Preparation and Photocatalytic Activity of Ag-Modified SnO$_2$@TiO$_2$ Core-Shell Composites

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Abstract
Photocatalytic degradation is an important method to mediate organic pollution in the environment. This article reports Ag-modified SnO$_2$@TiO$_2$ core-shell composite photocatalysts prepared via a hydrothermal method. The composite materials were characterized by X-ray diffraction, transmission electron microscopy, energy dispersive X-ray spectroscopy, thermogravimetry, X-ray photoelectron spectrometry, and UV-vis diffuse reflectance spectroscopy. The Ag modification and core structure in the composite enhanced the photocatalytic activity and stability of TiO$_2$, for Rhodamine B degradation under visible light irradiation. The composite modified in 0.15 M AgNO$_3$ showed an optimal level of photocatalytic activity, as it degraded 99.14% of Rhodamine B in 60 min while pure TiO$_2$ only degraded 45.7% during the same time.

Keywords: Core-shell composites; Hydrothermal method; Photocatalytic activity

Abbreviations: PT: Pure TiO$_2$; AgT: Ag-modified TiO$_2$; ST: SnO$_2$@TiO$_2$; AgST: Ag-modified SnO$_2$@TiO$_2$; AgST-M: Ag-modified SnO$_2$@TiO$_2$ prepared with M mol L$^{-1}$ AgNO$_3$

Introduction
Recently, titanium dioxide (TiO$_2$) has attracted great interest for the degradation of pollutants [1-3], such as most organic compounds and inorganic ions [4,5]. However, the photocatalytic performance of TiO$_2$ is greatly restricted by its wide band gap (3.2 eV) and high electron-hole recombination rate. Proposed solutions to these problems include doping with metallic or nonmetallic ions [6,7], dye photosensitization on the TiO$_2$ surface [8], deposition of noble metals [9,10], and semiconductor modification [11].

Modifying TiO$_2$ with semiconductors such as SnO$_2$ has proven to be an effective way to improve the photocatalytic activity, by using the transport and separation of photo produced carriers between two semiconductors with different energy gaps. Separately, Ag or other noble metals deposited on the surface of TiO$_2$ form a short-circuit battery with TiO$_2$, which leads to effective separation of the generated electrons/holes and a lower potential in the reduction reaction, thus greatly improving the photocatalytic activity.

In this paper, Ag-modified SnO$_2$@TiO$_2$ core-shell composites were fabricated in two steps: first the synthesis of SnO$_2$@TiO$_2$ composite using a hydrothermal method, and then surface modification of the composite with Ag. The Ag-modified SnO$_2$@TiO$_2$ core-shell composites demonstrated excellent photocatalytic activity and cycle stability under visible light.

Materials and Methods
Preparation of Ag-modified SnO$_2$@TiO$_2$ core-shell composites

Preparation of SnO$_2$:
SnCl$_4$·5H$_2$O and polyethylene glycol (PEG) were added into deionized water and magnetically stirred. When SnCl$_4$·5H$_2$O was completely dissolved, excessive ammonia was added dropwise into the solution and stirred well. After filtration, the precipitate was washed with absolute alcohol, and calcined at 400°C for 2 h to obtain the SnO$_2$ powder.

Preparation of SnO$_2$@TiO$_2$ core-shell composites:
SnCl$_4$·5H$_2$O was completely dissolved, excessive ammonia was added into deionized water and magnetically stirred. When the solution was clear, titania precursor was added dropwise into the solution and stirred well. After filtration, the precipitate was washed with absolute alcohol, and calcined at 400°C for 2 h to obtain the SnO$_2$@TiO$_2$ powder.

Preparation of Ag-modified SnO$_2$@TiO$_2$ core-shell composites: Tetrabutyl titanate, acetic acid, and anhydrous alcohol were mixed together, and then alcohol-water solution was slowly added to the mixture and stirred for 30 min. SnO$_2$ was then added, followed by another 30 min of stirring. The obtained solution was transferred to a 100-mL Teflon-lined autoclave and kept in an oven at 150°C for 4 h. After cooling to room temperature, the precipitate was collected by centrifugation (6000 rpm, 20 min), washed with anhydrous alcohol, and then dried at 60°C overnight. The obtained SnO$_2$@TiO$_2$ sample is designated as ST.

Preparation of Ag-modified SnO$_2$@TiO$_2$ core-shell composites:
The ST composite was added to AgNO$_3$ solutions of given concentrations and irradiated under a 500 W mercury lamp. The solids were collected by centrifugation and dried at 60°C overnight to obtain Ag-modified SnO$_2$@TiO$_2$ core-shell composites. These samples are designated as AgST-M, where M is the molar concentration of AgNO$_3$ solution used. For comparison, pure TiO$_2$ and Ag-modified TiO$_2$ were synthesized separately, and designated as PT and AgT, respectively.

