

Photochemical Preparation of Ag/SnO₂ Composites and their Photocatalytic Properties

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Abstract—In this study, a simple photochemical method for preparation of Ag/SnO₂ composites is presented. Ag nanoparticles were grown on the surface of SnO₂ particles in situ by UV light induced photoreduction of silver nitrate. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray powder diffraction (XRD) were applied to characterize the composites. The effects of concentration AgNO₃ solutions on the properties of the composites were analyzed. The photocatalytic activity of the composites was investigated by photodegrading methyl orange (MO) in aqueous solution under the metal halide lamp irradiation. The results showed that the Ag/SnO₂ composites with a suitable amount of silver have much higher photocatalytic activities than that of pure SnO₂. The Ag/SnO₂ composites obtained in 3mM AgNO₃ by photochemical routine has the best photocatalytic activity for degrading MO.

Keywords—Photochemical preparation; SnO₂; Ag nanoparticles; composites; photodegradation

I. INTRODUCTION

Photocatalytic technology is an effective way to get clean energy and environmental pollutant removal. In recent years the development of efficient photocatalysts caused widespread concern [1-3]. Oxide semiconductors (such as TiO₂ [4-6], SnO₂ [7,8] and ZnO [9,10], etc.) are commonly used as photocatalysts. However, because they often have a large band gap and high rate recombination of photogenerated electron-hole pairs, the application and the efficiency of photocatalytic degradation is limited to some extent. To improve photocatalytic efficiency of the pure oxide, the noble metal depositing on oxide semiconductor is one of the effective methods [6,9-13]. When the noble metal deposited on the semiconductor photocatalyst, it can increase the separation efficiency of the light-generated charge effectively through trapping photogenerated electrons and inhibiting fast recombination of electron-hole [9,12]. For this purpose, Ag is often used because of its low cost compared to other noble metals. There are many researches with respect to prepare such Ag/semiconductor oxide composite photocatalysts [6,9,14], for the purpose of improving photocatalytic efficiency. There are several methods to fabricate noble metal oxide nanocomposites. Photochemical reduction noble metal on the surface of oxide is an often used route to prepare such nanocomposites [11,12]. Using this way, when an oxide

semiconductor is excited with light irradiation, some electrons are excited from valence band to conduction band, meanwhile forming an equal number of holes. These produced photo-generated electrons are strongly reducing agents, which could in situ reduce metal ions on the oxide surface to form composite nanostructure. Up to now, using this method, several composites including Ag/ZnO [9,10], Ag/TiO₂ [6,14-16] and Ag/Cu₂O [11] etc are prepared. However, in these studies, the involved oxide semiconductor materials are mainly TiO₂ and ZnO. SnO₂ is another important semiconductor material, the related work reported less.

In this paper, the authors plan to modify the surface of SnO₂ with Ag nanoparticles by photochemical method at room temperature. The method consists of a photochemical reduction and deposition process under UV irradiation. The photocatalytic activity of the obtained Ag/SnO₂ composites was investigated by degradation of MO dye solution under the metal halide lamp irradiation. It is believed that the present work would offer a simple and cost-effective route for producing SnO₂ composite photocatalysts.

II. EXPERIMENTAL SECTION

A. Preparation of Ag/SnO₂ composites

SnO₂ was prepared according to the photochemical method reported in the literature [10]. 0.6g as-prepared SnO₂ was dispersed in a beaker filled with 100ml 0.5–30mM AgNO₃ aqueous solution. The dispersions, while being stirred, were irradiated by UV lamp (Philips, 254nm, 8W) for 19h at room temperature. After irradiation, the black powder was collected, rinsed with distilled water repeatedly to purify the product, then washed with ethanol three times, and finally dried at 100°C. Ag/SnO₂ powder samples were obtained. In order to distinguish these samples, they were named as S1, S2, S3, S4, S5, and S6, respectively, according to the concentration of AgNO₃ 0.5mM, 1mM, 3mM, 5mM, 10mM, and 30mM in the solution. For comparison, the control SnO₂ without Ag was named as S0.

B. Characterization of Ag/SnO₂ composites

The morphologies of the samples were characterized using a JSM-7001F field emission scanning electron microscope (SEM). The elemental compositions were

obtained on OXFORD energy-dispersive X-ray spectra (EDS). The phase identification of the resulting samples was characterized by X-ray powder diffraction (XRD, X'pert Powder, with Cu-K α radiation).

C. Evaluation of photocatalytic activity

Photocatalytic activity measurement was carried out for degrading MO aqueous solution at 20°C. 0.05g photocatalyst was dispersed in 300ml of 3 \times 10⁻⁵M MO aqueous solution, and then the mixture was put into a column-like container with magnetic stirring. A 250W metal halide lamp was used for the light source. For quantitative analysis of MO concentration, about 5 mL of samples were withdrawn from the reaction bottle followed by separation of photocatalyst particles using a centrifuge. The absorbance of MO solution was then measured by UV-Vis spectrophotometer (UV-2502PC) to study degradation rate as function of photocatalytic reaction time. The intensity of the absorbance peak at 464 nm was taken to calculate concentration of residual MO in the solution. The absorbance peak of MO solution used in this study was also measured as control corresponding to initial MO concentration in the absence of photocatalyst.

