Research Article

Synthesis of Hollow CdS-TiO$_2$ Microspheres with Enhanced Visible-Light Photocatalytic Activity

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CdS-TiO$_2$ composite photocatalyst in the shape of hollow microsphere was successfully synthesized via the hard-template preparation with polystyrene microspheres followed by ion-exchange approach. The hollow CdS-TiO$_2$ microspheres significantly extended the light adsorption into visible light region, comparing to TiO$_2$ microspheres. It led to much higher photocatalytic activities of hollow CdS-TiO$_2$ microspheres than that of TiO$_2$ during the photodegradation of rhodamine B under visible light irradiations. Furthermore, the well-remained hollow structure could achieve light multireflection within the interior cavities and the separation of photo-induced electrons and holes is efficient in CdS-TiO$_2$, which were facilitated to improving the photoactivity.

1. Introduction

Photocatalysis has attracted considerable scientific interest owing to its potential applications in environmental purification and H$_2$ energy production [1]. TiO$_2$ is the most promising photocatalyst owing to its various advantages including nontoxicity, low cost, high activity, and strong stability. However, its practical application has been restricted by the wide band gap (3.2 eV) and low quantum efficiency [2]. Up to now, various methods have been developed to extend the light absorbance of TiO$_2$ into visible light region and thus improve the photocatalytic efficiency, such as doping with other impurities [3], depositing noble metals on TiO$_2$ [4], and combining TiO$_2$ with other semiconductors [5]. Cadmium sulfide (CdS) with band gap of 2.4 eV has been widely used to sensitize TiO$_2$ to realize visible-light absorbance and improve the charge separation efficiency [6]. Meanwhile, it is well known that the design of well-defined structure is a promising way to achieve high photocatalytic activity via increasing specific surface area and promoting light harvesting [2]. Considerable efforts have been devoted to obtain the unique morphology, such as wires, tubes, core-shell microspheres, and hollow microspheres [7–10]. Hollow microspheres have attracted an immense interest for their high surface area, low density, and large light-harvesting efficiency [10]. Various methods have been developed for preparing hollow microspheres, including spray-drying method, photochemical preparation, and hard-template method [11–13]. Among these techniques, hard-template process is a general and effective approach for preparing hollow microspheres via using polymer, carbon, and silica microspheres as templates. As we know, the polymeric polystyrene (PS) microspheres are easy to be removed by calcination. Additionally, it is more convenient to achieve the uniform diameter of polystyrene microspheres than other microspheres.

Herein, we report the preparation of hollow CdS-TiO$_2$ microspheres via the hard-template process with PS microspheres followed by the ion-exchange approach. The ion-exchange is a convenient and flexible method to convert CdO into CdS [14, 15]. The introduction of CdS can effectively extend the photoresponse of TiO$_2$ to visible-light region and improve the photocatalytic activity of decomposition of rhodamine B (RhB) in aqueous solution.

2. Experimental Details

2.1. Catalyst Preparation. All the chemicals were of analytic purity and used without further purification. The synthetic approach included two steps. (1) hollow CdO-TiO$_2$ microspheres prepared using polystyrene microspheres as hard
template. Monodisperse PS microspheres were synthesized by emulsifier-free batch emulsion polymerization according to the previous report [16]. 0.27 g Cd(Ac)₂·2H₂O was dissolved in the mixture of 80.0 mL 2-propanol and 5.0 mL ethanol. Then a 5.0 mL prepared PS microspheres latex was dropped into the solution followed by stirring at 55°C for 30 min. After the solution was cooled down to room temperature, 4.0 mL 0.2 M aqueous NaOH solution was added. Then, the mixture was cooled down to room temperature after reacting at 55°C for 20 min followed by the centrifugation and wash in ethanol for three times. 0.10 g obtained powder was dispersed into the solution of 1.3 mL water and 5.0 mL ethanol. Another solution was mixed with 76.0 μL Ti(OBu)₄ and 20.0 mL ethanol via being refluxed at 75°C for 2 h. Subsequently, two solutions were mixed together and reacted for 20h. The obtained composites were washed in ethanol for three times and dried at 40°C. In order to remove the polymer template, the obtained powder was heated at 550°C for 4 h. (2) Converting CdO to CdS at room temperature. 0.3 g above-prepared powder was dispersed in 50.0 mL 0.2 M Na₂S aqueous solution with stirring for 2 h at room temperature followed by filtration and wash. The collected products were designated as CdS-TiO₂. For comparison, TiO₂ sample was prepared according to the same process without Cd(Ac)₂·2H₂O.

2.2. Characterization. The sample composition was determined by inductively coupled plasma (ICP, Varian VISTA-MPX). The surface morphologies were observed using field emission scanning electron microscopy (FESEM, HITA-CHI S4800). X-ray diffraction patterns were recorded to confirm the composition of crystallite using a Rigaku Dmax-3C with Cu Ka radiation (λ = 1.5418 Å). The UV-vis diffuse reflectance spectra (DRS) of the samples over a range of 200–800 nm were collected on a UV-2450 instrument. Photoluminescence measurements were carried out on Varian Cary-Eclipse 500.

