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Synthesis of core-shell structured CdS@CeO$_2$ and CdS@TiO$_2$ composites and comparison of their photocatalytic activities for the selective oxidation of benzyl alcohol to benzaldehyde

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ABSTRACT

Core-shell structured CdS@CeO$_2$ and CdS@TiO$_2$ composites were fabricated, with the aim of systematically comparing the influence of shell layer composition on the photocatalytic activity of CdS. The obtained samples were characterized by the means of transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nitrogen adsorption–desorption, and UV–vis diffuse reflectance spectroscopy (DRS). It was found that the core-shell structured CdS@CeO$_2$ and CdS@TiO$_2$ have been successfully constructed and the absorption edge exhibits a slight blue-shift after coating CeO$_2$ or TiO$_2$ shell layer. The selective oxidation of benzyl alcohol indicates that the photocatalytic activities of the synthesized samples show an increasing tendency in the order of CeO$_2$ < CdS < CdS@TiO$_2$ < CdS@CeO$_2$-90 < CdS@CeO$_2$-180 (CdS@CeO$_2$ samples treated at 90 °C and 180 °C were denoted as CdS@CeO$_2$-90 and CdS@CeO$_2$-180, respectively). It was revealed that the redox couple Ce^{4+}/Ce^{3+} in CeO$_2$ shell not only promotes the separation of electron-hole pairs but also favors the transfer of electrons from the inner layer of CeO$_2$ shell to its outer layer. Hydrothermal treatment can increase the contents of Ce^{3+} and chemisorbed oxygen, by which the photocatalytic activity can be enhanced. The radical scavenging experiments proved that in acetonitrile solution $^{\bullet}O_2^-$ and hole are the main reactive species responsible for the transformation from benzyl alcohol to benzaldehyde.

1. Introduction

Semiconductor photocatalysis has attracted much attention as a promising solution to solve the worldwide environmental and energy issues [1–6]. Amongst the various semiconductor materials, TiO$_2$ has been widely studied because of its low-cost, nontoxicity, and high photostability [7–9]. However, the practical applications of TiO$_2$ have been suppressed by their two drawbacks, one of which is the poor solar efficiency that is determined by their wide band gap; the other is the low quantum yield that arises from the rapid recombination of photo-generated electrons and holes. Therefore, considerable efforts have been devoted to exploiting more efficient visible-light-active photocatalysts to meet the requirements of environment and energy.

As a classical semiconductor with narrow band gap (Eg = 2.4 eV), CdS has been extensively studied due to its excellent capability for visible light response. So far, it has been successfully used in the fields of pollution degradation, solar cells, hydrogen production, and selective organic synthesis [10–15]. However, CdS also meets the issue of high recombination rate of photogenerated electrons and holes. To solve this problem, many strategies, such as doping with metals or nonmetals, loading of noble metals, and coupling with other semiconductors, have been adopted [16–19]. Among these techniques, constructing core-shell structure composites with other semiconductors has received much attention because the core-shell structure often shows superior efficiency in the separation of electrons and holes [20–22]. For the coupled semiconductor materials, TiO$_2$ is considered to be one of the most suitable candidates owing to its matched conduction band and high chemical stability. After absorbing visible light, the photogenerated electrons can be transferred from the conduction band of CdS to that of TiO$_2$ while holes remain in CdS, by which the photo quantum efficiency can be improved [23]. For instance, Liu et al. reported that TiO$_2$ shell layer with suitable thickness can improve the photocat-

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alytic activity of CdS nearly 60% in terms of the selective oxidation of benzyl alcohol [24]. Lee et al. found that the H_2 evolution rate over core-shell structured CdS@TiO_2 increased nearly 6 times compared with bulk CdS [24]. Alternatively, CeO_2 is also a suitable coupler used to improve the photocatalytic activity of CdS because the redox couple Ce^{4+}/Ce^{3+} in CeO_2 can effectively separate the photogenerated electrons and holes [25,26]. For example, Tang's group found that the conversion rate of nitroaromatics over CdS@CeO_2 nanowires was more than twice as much as that of blank CdS nanowires under visible light irradiation [25]. Yuan et al. disclosed that the degradation of Rhodamine B over CdS@CeO_2 nanorods was improved ∼50% than that over CdS nanorods [26]. Although the previous studies have confirmed that both TiO_2 and CeO_2 shell layer can improve the photocatalytic activity of CdS core, the effects of TiO_2 and CeO_2 shell layer on the photocatalytic activity have never been systematically compared. Since the researchers' experiments were conducted under different conditions, it is hard to obtain a defined conclusion about the effects of TiO_2 and CeO_2 shells on improving photocatalytic activity.

In the present work, we constructed core-shell structured CdS@CeO_2 and CdS@TiO_2 composites and systematically comparing their photocatalytic activities in terms of the selective oxidation of benzyl alcohol (BA) to benzaldehyde (BAD). On the basis of a series of characterization and experiment results, the photocatalytic oxidation mechanism of BA over CdS@CeO_2 was proposed. It was revealed that the redox couple Ce^{4+}/Ce^{3+} in CeO_2 not only promotes the separation of photogenerated electrons and holes but also facilitates the transfer of electrons from the inner layer of CeO_2 shell to its outer layer. Moreover, we also investigated the influence of hydrothermal treatment on the photocatalytic activity of CdS@CeO_2.