III. RESULTS AND DISCUSSION

When irradiating the precursor solution with 254 nm UV light, as shown in (1), SnO₂ dispersed in the precursor solution can be excited to produce electrons from the valance band to the conduction band. The potogenerated electrons on SnO₂ are powerful reductants and can immediately reduce Ag⁺ in the solution to produce Ag on the surface of SnO₂ to form Ag nuclei (see (2)). Once the Ag nuclei are formed, the followed produced Ag will grow on Ag nuclei. As a result, Ag nanoparticles can be loaded on the surfaces of SnO₂ particles in situ. The photochemical reaction processes for the formation of Ag/SnO₂ composites can be written as follows.

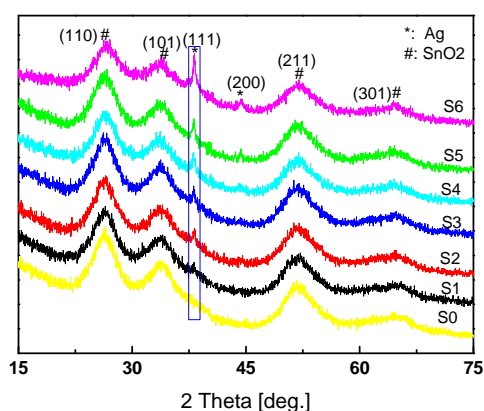
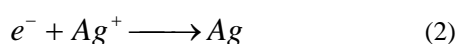
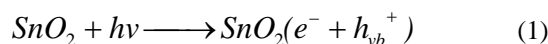


Figure 1 XRD spectra of SnO₂ (S0) and Ag/SnO₂ (S1-S6) composites obtained from different concentration AgNO₃ solutions.

The XRD patterns of Ag/SnO₂ and pure SnO₂ powders are shown in Fig.1. S0 has four diffraction peaks (26.43°, 33.97°, 52.15°, 65.5°) indexed to (110), (101), (211), and (301) crystal planes of the tetragonal cassiterite SnO₂, respectively. Comparing S0 with Ag/SnO₂ Fig. 1(S1-S6,) aside from the characteristic diffraction peaks of SnO₂, two new and weak diffraction peaks at 38.12° and 44.15° are observed, which corresponded to Ag (111) and Ag (200) plane. This shows that the prepared composite samples contain SnO₂ and Ag. With increasing the concentration of AgNO₃, the intensity of the diffraction peaks at 38.12° was gradually increased, which means the Ag content increase in the composite. These confirm that the amount of silver can deposited on SnO₂ to form composites with UV light irradiating different AgNO₃ precursor solution.

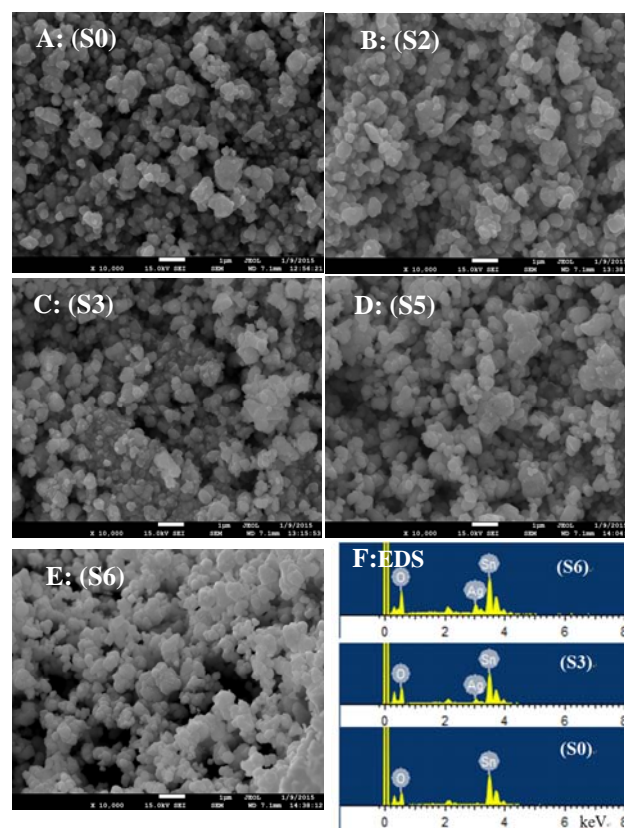


Figure 2 SEM images of Ag/SnO₂ composites (A-E), and (F) is the EDS images with S6, S3 and S0

