$ for determining the optical band gap of the as-prepared samples.

edge to the visible light range and, additionally, greatly enhances its light absorption ability. The optical band gap energy of a semiconductor can be estimated from the Tauc plot (i.e., the curve of the converted $(\alpha h\nu)^n$ versus $h\nu$ from the UV-vis spectrum, in which α , h and ν are the absorption coefficient, Planck constant and light frequency, respectively, and $n = 2$ for a direct band gap material and $n = 1/2$ for an indirect band gap material [34]). Here, the value of n was selected as 2 and Fig. 5(b) shows a good linear fit when the value $n = 2$ was applied. The E_g values of U-Ag₂WO₄ and U-Ag₂S were thus determined to be 3.29 and 2.19 eV, respectively, by measuring the x-axis intercept of the extrapolated line from the linear regime of the curve. The loading of Ag₂S resulted in a decrease in the E_g . The value of E_g for U-Ag₂S/Ag₂WO₄ was determined to be 1.88 eV.

3.5. PL properties

PL analysis was performed to investigate the separation efficiency of the photogenerated electrons and holes. Fig. 6 displays the typical PL spectra of Ag₂WO₄, Ag₂S/Ag₂WO₄ and U-Ag₂S/Ag₂WO₄. The emission peak appearing at 468 nm could be attributed to the radiative recombination process of the photo-excited carriers in Ag₂WO₄. Fig. 6 shows that pure Ag₂WO₄ displays the strongest intensity PL peak among the three samples, indicating that the highest recombination probability of the charge carrier is in Ag₂WO₄. The positions of the emission band for Ag₂S/Ag₂WO₄ and U-Ag₂S/Ag₂WO₄ are similar to Ag₂WO₄, while the PL peak intensity of U-Ag₂S/Ag₂WO₄ is

Fig. 6. PL spectra of Ag_2WO_4 , $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ and $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$.

the weakest, indicating that both the coupling of Ag_2S and ultrasonic irradiation could promote the separation of charge carriers.

3.6. Photocurrent responses

The charge separation efficiency was further investigated by the transient photocurrent response. The transient photocurrent responses were monitored by electrodes consisting of Ag_2S , Ag_2WO_4 , $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ and $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ samples. Fig. 7 shows the comparison of the photocurrent–time (I – t) curves of the samples with several on–off cycles under intermittent irradiation from a Xe lamp. Fast photocurrent responses were observed in the samples when the light was turned on, and the photocurrent rapidly decayed when the light was turned off. This indicates that most of the photogenerated electrons are transported back to the contact across the sample to produce photocurrent under Xe lamp irradiation. $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ and $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ exhibited a much higher photocurrent intensity than that of Ag_2WO_4 and Ag_2S . It is proposed that the stronger photocurrent intensity reveals a higher separation efficiency of electrons and holes. This result further demon-

Fig. 7. Transient photocurrent responses of Ag_2S , Ag_2WO_4 , $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ and $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ samples in 0.1 mol/L Na_2SO_4 aqueous solution under irradiation from a Xe lamp.

strates that a noticeable improvement in the separation of photogenerated electrons and holes, realized by coupling of Ag_2S and ultrasonic irradiation, could also largely benefit the boosting of photocatalytic activity.

3.7. Photocatalytic performance

MB was used as the photodegradation target under metal halide lamp illumination. Fig. 8(a) and (b) shows that the addition of Ag_2S as a photocatalyst did not result in an obvious degradation reaction for MB, suggesting the poor photocatalytic activity of Ag_2S . Ag_2WO_4 displays an obvious photocatalytic activity for MB decomposition. The highest degradation rate of MB (99%) was observed over $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$. Fig. 8(c) shows the degradation dynamics curves of MB over the as-prepared samples. The largest degradation rate constant over $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ was 0.149 min^{-1} , which is 4.7 times and 29.8 times higher than that of bare Ag_2WO_4 (0.032 min^{-1}) and Ag_2S (0.005 min^{-1}), respectively. Fig. 8(d) shows the UV-vis absorption spectra of MB with different reaction times in the presence of $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$.

The photocatalytic activities of the as-prepared samples were further evaluated by the degradation of another dye. Fig. 9(a) and (b) display the concentration changes of MO over different samples. Both Ag_2S and Ag_2WO_4 did not exhibit good photocatalytic performance. After ultrasonic treatment, $\text{U-Ag}_2\text{S}$ displayed a significant improvement in the photocatalytic activity. Once Ag_2S was loaded into Ag_2WO_4 , $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ showed a large enhancement in the photocatalytic activity. Especially, $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ showed the highest photocatalytic activity, and the degradation rate of MO over it reached 75%.

