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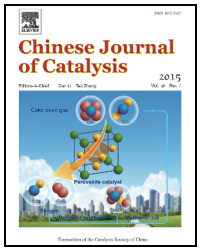

Article

Mild, one-step hydrothermal synthesis of carbon-coated CdS nanoparticles with improved photocatalytic activity and stability

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ABSTRACT

Carbon-coated CdS (CdS@C) nanoparticles were conveniently prepared by a one-step hydrothermal carbonization method at temperature as low as 130 °C, in which cadmium acetate and glucose were used as the cadmium and carbon sources, respectively, and thiourea was used as the sulfur source and catalyst for the hydrothermal carbonization of glucose. The prepared CdS@C particles possess a smaller size, better dispersion, and more uniform distribution than pure CdS particles prepared under the same conditions. Furthermore, the hydrothermal carbonization of glucose easily induces the prior formation of metastable cubic CdS crystals. In addition, the carbonaceous species coated on the surface of CdS expands the range of absorption light and slightly decreases the band gap of CdS, as well as reduces the recombination of the photogenerated electron-hole pairs of CdS and its photo-oxidative corrosion, which can improve the photocatalytic activity and stability of CdS for the photo-oxidative degradation of methyl orange in aqueous solution under visible light irradiation.

1. Introduction

During the past few decades, photocatalytic oxygenation has attracted extensive interest because of its potential application in environmental treatment and the synthesis of fine chemicals [1–3]. Meanwhile, a large number of metal oxide and sulfide semiconductors have been found to be effective photocatalysts in the purification of wastewater and the removal of waste gas [4–6]. Cadmium sulfide (CdS) as a II-VI n-type semiconductor material possesses a low band gap energy (2.4 eV) and good visible light absorption as well as unique photo-electrochemical and photo-physical properties [7–10], and therefore it has been extensively applied to photoelectric conversion, nonlinear optics, optical sensors and, especially, in the field of photocatalysis [11–17]. However, CdS is prone to light corrosion reactions in aqueous solution, which shortens its photocatalytic lifetime and results in environmental pollution [18,19]. In addition, the photocatalytic activity of CdS is limited owing to its poor adsorption of the organic dye and the rapid recombination rate of its photogenerated electron-hole pairs. Some effective methods have been developed to improve the photocatalytic activity of CdS, such as precious metal deposition [20], metal cation doping [21,22], and semiconductor composites [23–25].

Recently, amorphous carbon as a coating material has received considerable attention because of its aromatic carbon sheet structure and its abundant surface –OH and –COOH

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groups that can efficiently reduce the photogenerated electron-hole pair recombination of CdS by accelerated electron transfer and can improve the adsorption capacity for organic contaminants in wastewater [26–28]. Moreover, the amorphous carbon-coated semiconductors can expand the light absorption range *via* a photosensitizing effect [27,29–31]. The amorphous carbon material is easily prepared by a simple hydrothermal or solvothermal process at a temperature higher than 160 °C using glucose or cellulose as a precursor [27,29,32–35]. To the best of our knowledge, however, the hydrothermal carbonization of glucose at lower temperatures has not yet been reported. Here, we report the preparation of carbon-coated CdS (CdS@C) nanoparticles by one-step hydrothermal carbonization of glucose under mild conditions and their photocatalytic performance in the visible light triggered-oxidative degradation of methyl orange (MO) aqueous solution.

2. Experimental

2.1. Preparation of catalyst

All chemicals were of analytical reagent grade purchased from Sinopharm and were used without further purification. Deionized water was used in all experiments. CdS@C hybrid particles were prepared by a one-pot hydrothermal method where, in a typical synthesis, $Cd(OAc)_2{\cdot}2H_2O$ (20 mmol), $(NH_2)_2CS$ (24 mmol), and $C_6H_{12}O_6{\cdot}H_2O$ (20 mmol) were dissolved in deionized water (80 mL) under ultrasonication to form a homogeneous aqueous solution, after which the solution was removed to a 100-mL Teflon-lined stainless autoclave. The sealed autoclave was heated to 130 °C and maintained at this temperature for various heating times. After cooling to room temperature, the resulting solid particles were collected and washed several times with distilled water and ethanol and subsequently dried in air at 60 °C for 12 h. Corresponding to the heating time used (8, 10, 14, 18, 20, and 22 h), the catalyst sample was designated as CdS@C-8, CdS@C-10, CdS@C-14, CdS@C-18, CdS@C-20, and CdS@C-22. For comparison, a pure CdS-18 sample was prepared using the same hydrothermal conditions as for sample CdS@C-18 in the absence of glucose. A typical photocatalyst P25 was purchased from Sinopharm.

