

Preparation of Ag₂SO₃ sub-microparticles with high visible-light photocatalytic activity

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A visible-light sensitive Ag₂SO₃ semiconductor photocatalyst with size of ca. 500 nm was prepared by a simple precipitation method. This photocatalyst exhibits high-efficiency degradation ability for typical three dyes, which can be ascribed to the efficient photosensitised electron injection and slow electron recombination. The photocatalytic reaction follows a pseudo-first-order reaction and the rate constant of Ag₂SO₃ for the degradation of rhodamine B is estimated to be 1.7 times that of commercial TiO₂. The stability of unstable Ag₂SO₃ was remarkably enhanced by the addition of Na₂SO₃. The h⁺ and •O₂⁻ played relatively major roles during the photocatalytic reaction.

1. Introduction: Nowadays, organic pollutants are inevitably released into the environment because of their huge production by the textile industry [1, 2]. Degradation of organic pollutants in wastewater through photocatalysis has received increasing attention in recent years [3, 4]. In previous reports, TiO₂ has exhibited excellent photocatalytic activity and stability [5, 6], but it is a semiconductor with a large bandgap of 3.2 eV, active only under ultraviolet (UV) light irradiation [7]. It is necessary to find novel semiconductor photocatalysts that can make full use of solar energy, even indoor light. The Ag₂O semiconductor with a narrow bandgap of 1.3 eV is a promising visible-light-sensitive catalyst [8], and its bandgap can be broadened by doping other elements. Up to now, p-block metallic and non-metallic elements doped Ag₂O, such as α-AgGaO₂ [9, 10], Ag₃VO₄ [11, 12], AgSbO₃ [13, 14], Ag₃PO₄ [15–17] and Ag₂CO₃ [18–20], have exhibited high visible-light-driven photocatalytic activity. S element doped Ag₂O such as Ag₂SO₃/Ag₂SO₄/Ag₂S, Ag₂SO₃/Ag₂SO₄/AgX (X = Cl, Br) [21] were prepared by a two-step route, including mild gas–liquid reaction and a simple ion-exchange method and exhibited photocatalytic behaviour for the degradation of rhodamine B (RhB) under visible light irradiation.

In the work reported in this Letter, Ag₂SO₃ particles with size of 500 nm were prepared by a simple precipitation method, and showed high-efficiency degradation ability for RhB, methyl orange (MO) and methylene blue (MB) under visible light irradiation. In addition, the recyclability and stability, reaction kinetics and active species were also investigated. To the best of our knowledge, this is the first reported systematic study of the photocatalytic activity of Ag₂SO₃ sub-microparticles.

2. Experimental

2.1. Synthesis: All the chemicals were of analytical grade and used as received without further purification. The Ag₂SO₃ samples were prepared by a precipitation method. In brief, 10 ml of Na₂SO₃ (0.1 M) was added dropwise into 10 ml of AgNO₃ (0.2 M) in a beaker under vigorous stirring. After stirring for another 30 min, the white precipitates were collected by centrifugation, washed with deionised water and anhydrous ethanol for several times and finally dried under vacuum at room temperature.

2.2. Characterisation: The structure, morphology and composition of the products were characterised by X-ray diffraction (XRD, Philips X'Pert PRO), scanning electron microscopy (SEM, Hitachi S-4800) and energy-dispersive X-ray spectrometry (EDX, INCAx-Sight OXFORD) attached to SEM, respectively. UV-visible diffuse reflectance spectra (DRS) were recorded by a Shimadzu UV-2450 spectrometer at room temperature. The photoluminescence spectra for solid samples dispersed in absolute ethanol were investigated with an excitation wavelength of 300 nm on a Hitachi F-4500 fluorescence spectrophotometer.

2.3. Photocatalytic evaluation: The optical system for the photocatalytic reaction was composed of a 300 W Xe lamp (Shanghai Lanpu Light, China) with a light intensity of 40 mW/cm² and a cutoff filter (λ > 400 nm). Dye solutions (30 ml, 5 mg/l) containing 50 mg of catalyst were put in a sealed glass beaker and first ultrasonicated for several minutes, and then stirred in the dark for 30 min to ensure absorption–desorption equilibrium. After visible light illumination at regular time intervals, the absorbance of RhB solution was monitored by A Hitachi U-4100 UV–vis spectrophotometer.