To explore the degradation mechanism, radical capture experiments were carried out. Generally, hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$) and photogenerated holes (h^+) are the main radicals for the photocatalytic degradation of organic pollutants. Here, a series of radical capturing experiments were performed by using *tert*-butyl alcohol (TBA, a quencher of $\cdot\text{OH}$) [35], benzoquinone (BQ, a quencher of $\cdot\text{O}_2^-$) [36] and triethanolamine (TEOA, a quencher of h^+) [37] in the $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ reaction system. Fig. 10 shows the effect of the addition of quenchers on the photocatalytic degradation of MO over $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$. It was shown that the degradation rate of MO was maintained around 75% in the presence of TBA, which means that $\cdot\text{OH}$ has little effect on the photodegradation of MO. When the TEOA or BQ was added into the reaction solution, the photocatalytic degradation rate was substantially decreased. It was proposed that h^+ and $\cdot\text{O}_2^-$ are the major reactive species in this $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ system.

We proposed a possible mechanism to explain the enhanced activity over the $\text{U-Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite. As shown in Fig. 11, upon light irradiation, electrons (e^-) in the valence band (VB) will be excited to the conduction band (CB) and holes (h^+) will be left in the VB. Then, the photogenerated e^- in the CB will be trapped by adsorbed O_2 to produce $\cdot\text{O}_2^-$ radicals. Both $\cdot\text{O}_2^-$ and h^+ are powerful oxidative species which can break down the chromophores of organic pollutants into small molecules, for example, CO_2 and H_2O . Moreover, the intimate interface of

Fig. 8. (a) The photocatalytic performance of samples for the degradation of MB; (b) The comparison of degradation rates of MB for the different samples; (c) Reaction kinetics of the degradation of the MB over different samples; (d) UV-visible absorption spectra of MB with different reaction times in the presence of $U-Ag_2S/Ag_2WO_4$.

Fig. 9. (a) The photocatalytic performance of samples in the degradation of MO; (b) The comparison of the degradation rates of MO over different samples.

Ag_2S/Ag_2WO_4 , with a matched band energy structure between Ag_2S and Ag_2WO_4 phases, could promote the transfer of charge carriers between Ag_2WO_4 and Ag_2S . Thus, a relatively large separation of photogenerated holes and electrons was obtained over $U-Ag_2S/Ag_2WO_4$, which was confirmed by the former PL and transient photocurrent tests. The radical capture experiments suggested that h^+ and $\cdot O_2^-$ are the major reactive species

in the $U-Ag_2S/Ag_2WO_4$ system. The relatively large separation of the photogenerated holes and electrons provide more active substances (e.g., h^+ and $e^- \rightarrow \cdot O_2^-$) to decompose the dye molecules.

The stability of the catalyst is an important factor to evaluate its potential for practical applications. Therefore, the performance of Ag_2WO_4 , Ag_2S/Ag_2WO_4 and $U-Ag_2S/Ag_2WO_4$ was

Fig. 10. Effect of the addition of quenchers on the photocatalytic degradation of MO over U-Ag₂S/Ag₂WO₄.

Fig. 11. Scheme of photocatalytic mechanism of U-Ag₂S/Ag₂WO₄.

compared through recycling degradation reactions. Fig. 12 shows that after three cycles, the activity of pure Ag₂WO₄ decreased substantially. The degradation rate was reduced from 61.5% to 5.6%. Compared with Ag₂WO₄, the stability of the Ag₂S/Ag₂WO₄ was greatly improved. U-Ag₂S/Ag₂WO₄ yielded the highest stability. After three cycles, the degradation rate of MB over it was still maintained at ~80%.

4. Conclusions

Ag₂S/Ag₂WO₄ composite microrods were fabricated by a sonochemical route. Ultrasonic irradiation resulted in an obvious improvement of the textural properties, for example, the increase in crystallinity and surface area. Moreover, sonochemically fabricated Ag₂S/Ag₂WO₄ microrods exhibited strong visible light absorption and a transient photocurrent response. The produced intimate Ag₂S/Ag₂WO₄ interface between Ag₂S and Ag₂WO₄ phases was able to promote the separation of photogenerated h⁺ and e⁻. A high photocatalytic activity and stability were obtained over U-Ag₂S/Ag₂WO₄ composite microrods. The degradation rate constant of U-Ag₂S/Ag₂WO₄ was 4.7 times and 29.8 times higher than that of bare Ag₂WO₄ and

Fig. 12. The stability test of the samples in the recycling reactions for the degradation of MB.

