Preparation of spherical and dendritic CdS@TiO2 hollow double-shelled nanoparticles for photocatalysis

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Abstract
Spherical and dendritic CdS@TiO2 hollow double-shelled nanoparticles (HDNPs) with visible light photocatalytic activity were synthesized via sol–gel and wet-chemical approach respectively. The morphologies, composition, size of the nanoparticles and crystal structure of the synthesized CdS@TiO2 HDNPs were characterized by XRD, TEM, and SAED. The results showed that morphologies and crystalline phases of as-prepared CdS@TiO2 HDNPs mainly depended on the synthesis conditions such as temperature and pressure. Compared with the typical core–shell of PS@TiO2 and PS@CdS, CdS@TiO2 HDNPs, their photocatalytic activity was obviously enhanced with maximum degradation efficiency of RhB as high as 99.9%.

1. Introduction
In recent years, the core–shell nanoparticles have aroused great interest due to the tremendous demands of modern technology for more advanced materials, particularly in the photocatalysis field [1,2]. Previously researchers synthesized CdS@TiO2 core–shell structure samples exhibited greatly enhanced photocatalytic activity toward the degradation of Rhodamine B (RhB) and 4-chlorophenol aqueous solution under visible light irradiation (λ > 420 nm) [3]. The enhanced photosensitivity and catalytic properties of the combination of CdS and TiO2 resulted from reducing electron-hole recombination rate via photoexcited electron transporting from the TiO2 shell to the CdS core.

However, in the case of the heterogeneous photocatalytic reaction, low surface-to-volume ratio of solid nanoparticle greatly affects its catalytic effect for containment removal [4]. Recently, hollow microspheres nanomaterials have been proved to be a promising structure to make up for the deficiency with high surface area, low density, excellent loading capacity and high light-harvesting efficiency [5,6].

In this paper, we report an ultrasonic-assisted reaction followed by a subsequent sol–gel or wet-chemical method for preparing CdS@TiO2 HDNPs with spherical and dendritic morphologies and estimate their photocatalytic performance.

2. Experimental details
2.1. Preparation of spherical and dendritic CdS@TiO2 HDNPs
The hydrolysate of Ti (VI) source as TiO2 precursor was coated on PS@CdS in our previous work [7, 8]: As-prepared PS@CdS powder of 0.2 g was ultrasonic dispersed in 50 mL of ethanol and then 0.08 mL of tetrabutyl titanate (TBT) was added into the mixture. Subsequently, the de-ionized water dropwise in the solution above, which next heated at 60 °C for 2 h. To obtain the spherical ones, the solution above needed continual heating at 60 °C for 15 h. To obtain the dendritic ones, the mixture was transferred into hydrothermal reactor and heated at 180 °C for 15 h. At last, the CdS@TiO2 HDNPs were obtained by calcining at 550 °C for 4 h to remove polymer cores and crystallize TiO2. A comparison, we also prepared the PS@TiO2 core–shell by sol–gel process.

2.2. Material characterization
Microstructural characterizations of the core–shell nanoparticles were carried out by transmission electron microscopy (TEM, JEOL: JEM-2100UHR) operated at an accelerating voltage of 200 kV. Phase determination of the core–shell nanoparticles was carried out by an X-ray diffractometer using Ni-filtered Cu Kα radiation at 40 kV and 40 mA in the 2θ range of 20–80°, with a scan rate of 0.02° per second (wavelength = 1.54056 Å).
3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of PS@CdS, PS@TiO$_2$ core–shell and spherical and dendritic CdS@TiO$_2$ HDNPs samples and examines the crystallographic structure of the as-prepared samples. A comparison of the XRD patterns of PS@TiO$_2$ and PS@CdS with two kinds of CdS@TiO$_2$ HDNPs (blue and red) reveals an increase in the intensity of the TiO$_2$ peak in CdS@TiO$_2$ HDNPs and peak at 25.3° so then concluding a successful combination of TiO$_2$ and CdS nanoparticles in spherical and dendritic CdS@TiO$_2$ HDNPs. In addition, a typical diffraction peak of anatase’s TiO$_2$, located at 2θ=25.3°, is observed in dendritic CdS@TiO$_2$ HDNPs, which is more intense than spherical one due to its higher content of the (101) crystal plane of anatase-phase TiO$_2$.

Detailed morphological features and crystallinity of the PS@CdS and CdS@TiO$_2$ HDNPs were investigated using TEM and SAED analyses, as is shown in Fig. 2. Fig. 2a and b show that the CdS-coated shell thickness was approximately 40 nm and the formation of double shell spherical structures with shells of about 90 nm in thickness. Fig. 2c presents that the growing pattern of TiO$_2$ nanoparticles changed and adendritic morphology can be distinguished with increasing reaction temperature up to 180 °C. Insets in Fig. 2d and e display the high-resolution TEM (HRTEM) and SAED images of spherical and dendritic CdS@TiO$_2$ HDNPs. The identified lattice spacings of 0.351, 0.458 and 0.356 nm in HRTEM images of insets in Fig. 2d and e correspond to the (101) plane of anatase TiO$_2$, (001) plane of rutile TiO$_2$ and (100) plane of hexagonal CdS phase, respectively.