The repeated experiments were conducted as follows. At the end of each cycle, the suspension was centrifuged at 10 000 rpm for 10 min and the supernatant was discarded. The recovered catalyst was then washed with deionised water three times and dried at ambient temperature under vacuum.

3. Results and discussion

3.1. Structure and optical properties: Fig. 1a shows the XRD pattern of Ag₂SO₃ obtained by drying in vacuum; most of the diffraction peaks can be indexed to a monoclinic phase Ag₂SO₃ (JCPDS No. 70-1910). Besides, the weak diffraction peaks at 28.1°, 31.1° and 33.9° could be assigned to the (040), (113) and (220) characteristic peaks of Ag₂SO₄ (JCPDS No. 07-0203), respectively. The above result indicated that the as-obtained Ag₂SO₃ might be gradually oxidised in air and contained tiny amounts of Ag₂SO₄. The chemical composition was further determined by EDX spectrometry (Fig. 1b) and the only detectable elements are Ag, O and S (the C element comes from the conductive tape), which are mainly ascribed to Ag₂SO₃. The morphology of the as-obtained Ag₂SO₃ was studied by SEM. As

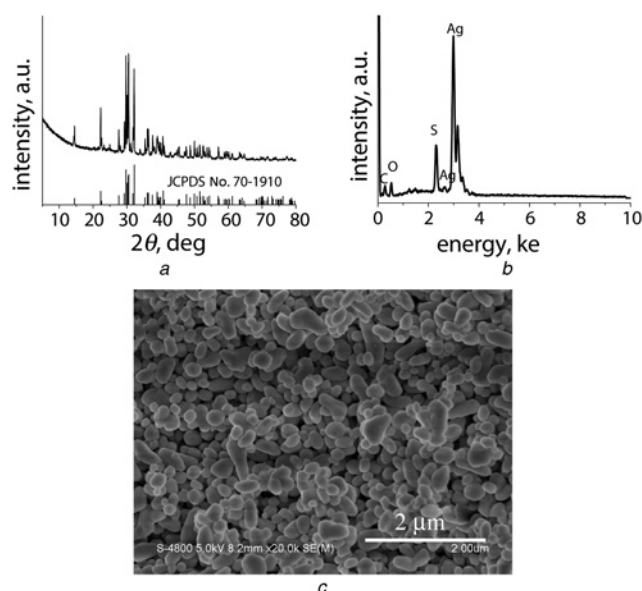


Figure 1 XRD pattern (Fig. 1a), EDX spectrum (Fig. 1b), and SEM image of as-prepared Ag_2SO_3 (Fig. 1c)

shown in Fig. 1c, Ag_2SO_3 is composed of particles with an average size of ca. 500 nm.

The optical absorbance of Ag_2SO_3 was measured by UV–vis diffuse reflectance spectroscopy (Fig. 2). It was found that Ag_2SO_3 exhibits relatively strong absorption in the UV region, and extremely weak absorption in the visible light region before sunlight irradiation. After visible light irradiation for about 40 min, an absorption peak at ca. 460 nm appeared for Ag_2SO_3 (Fig. 2a), which can be ascribed to the surface plasmon absorption of Ag nanoparticles (NPs) since Ag^+ ions could be reduced under visible light irradiation [21, 22]. From the plot of the transformed Kubelka-Munk function of light energy $(\alpha h\nu)^{1/n}$ against energy $(h\nu)$ [18, 19] of Ag_2SO_3 (Figs. 2b and c), the bandgaps of Ag_2SO_3 could be estimated to be 3.38 eV (indirect bandgap, $n = 2$) and 3.60 eV (direct bandgap, $n = 1/2$), respectively. Therefore it is believed that Ag_2SO_3 cannot absorb visible light.