Characterization of the photocatalysts
The chemical composition of the photocatalyst samples was analyzed by energy dispersive X-ray spectroscopy (EDX, INCA). Transmission electron microscopy (TEM, JEM-2100, JEOL) was used for morphology characterization. The crystalline structures of the samples were determined by X-ray diffraction (XRD, XRD-6000, Japan Shimadzu) using Cu Ka radiation ($\lambda=0.154$ nm) at 40 kV, 250 mA at room temperature. An X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250, Waltham, MA, USA) was used to analyze the elemental composition and valence states. UV-vis diffuse reflectance spectrophotometry (DRS, Shimadzu, Japan) was used to characterize the electronic and optical properties of the samples.

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spectra (DRS) of the samples were recorded in the range of 200–800 nm using a Shimadzu UV240 spectrophotometer (Kyoto, Japan) equipped with an integrating sphere, and BaSO$_4$ was used as the reference. Thermogravimetry and differential thermal analysis (TG-DTA) were performed by a Pyris Diamond 851e analyzer (PerkinElmer) at a heating rate of 200$^\circ$C min$^{-1}$ under N$_2$ environment, with a flow rate of 40 mL min$^{-1}$.

**Photocatalytic activity**

The photocatalytic activities of the samples were evaluated by the degradation of Rhodamine B in a 500-mL jacketed beaker, a 500 W mercury lamp was selected as the visible light source. In a typical experiment, 0.05 g of the photocatalyst sample was dispersed in the Rhodamine B solution (40 mL, 5 mg L$^{-1}$). The solution was then maintained in the dark for 30 min prior to irradiation, in order to reach the adsorption–desorption equilibrium. During irradiation, 4 mL of the sample solution was taken out every 10 min and the Rhodamine B concentration was measured by UV-vis spectroscopy. The degradation rate of Rhodamine B can be calculated via the formula:

$$\eta = (1 - A_i / A_0) \times 100\%$$

where $A_0$ is the initial absorbance of the solution, and $A_i$ is the absorbance after different reaction times.

**Results and Discussion**

**Phase structure and morphology characterization**

The XRD spectra of Ag-modified SnO$_2$@TiO$_2$ and other samples were shown in Figure 1. The diffraction patterns of ST and AgST displayed the anatase peak of TiO$_2$ at 2$\theta = 25.3^\circ$. However, we could not confirm the anatase phase since only one peak was detected, probably due to the low amount of TiO$_2$ in the particles. Similarly, no Ag peaks were detected in the patterns of AgT and AgST, likely due to the low amount of Ag [12-14].

Figure 2 showed three typical TEM images of AgST-0.15. The as-prepared sample consisted of many decentralized nanoparticles of uniform size (30–50 nm in diameter). The core-shell nanostructures could be observed in Figure 2(c), as the surface of the SnO$_2$ nanoparticles was coated with a layer of TiO$_2$.

**Thermogravimetric analysis**

TG-DTA curves of the AgST-0.15 nanoparticles were exhibited in Figure 3. The results showed that the nanoparticles underwent a multistep decomposition process in the temperature range of 25–800$^\circ$C. The endothermic peak in the range of 25–90$^\circ$C was related to the desorption of physically adsorbed free water and residual ethanol, which together accounted for 8% of the weight loss. The sharp exothermic peak in the temperature range of 200–300$^\circ$C (about 5% weight loss) was due to the combustion of organics on the surface of the sample. In the temperature range of 300–400$^\circ$C, there was another exothermic peak owing to further carbonization of organics and the removal of constitution water. These results indicated that the as-prepared Ag-modified SnO$_2$@TiO$_2$ core-shell composite exhibited high thermal stability.

**Elemental analysis**

XPS analysis: AgST-0.15 was further analyzed by XPS to determine the main elements on the TiO$_2$ surface and their chemical states. The survey spectrum was shown in Figure 4(a). The binding energies obtained in the analysis were corrected for specimen charging by C ls (284.8 eV) [15]. The results indicated the presence of five elements: C, Ti, O, Sn, and Ag. In Figure 4(b), the two Sn 3d peaks centered at 495.2 and 486.9 eV were assigned as Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$, respectively. The binding energy of Sn 3d$_{5/2}$ (486.9 eV) matched the typical values for SnO$_2$ [16,17], indicating that the Sn$^{4+}$ dopant was incorporated into TiO$_2$ to form SnO$_2$. In the spectrum of Ag 3d (Figure 4(c)), the binding energies of 368.2 and 374.2 eV were respectively attributed to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$. The 6.0 eV splitting within the Ag 3d doublet indicated the formation of metallic Ag on the surface of TiO$_2$ [18,19]. The Ag content of AgST-0.15 estimated from XPS was 3.76%. The atomic ratio of O/Ti
determined from XPS was 2.82:1, suggesting the existence of oxygen vacancies on the surface of TiO$_2$.