3.2. Growth mechanism

In this work, we described that the preparation of CdS@TiO$_2$ HDNPs with sol–gel or wet-chemical method after the ultrasound-assisted synthesis of PS@CdS core–shell structure. The formation mechanism of PS@CdS core–shell structure has been clarified in our previous work [7]. In the growth progress of TiO$_2$ onto CdS layer surface, the temperature is an important factor of controlling the crystal type and microstructural aspect of TiO$_2$. The previous studies indicated that TiO$_2$ nanoparticles were prepared by the sol–gel process from a condensed Ti(OH)$_4$ gel preformed by the hydrolysis of a Ti(VI) source. It took about a few hours or more for hydroxide ions to reach the adsorption equilibrium with Ti(OH)$_4$ precipitate at a lower temperature, but it was promoted and greatly accelerated at a higher temperature [9]. It is a slow and less severe process to form TiO$_2$ particles at the reaction temperature of 60 °C under atmospheric condition which could form a smooth TiO$_2$ layer. To gain mixed precursor of TiO$_2$, the solution was placed under this condition for 2 h in the first step. With the increasing of reaction temperature, as one can imagine, the violence of the reaction gets higher step by step. While reaching 180 °C, the growth of TiO$_2$ is so fast that the newly generated particles seek to expand. In the case of dendritic CdS@TiO$_2$ HDNPs, the formation of dendritic TiO$_2$ nanorods probably attributes to the remainder PVP of extending on the CdS surface and PVP plays a role of surfactant to assist TiO$_2$ nanorods to extend vertically on the CdS surface. Meanwhile, we discovered that the longer of the reaction time in the hydrothermal process was, the longer of TiO$_2$ nanorods were.

3.3. Photocatalysis test

To evaluate the photocatalytic activity of the as-prepared samples, 40 mg of the powder was dispersed in 200 mL deionized water containing 5 mg/L RhB. A 500W Xenon lamp with a cutoff filter (λ > 400 nm) was used as the visible source. Before each irradiation, the solutions were kept in the dark for 1 h in order to reach the adsorption equilibrium. The photocatalytic performances of the four as-prepared samples have been shown in Fig. 3.

It can be observed obviously that the photocatalytic activity of different catalysts decreased in the following order: dendritic CdS@TiO$_2$ > PS@CdS > spherical CdS@TiO$_2$ > PS@TiO$_2$. The dendritic CdS@TiO$_2$ HDNPs demonstrated significantly improved photocatalytic performance in comparison with PS@CdS for photocatalytic redox reactions. It was clear that the enhancement of photocatalytic performance of these combined nanoparticles was mainly resulted from the charge transformation at the interfaces between CdS and TiO$_2$ with matched band structure, which accordingly favored an effective photoexcited electron hole separation in these two layers [10]. The photoinduced electrons on the CdS surface can transfer easily to conduction band (CB) of TiO$_2$. Likewise, photoinduced holes on the TiO$_2$ surface will migrate to CdS due to different valence band (VB) edge potentials. However, when the density of the TiO$_2$ outer shell is reach a high-value, even CdS was entirely covered (spherical CdS@TiO$_2$), its surface active sites for the holes will be occupied. This moment the surface TiO$_2$ layer would be excited first by the light and injected electrons into the CB of CdS, causing a suppression of the generation of excitons from CdS, resulting in a lower photocatalytic activity even than pure PS@CdS [11]. For the dendritic CdS@TiO$_2$ HDNPs, only parts CdS are covered by TiO$_2$, which exposes more active sites. The dendritic CdS@TiO$_2$ HDNPs have not only hollow double-shelled structure but also abundant sharp corners and edges and result in higher surface area. By and large, in addition, the anatase of TiO$_2$ exhibits higher photocatalysis activity than crystal shape of rutile and dendritic samples contain more anatase of TiO$_2$. The above reasons cooperate to make the dendritic CdS@TiO$_2$ HDNPs possess the highest photocatalytic effect and superior electrochemical properties compared to other nanoparticles with smooth surfaces.

4. Conclusions

In this work, two novel types of CdS@TiO$_2$ HDNPs were successfully synthesized based on a strategy of controlling the hydrolysis extent of the precursor of TiO$_2$ chiefly and tested for their photocatalytic activity. Dendritic CdS@TiO$_2$ HDNPs exhibited higher photocatalytic activity than PS@CdS core–shell and
thus, dendritic CdS@TiO2 HDNPs are promising materials for application in degradation of dye wastewater. This paper opens up a new way to synthesize CdS@TiO2 HDNPs and to further improve the photocatalysis performance of CdS@TiO2-based devices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.11.127.

References