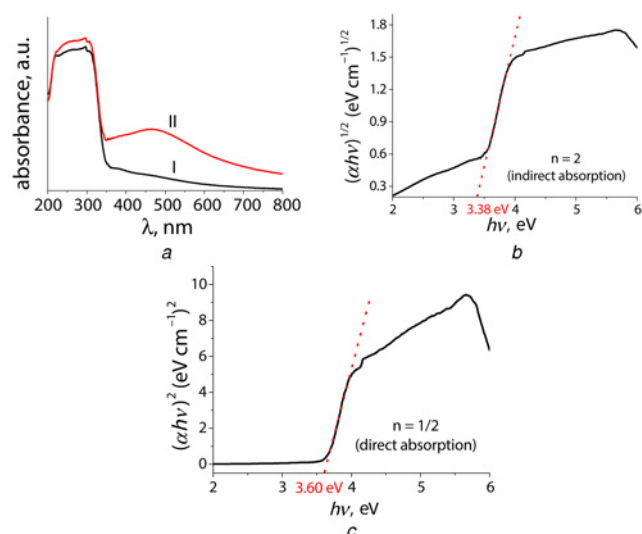


Figure 2 UV–vis DRS of as-prepared Ag_2SO_3 (I: before visible light irradiation; II: after visible light irradiation) (Fig. 2a), and plot of $(\alpha h\nu)^{1/2}$ against $h\nu$ (Fig. 2b) and plot of $(\alpha h\nu)^2$ against $h\nu$ (Fig. 2c) of Ag_2SO_3

3.2. Photocatalytic activity and stability of Ag_2SO_3 : The photocatalytic activity of the as-prepared Ag_2SO_3 was evaluated by degradation of RhB under visible light irradiation. For comparison, the photocatalytic activity of commercial TiO_2 (Degussa P25) was also measured. The photodegradation of RhB against irradiation time in different systems are shown in Fig. 3a. In the absence of Ag_2SO_3 or with it in the dark, the RhB aqueous solution hardly degraded. It was also observed that Ag_2SO_3 could degrade more than 94% of RhB after sunlight irradiation of 40 min (Fig. 3b), while P25 degraded only 80% of RhB under the same condition. The absorption intensity of RhB gradually decreased with increasing irradiation time without any shift of the absorption wavelength, suggesting a complete cleavage of RhB chromophores. The photocatalytic reaction follows a pseudo-first-order reaction because of the low concentration of dye solutions; the relevant equations are listed as follows: $-\ln(C_t/C_0) = kt$, where C_0 and C_t are the concentrations of the reactant at time 0 and t , respectively, and k is the first-order reaction rate constant [23, 24]. Ag_2SO_3 has a better degradation ability than that of P25, and its rate constant is estimated to be 1.7 times that of P25 (Fig. 3c).

The recyclability and stability for one photocatalyst is important for practical use. Therefore, the recycled experiments of Ag_2SO_3 for the photodegradation of RhB were investigated, and the results are shown in Fig. 3d. The photocatalytic activity of Ag_2SO_3 decreased dramatically for three cycles in the absence of sacrificial reagents (red line II in Fig. 3d), which can be attributed to photocorrosion [19]. With the increasing of the irradiation time, the quantity of Ag_2SO_3 decreased, and excessive Ag atoms are produced. To suppress the photocorrosion process, Na_2SO_3 (0.01 M) was added in the RhB/ Ag_2SO_3 suspension during the photocatalytic process. The results shown in Fig. 3d (black line I) indicated the stability of Ag_2SO_3 was remarkably enhanced after adding Na_2SO_3 .

3.3. Effects of different factors on degradation of dye by Ag_2SO_3

3.3.1 Effects of different dyes: The typical organic dyes such as RhB, MO and MB were used for target molecules to evaluate the photodegradation performance of Ag_2SO_3 (Fig. 4). The degradation of more than 93% of MO, 97% of MB and 99% of RhB molecules after 60, 80 and 80 min simulated sunlight irradiation was observed, respectively. It is also noted that MB molecules are easier to be adsorbed than MO and RhB molecules [23].