**EDX analysis:** The AgST-0.15 sample was analyzed by EDX in order to determine its composition (Figure 5). Elemental analysis results (Table 1) showed only Ti, O, Ag and Sn with no detectable impurities, which are in agreement with the XPS results.

**Photoelectrochemical performance**

**UV-Vis DRS analysis:** The activity of a photocatalyst mainly depends on the width of its band gap, and the recombination rate of electron-hole pairs. From the UV-vis DRS results in Figure 6, the band gaps for PT, AgT, ST, and AgST-0.15 were estimated to be 3.17, 3.06, 3.02, and 2.85 eV, respectively. Compared to PT, both AT and ST exhibited enhanced absorption extending towards the visible region. AgST-0.15 exhibited significant absorption in both UV and visible regions, revealing the synergistic effects of SnO$_2$ addition and Ag modification in narrowing the band gap of TiO$_2$. This obtained result could be ascribed to the following mechanisms: (1) electron transfer from TiO$_2$ surface to SnO$_2$, which reduced the electron density on the TiO$_2$ surface, as well as the rate of recombination of photogenerated holes and electrons [20,21], (2) Ag with its high electrical conductivity can transfer electrons during the photocatalytic reaction, thereby dispersing the electrons and photogenerated holes [22].

**Photocatalytic activity in Rhodamine B degradation:** The photocatalytic activities of the samples were evaluated by the degradation of Rhodamine B under visible light irradiation, with the results shown in Figure 7. The degradation rates were relative to the Rhodamine B concentration at adsorption equilibrium (after 30 min in the dark). Compared with PT, all modified TiO$_2$ samples showed improved photocatalytic performance, especially the Ag-modified SnO$_2$@TiO$_2$ core-shell composites, which remarkably accelerated the photodegradation. Importantly, the photocatalytic efficiency initially increased with the concentration of AgNO$_3$ used for treatment, from 0 to 0.1 and then 0.15 M. Afterwards, the efficiency decreased with AgNO$_3$ concentration up to 0.3 M. The AgST-0.15 sample exhibited the best catalytic efficiency, degrading 99.14% of Rhodamine B in 60 min while PT only degraded 45.7% during the same time period.

**Photochemical stability of the catalysts**

Figure 8 compared the cycle stability of AgST-0.15, the most
Ag-modified SnO$_2$@TiO$_2$ core-shell composites were successfully prepared by a hydrothermal method. Compared with pure TiO$_2$, the composite sample had significantly higher photocatalytic activity in visible light due to the synergistic effect of Ag modification and SnO$_2$ addition. The photocatalytic activity of Ag-modified SnO$_2$@TiO$_2$ core-shell composites was better than the published results for TiO$_2$-SnO$_2$ [23]. Since Ag has good electrical conductivity, it can facilitate the electron transfer during the photocatalytic reaction, and disperse the electrons and photogenerated holes. However, excess Ag may cover the surface of TiO$_2$, thereby reducing the photocatalytic rate. Hence, there was an optimal Ag content for photocatalysis, beyond which the efficiency would decrease. The sample modified with 0.15 M AgNO$_3$ possessed the best photocatalytic performance, as well as cycle stability.

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### Table 1: The elemental composition of AgST-0.15.

| Element | Weight percent (%) | Atomic percent (%) |
|---------|--------------------|--------------------|
| O K     | 50.32              | 82.85              |
| Ti K    | 18.10              | 9.95               |
| Ag L    | 8.71               | 2.13               |
| Sn L    | 22.87              | 5.08               |
| Total   | 100.00             | 100.01             |

### Figure 6: UV-vis diffuse reflectance spectra of different photocatalyst samples.

### Figure 7: The degradation curves of Rhodamine B under visible light irradiation with different photocatalysts.

### Figure 8: Photochemical stability of AgST-0.15 and PT. The degradation rate is based on 60 min of reaction time.

### Conclusion

Ag-modified SnO$_2$@TiO$_2$ core-shell composites were successfully prepared by a hydrothermal method. Compared with pure TiO$_2$, the composite sample had significantly higher photocatalytic activity in visible light due to the synergistic effect of Ag modification and SnO$_2$.
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