The morphology of pure SnO₂ (S0) and the as-prepared Ag/SnO₂ (S2,S3, S3,S6) is shown in Fig 2. It shows that the products from different concentration AgNO₃ solutions have similar morphology. The pure SnO₂ (S0) amorphous particles are approximately 200 nm in size, composed of numerous smaller SnO₂ nanocrystals. Comparing with S0, the resulting composites (S2, S3, S5, S6) from different concentration AgNO₃ solutions have similar morphology. For further detecting the composition of composites, the content of Ag on SnO₂ was also studied by EDS. EDS analyses of chosen regions which includes full slected region of S0, S3 and S6 are shown in Fig. 2F. It shows that no clear Ag phase was detected in pure pure SnO₂ (Fig. 2F, S0) which means tin and oxygen are the dominant elements. However for S3 and S6, additional peaks

corresponding to Ag appeared in Ag/SnO₂ as shown in Fig. 2F, which indicates that composites are mainly composed of SnO₂ and a little metallic silver. With increasing AgNO₃ concentration, Ag content increased according to the increasing peaks intensity corresponding to Ag. The calculated Ag: Sn molar ratios of S6 and S3 are 1.18: 1 and 1.04: 1 respectively. It also confirms that Ag was successfully deposited on SnO₂ surface by photochemical method.

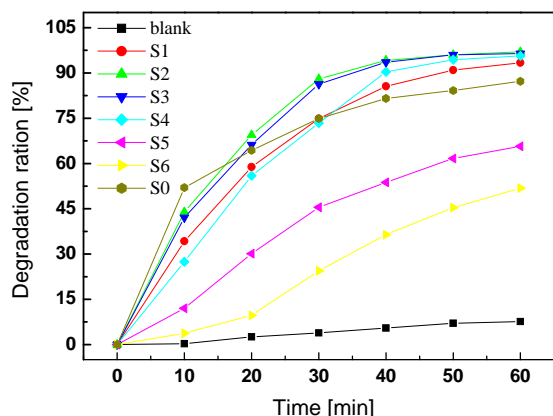


Figure 3 Photodegradation of MO by SnO₂ (S0) and Ag/SnO₂ (S1–S6)

The photocatalytic activities of the prepared composites were evaluated by degrading MO under the metal halide lamp irradiation for 60 min. The relationships between the MO degradation ratios and irradiation time for different composites are shown in Fig. 3. For comparison, the blank experiment is carried out in the presence of irradiation without photocatalyst. Without any catalyst, only about 6% MO degradation ratio was detected under irradiation for 60 min (see Fig. 3b line blank). Obviously, the addition of photocatalysts accelerates the degradation of MO. The degradation ratio all increase with the prolonged irradiation times for different catalysts. Comparing with pure SnO₂, although pure SnO₂ has the highest MO degradation ratio at initial 10 min, however, with further increase time, the composites S1–S4 have higher degradation rate than S0. Degradation efficiency of MO in the presence of composites (S1–S4) is higher than that in the presence of pure SnO₂. When using S5 and S6 as catalyst, the MO degradation efficiency is lower than that using S0. It means that the load of proper Ag on SnO₂ can improve the photocatalytic performance to some degree. The degradation efficiency can reach to 96.01% under the light illumination for 50 min for S2 and S3. For irradiation 60 min, the MO degradation ratio is about 93.38%, 96.98%, 96.41%, 95.63%, 65.72%, 51.86% and 87.21% with using S1, S2, S3, S4, S5, S6 and S0, respectively. Obviously, when using the concentration range between 1–5 mM of AgNO₃ to prepare composites, we can obtain higher composite catalytic photocatalyst. The 3 mM is the best concentration to prepare Ag/SnO₂ composite photocatalyst. The improved activity is mainly ascribed to the better charge separation of nanocomposites than that of pure SnO₂ [9]. During the photodegradation of MO solution, the photogenerated electrons can be captured by

Ag and subsequently transferred to dissolved oxygen in the solution. However, the photocatalytic activity decreases with the further increase of Ag content in the nanocomposites. It maybe attributes to the decrease of photogenerated electrons because of too much nano Ag covered on the surface of SnO₂.

IV. CONCLUSIONS

In summary, we have prepared Ag/SnO₂ composites by UV light irradiating precursor solution containing silver nitrate and SnO₂. The morphologies, composition and photocatalytic activity were investigated. The presence of metallic silver on the surface of SnO₂ can help the electron-hole separation by attracting photoelectrons. Suitable amount of Ag nanoparticles loaded on SnO₂ is able to enhance the photocatalytic activity of SnO₂. The Ag/SnO₂ composites obtained in 3 mM AgNO₃ by photochemical routine has the best photocatalytic activity for degrading MO. It is indicated that the photochemical route is a very facile and promising approach to synthesize noble nanoparticles loaded semiconductor photocatalyst materials.

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