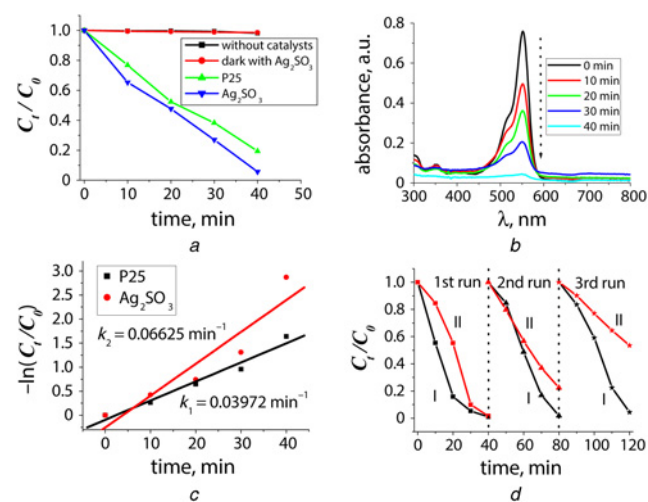


Figure 3 Photodegradation efficiencies of RhB solution (5 mg/l) against irradiation time in different systems (Fig. 3a); UV–vis spectral changes of RhB in aqueous Ag_2SO_3 dispersions against irradiation time (Fig. 3b); rate constants of RhB in aqueous Ag_2SO_3 and P25 dispersions (Fig. 3c); cycling runs in the photodegradation of RhB by Ag_2SO_3 in presence of Na_2SO_3 (0.01 M, I) and without Na_2SO_3 (II) (Fig. 3d)

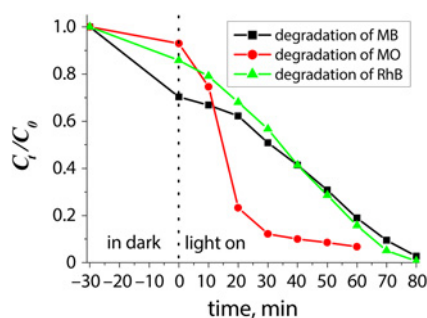


Figure 4 Photocatalytic degradation of three kinds of dyes (10 mg/l) by Ag_2SO_3

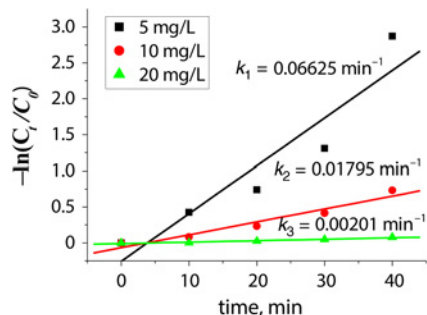


Figure 5 Plot of $-\ln(C_t/C_0)$ against irradiation time for degradation of RhB by Ag_2SO_3 at different initial concentrations

3.3.2 Effects of different initial concentrations of RhB: As shown in Fig. 5, for different initial concentrations of RhB solutions, the values of degradation rate constant are 0.06625 min^{-1} for 5 mg/l, 0.01795 min^{-1} for 10 mg/l and 0.00201 min^{-1} for 20 mg/l, respectively. When the initial concentration of the dye solution is much lower, the degradation efficiency is much higher, which is consistent with previous reports for RhB degradation by Ag_3PO_4 [2], TiO_2 [25] and Bi_2WO_6 [26].

3.3.3 Effects of different scavengers: It is generally accepted that the dyes and organic pollutants can be photodegraded via photocatalytic oxidation process, in which a large number of main reactive oxygen species including hydroxyl radical ($\bullet\text{OH}$) and superoxide radical ($\bullet\text{O}_2^-$) and hole (h^+) are involved [27–29].

Isopropanol (IPA), benzoquinone (BQ) and ethylene diamine tetraacetic acid (EDTA) were commonly used as scavenger for $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and h^+ , respectively [4]. From Fig. 6, it can be found that the degradation rate of RhB was not quenched obviously in the presence of 1 mM IPA, while in the presence of 1 mM BQ or EDTA, an evident decreasing of the photocatalytic activity of Ag_2SO_3 was observed. Therefore, the degradation of RhB with Ag_2SO_3 was mainly attributed to $\bullet\text{O}_2^-$ and h^+ , whereas $\bullet\text{OH}$ only played a relatively minor role in the process.

3.4. Proposed photodegradation mechanism: From the above results, we know that as-prepared Ag_2SO_3 has a direct bandgap of 3.38 eV ($\sim 367 \text{ nm}$) and an indirect bandgap of 3.60 eV ($\sim 344 \text{ nm}$), so it cannot adsorb visible light under the present condition ($\lambda > 400 \text{ nm}$). However, in fact, Ag_2SO_3 showed high photocatalytic degradation activity under visible light irradiation. Therefore, the photodegradation of dyes over Ag_2SO_3 under visible light must be ascribed to the surface plasmon absorption of Ag NPs [22, 30, 31] or the dye-photosensitised electron injection [32–34].