2.3. Photocatalytic Test. Liquid-phase photocatalytic degradation of RhB was carried out at 30°C in an 80 mL self-designed quartz photochemical reactor containing 50.0 mg catalyst and 50.0 mL 10.0 mg/L RhB aqueous solution. The suspension was magnetically stirred continually. After adsorption-desorption equilibrium for 1 h, the photocatalytic degradation of RhB was initiated by irradiating the reaction mixture with a one 500 W xenon lamp (CHF-XM500, light intensity = 600 mW/cm²), a 420 nm glass filter (JB-420) was used to remove the radiation in the UV region. The light source was located at 18 cm away from the reaction solution. Each experiment was lasted for 3 h and the concentration was measured at a time intervals of 30 min. the RhB concentration was determined by measuring absorbance using a UV-vis spectrophotometer (UV-7502PC) at its characteristic wavelength of 553 nm. Preliminary tests demonstrated a good linear relationship between the light absorbance and RhB concentration. The degradation yield can be calculated using the following equation:

\[
\text{Degradation yield} = \frac{C_0 - C}{C_0} \times 100\%.
\]  

Here, \(C_0\) was the initial concentration of RhB and \(C\) was the concentration of RhB remaining in the solution. Meanwhile, experimental results also confirmed that only less than 6.0% RhB was removed in the absence of catalyst or light irradiation and thus could be neglected in comparison with the photocatalysis process.

3. Results and Discussion

3.1. Characterization of CdS/TiO₂ Composites. The ICP result demonstrated that the molar ratio of CdS to TiO₂ was 12.3% in CdS-TiO₂ composites. The crystal phase of calcined CdS-TiO₂ and TiO₂ samples were characterized by wide-angle powder XRD method as shown in Figure 1. The principal peaks of anatase TiO₂ were found (ICPDS 21–1272), indicative of the well crystallization. The diffraction peak of CdS could be corresponded to the hexagonal CdS crystal (JCPDF 41–1049). The peak of CdS was weak possibly due to the package of exterior TiO₂. No other crystalline impurities including CdO crystal could be detected, indicative of the complete ion exchange converting from CdO to CdS. Meanwhile, no significant shift of principal peaks of either the CdS or the TiO₂ was observed, confirming that the CdS was present in a separated phase rather than in the TiO₂ lattice.

FESEM images in Figure 2 displayed the formation process of CdS-TiO₂ composites in the shape of hollow microsphere via the hard template of PS microspheres. All the microspheres covered with precursor revealed uniform size and smooth surface, indicating that both Cd and Ti precursors were successfully coated on PS microspheres. Furthermore, the size of microspheres after coating with Ti precursor was larger than that of microspheres only coated with Cd precursor with the increased diameter from about 300 nm to 340 nm. After calcination and ion exchange from CdO to CdS, CdS-TiO₂ sample showed the slightly decreased size with the diameter of about 300 nm. The hollow structure was formed with the shell thickness of about 30 nm. It is clear that
the hollow structure was maintained well after calcination without any destroying and collapse. The decreased diameter of hollow CdS-TiO2 microspheres was attributed to the shrinkage during the removal of PS microsphere templates. It was suggested that hollow CdS-TiO2 microspheres could be successfully fabricated by the polymer hard-template method combined with anion-exchange approach.

From Figure 3, UV-vis DRS spectra of CdS-TiO2 and TiO2 samples indicated that TiO2 could only absorb UV light with wavelength less than 400 nm for its large energy gap of anatase (3.2 eV). The introduction of CdS in CdS-TiO2 sample can effectively shift the absorption range of TiO2 into visible light region of 400–550 nm due to the narrow band gap of CdS (2.4 eV). Therefore, the light-harvesting efficiency of CdS-TiO2 hollow microspheres was larger than that of TiO2 in visible light region, beneficial to the photocatalytic activity.

The efficiency of charge trapping and recombination of photo-induced electrons and holes in the semiconductor could be verified by PL spectra. According to PL spectra of both CdS-TiO2 and TiO2 samples in Figure 4 with the excitation wavelength of 360 nm, CdS-TiO2 exhibited much weaker intensity of peak at 720 nm than TiO2. It could be ascribed to the lower recombination probability of photo-induced electrons and holes [17, 18]. As we know, the efficient charge transfer from CdS to TiO2 conduction band could effectively separate photo-induced electrons from holes in the CdS semiconductor and thus inhibit their recombination, resulting in the enhanced charge density in the TiO2 conduction (Scheme 1).

3.2. Photocatalytic Performance. The photodegradation of RhB under visible-light irradiations ($\lambda > 420$ nm) was used as a probe to evaluate the performance of photocatalysts. According to the dependence of photodegradation rate on...
reaction time (Figure 5), the removal of RhB in the absence of photocatalyst could be neglected. After reaction for 3 h, CdS-TiO2 presented much higher degradation yield than TiO2 sample, which was up to 90%. The degradation result well demonstrated that the introduction of CdS could significantly extend light absorbance into visible-light region with high intensity and thus promote the photocatalytic activity under visible-light irradiations. The well-remained structure of hollow microsphere via polymer hard-template approach followed by ion-exchange could achieve light multireflection within the interior cavities, leading to more efficient light harvesting [19]. Furthermore, the lower recombination of photo-induced electrons and holes in CdS-TiO2 than that in TiO2 could lead to the improved quantum efficiency and facilitate the formation of active radicals which decomposed organic compounds.

4. Conclusions

Hollow CdS-TiO2 microspheres with uniform size were synthesized via hard-template process with PS microspheres followed by ion-exchange. During the photodegradation of RhB under visible light irradiations, CdS-TiO2 exhibited much higher photocatalytic activity than TiO2. It was attributed to the introduction of CdS which extended the photoreponse to the visible-light region and improved the separation of photo-induced charges.

Acknowledgments

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