2. Experimental

2.1. Synthesis of CdS nanospheres (NSPs)

Uniform CdS NSPs were synthesized by a simple hydrothermal method, similar to the previous reference [22]. In a typical procedure, 1.28 g (4.8 mmol) of cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$), 1.44 g (24 mmol) of thiourea (NH_2CSNH_2) and 60 mL of deionized water were added into a flask and stirred at room temperature to form a clear solution. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 140 °C for 24 h. After the autoclave had been cooled to room temperature, the yellow precipitate was collected by centrifugation and washed three times with deionized water and ethanol to remove the residual ions. Finally, the obtained CdS NSPs were further dried at 70 °C for 5 h.

2.2. Synthesis of core-shell structured CdS@CeO_2

Firstly, Stock solution A was beforehand prepared by dissolving 74.4 mg (0.2 mmol) of EDTA-2Na and 86.8 mg (0.2 mmol) of $Ce(NO_3)_3{\cdot}6H_2O$ in 20 mL of deionized water. Meanwhile, Stock solution B was prepared by dissolving 20 mL of concentrated ammonia (30%) into 80 mL of ethanol. For the preparation of core-shell structured CdS@CeO_2, 20 mg of CdS nanospheres and 0.4 g of CTAB were added into a flask containing 79 mL of deionized water, followed by ultrasonic irradiation for 20 min to form a uniform CdS suspension. Subsequently, 20 mL of Stock solution A and 1 mL of Stock solution B were sequentially added into the above CdS suspension under vigorous stirring. Then, the temperature of the mixed solution was elevated to 90 °C and kept at this temperature for 5 h under gentle stirring and O_2 atmosphere. Finally, the product was collected by centrifugation, washed repeatedly with deionized water, and dried in at 70 °C for 5 h, denoted as CdS@CeO_2-90.

33 mg CdS@CeO_2-90 in 60 mL of H_2O was transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 18 h. The product was washed with and dried in vacuum at 70 °C for 5 h, denoted as CdS@CeO_2-180.

2.3. Synthesis of core-shell structured CdS@TiO_2

Core-shell structured CdS@TiO_2 was synthesized according to the following procedure: Under ultrasound irradiation, 150 mg of CdS was dispersed in 100 mL of ethanol, followed by addition of 3.4 g (1 mmol) tetrabutyl titanate [27]. Subsequently, 30 μL of ammonium hydroxide was slowly added to the mixture and further stirred at 50 °C for 12 h. Then, the collected suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 18 h. Finally, the product was collected by centrifugation (4000 rmp, 20 min), washed repeatedly with deionized water, and dried in vacuum at 70 °C for 5 h.

2.4. Characterization

The crystal phases of the synthesized samples were analyzed by a Rigaku Ultima IV X-ray diffractometer equipped with a graphite monochromator, using Cu Kα radiation (α = 0.15406 nm), operated at 40 kV and 40 mA. The morphologies of the samples were observed with a JEOL JEM2000EX transmission electron microscope (TEM). The Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) were measured with an ASAP 2020 apparatus at 77 K. The pore sizes of the samples were determined by the Barret–Joyner–Halender (BJH) method. The UV–vis diffuse reflectance (DRS) spectra were tested using a SHIMADZU UV-2450 spectrophotometer equipped with an integrating sphere assembly, using $BaSO_4$ as the reference material. X-ray photoelectron spectroscopy (XPS) spectra of the samples were obtained with Thermo Fisher ESCALAB 250Xi system with Al Kα radiation, operated at 250 W. Binding energies were standardized by assigning the value of the C 1s peak to 284.8 eV.

2.5. Photocurrent and photocatalytic activity measurements

The transient photocurrents were measured with an electrochemical station (ZAHNER, Germany) by a standard three-electrode system, using the sample as the working electrode with an active area of 1.0 cm^2, a Pt foil as the counter electrode, 0.01 M Ag^+/Ag as the reference electrode, and 0.1 M Tetra-*n*-butylammonium hexafluorophosphate as the electrolyte, adding 0.5 bias voltage. In these tests, acetonitrile was chosen as the solvent to simulate photocatalytic oxidation reaction system. A 300 W Xe arc lamp with a UV cutoff filter ($\lambda \geq 420$ nm) was used as the visible light source.

The photocatalytic selective oxidation of BA was performed in a 25 mL three-necked flask at room temperature and oxygen atmosphere (1 bar). A 300 W xenon arc lamp with a UV-cutoff filter ($\lambda \geq 420$ nm) was used as the visible light source to drive the photocatalytic reaction. Acetonitrile was selected as the reaction medium for BA oxidation. For each measurement, 20 mg of photocatalyst sample was dispersed in the mixed solution of acetonitrile (8 mL) and BA solution (83 μL, 0.8 mmol) under ultrasound irradiation. Prior to light irradiation, the mixture was stirred in the dark for 30 min to attain the adsorption–desorption equilibrium for BA and dissolved oxygen on the surface of photocatalyst. The concentrations of BA and BAD were measured with a SHIMADZU SPD-M20A high-performance liquid chromatograph (HPLC). The conversion rate of BA, the yield of BAD, and reaction selectivity were calculated with the following equation:

$$\text{BA conversion rate}(\%) = \frac{(C_0 - C_1)}{C_0} \times 100$$

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