To understand the cause for enhancing the photocatalytic performance of the Ag_2SO_3 , some other characterisations have been

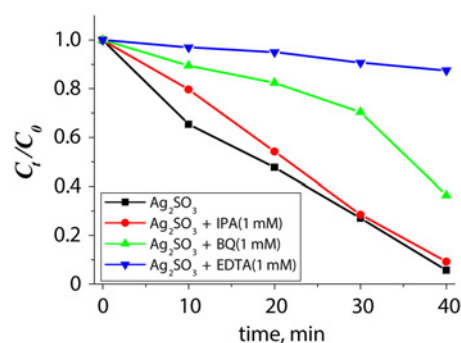


Figure 6 Effects of different scavengers on degradation of RhB (5 mg/l) in presence of Ag_2SO_3

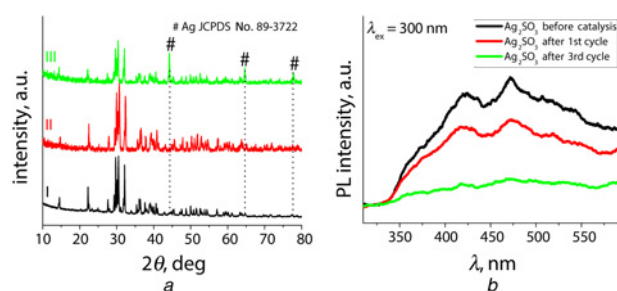


Figure 7 XRD patterns of as-prepared Ag_2SO_3 (I: before catalysis, II: after first cycle, III: after third cycle) (Fig. 7a), and photoluminescence spectra of Ag_2SO_3 sub-microparticles before catalysis, after first cycle and after third cycle with excitation wavelength of 300 nm (Fig. 7b)

performed, including XRD and photoluminescence spectra. As indicated in Fig. 7a, the amount of metallic Ag increased with the increase of the irradiation time. As displayed in Fig. 7b, under an excitation wavelength of 300 nm, for Ag_2SO_3 before catalysis, a broad band at 330–590 nm is detected, for Ag_2SO_3 after the first and the third cycle; the obviously decreased emission intensity represents an effective interfacial charge-transfer process, suggesting that an additional pathway for the disappearance of the charge carriers dominates, because of the interactions between the excited Ag_2SO_3 sub-microparticles and Ag NPs. This indicated that the Ag_2SO_3 -Ag composite has a lower recombination rate of electrons and holes. A control experiment showed that the degradation was not because of the excitation of Ag_2SO_3 as phenol that has no absorption in the visible light region was not degraded under the present experimental condition. Hence the photosensitised degradation mechanism based on the excitation of dye [32, 33] was proposed in this case. Namely, the dye molecule is firstly excited by visible light, followed by electron transfer from the excited dye (dye^*) to the conduction band of Ag_2SO_3 . Then, the electron is trapped by surface-adsorbed O_2 to generate various reactive oxidation species, such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$. Subsequently the dye^{*+} itself degraded and/or was degraded by $\bullet\text{O}_2^-$ and h^+ . The Ag NPs might act as the electron transport channel in this process.

4. Conclusions: In summary, a visible-light-sensitive Ag_2SO_3 photocatalyst was successfully prepared by a facile precipitation method, and it can effectively degrade the organic dyes (i.e. MO, MB and RhB) under sunlight irradiation. Ag NPs produced by visible light irradiation enhanced the photocatalytic activity of Ag_2SO_3 . The stability of Ag_2SO_3 was greatly improved after adding Na_2SO_3 into the photocatalytic system. The reaction kinetics results indicated that the lower the initial concentration of dye is, the higher the degradation efficiency. Furthermore, a

controlled experiment proved that the degradation of RhB followed the photosensitized electron injection mechanism, and was directly oxidised by h^+ and $\bullet O_2^-$, and $\bullet OH$ only played a relatively minor role.

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6 References

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