Ag₂S, respectively. This sonochemical route provides interesting information for the design of highly efficient visible light driven Ag-based semiconductor photocatalysts.

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Graphical Abstract

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Sonochemical fabrication, characterization and enhanced photocatalytic performance of $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrods

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The $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ composite microrod was fabricated by a facile sonochemistry route. The unique texture properties and the produced intimate $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ interface between Ag_2S and Ag_2WO_4 phases could promote the separation of photogenerated carriers lead to the high photocatalytic activity and stability.

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 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 微米棒的声化学合成、表征及其高光催化性能

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摘要: TiO_2 作为一种光催化剂广泛应用于各种污染物的降解。但是它较大的宽禁带 (~3.2 eV) 导致其很难吸收可见光, 因此寻找窄禁带的具有可见光响应的半导体光催化剂成为近年来光催化研究的热点。在众多窄禁带光催化剂中, 纯 Ag_2S 在降解污染物方面并不出色, 但是作为一种窄禁带的直接带隙半导体, 它在加快电子迁移和提高光量子效率方面表现出色。目前有许多高催化活性的 Ag_2S 异质结复合半导体光催化剂的报道, 如 $\text{Ag}_2\text{Mo}_3\text{O}_{10}-\text{Ag}_2\text{S}$, $\text{TiO}_2-\text{Ag}_2\text{S}$, $\text{ZnS}-\text{Ag}_2\text{S}$ 和 $\text{NiO}-\text{Ag}_2\text{S}$ 等。 Ag_2WO_4 是一种具有新颖物理化学性质的半导体材料, 在催化、传感器、抗菌和光致发光等方面有着广泛应用。但是, Ag_2WO_4 的理论带隙较宽, 约为 3.5 eV, 而且光照下 Ag_2WO_4 很容易产生光化学腐蚀而分解出单质银, 作为光催化剂存在太阳光利用率低和稳定性较差等缺点。

声化学是一种特殊纳米材料的合成方法。它主要是利用超声空化产生特殊的物理化学环境来强化化学键的生成, 同时实现半导体从无定形态到固定晶型转变。本文采用超声辅助共沉淀法制备了长为 0.2–1 μm 、直径为 20–30 nm 的 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 微米棒复合光催化剂。利用 X 射线衍射 (XRD)、 N_2 物理吸附、扫描电镜、透射电镜、光电子能谱、光致发光谱 (PL) 和紫外-可见漫反射吸收光谱 (UV-vis DRS) 和光电流等手段对所制 Ag_2S , Ag_2WO_4 和 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 进行了表征。结果表明, 合成的样品比表面积较小 (2.7–3.6 m^2/g)。UV-vis DRS 测试表明, 声化学处理能有效拓宽 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 在可见

光区的吸收范围,提高其可见光响应性能.另外,PL和光电流测试结果证实,在声化学制备的 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 体系中,光生电子(e^-)-空穴(h^+)的复合过程被极大地限制,具有较高的 e^- - h^+ 分离效率.

以金卤灯为光源进行了光催化降解染料亚甲基蓝的性能测试.结果表明,声化学合成的 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 的反应速率常数 (0.150 min^{-1}) 分别为单纯 Ag_2WO_4 (0.031 min^{-1}) 和 Ag_2S (0.004 min^{-1}) 的 4.7 和 29.8 倍.自由基捕获实验表明,在 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 光催化降解甲基橙过程中主要的活性物种为超氧自由基 (O_2^-) 和光生空穴 (h^+).此外,声化学合成的 $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 表现出很好的光催化稳定性.循环使用 3 次后,该样品对亚甲基蓝的光催化活性仍高达 80.4%,而纯 Ag_2WO_4 几乎完全失活. $\text{Ag}_2\text{S}/\text{Ag}_2\text{WO}_4$ 具有很高的光催化活性的原因,一方面是声化学处理提高了催化剂的结晶度,同时生成了独特的棒状结构;另一方面是在超声作用下, Ag_2S 和 Ag_2WO_4 两相紧密接触形成异质结,促进了可见光的吸收和光生 e^- 与 h^+ 的分离.

关键词: 声化学;微米棒;钨酸银;光催化;异质结

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