2.2. Characterization of catalyst

X-ray diffraction (XRD) analysis of the samples was carried out at room temperature on a Y-2000 X-ray diffractometer apparatus using Cu K_α radiation (λ = 0.15406 nm) and a graphite monochromator, operated at a voltage of 30 kV and a current of 20 mA. XRD patterns were recorded in the angular range of 20°–80° with a scanning rate 0.05°/s. Scanning electron microscopy (SEM) analysis was performed with a MIRA3 TESCAN using an accelerating voltage of 20 kV, and with the energy-dispersive X-ray spectrometer (EDX) attached to the SEM. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM-2100F instrument with a tungsten filament, using an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra of the samples were obtained on a Nicolet 310 spectrometer in the wavenumber range of 4000–400 cm^{-1}. Ultraviolet to visible light (UV-Vis) diffuse reflectance spectra (DRS) of the samples were recorded from 200 to 800 nm using a UV-Vis spectrophotometer (UV-3310) with $BaSO_4$ as a reference. Photoluminescence (PL) measurements of the samples were carried out on an F-4600 FL spectrophotometer with the excitation wavelength of 370 nm. Thermogravimetric analysis (TGA) curves were recorded in air flow on a Netzsch Model STA 409PC instrument with a heating rate of 20 °C/min from room temperature to 600 °C using α-Al_2O_3 as the standard material.

2.3. Photocatalytic activity test

Photocatalytic activity of the as-prepared samples for the oxidative degradation of an MO aqueous solution was performed in a photo-reactor built in-house and equipped with a water-cooled condenser (15 °C). A typical procedure was as follows. Catalyst powders (0.02 g) were dispersed into the MO aqueous solution (10 mg/L, 30 mL), and a 35-W tungsten-bromine lamp with a UV light filter (Osram brand) was immersed in the suspensions. Before illumination, the mixture was magnetically stirred in the dark for 30 min under pure O_2 atmosphere to ensure adsorption-desorption equilibrium of the MO dye onto the surface of the catalyst. After given illumination time intervals, the reaction solution (1 mL) was taken out and centrifuged to remove the catalyst. The obtained filtrate was subjected to an analysis of MO concentration on the UV-Vis spectrometer 1102 using a work wavelength of 465 nm.

3. Results and discussion

3.1. Characterization of photocatalyst

3.1.1. XRD results

Figure 1 shows the XRD patterns of the CdS and CdS@C materials. The CdS-18 exhibits characteristic XRD peaks at 2θ = 24.9°, 26.5°, 28.1°, 43.9°, 47.8°, and 52.0°, which respectively correspond to the (100), (002), (101), (110), (103), and (112) crystal planes of hexagonal CdS (JCPDS 41-1049). In addition, there are no miscellaneous peaks attributed to CdO, Cd, and other cadmium compound crystals evident in this XRD pattern, indicating that the CdS-18 synthesized under these hydrothermal conditions is of a high quality. The XRD patterns of three catalysts (CdS@C-14, CdS@C-18, and CdS@C-22) are very similar to each other, exhibiting three strong peaks at 2θ = 26.6°, 43.8°, and 52.1°, which are respectively assigned to the (111), (220), and (311) crystal planes of face-centered cubic (fcc) CdS (JCPDS 89-0440). In addition, a very weak peak at the 2θ value of 47.8° and an asymmetry of the (111) crystal plane peak are also noticed in these XRD patterns, which is indicative of the existence of a hexagonal CdS impurity in the hybrid samples. We propose from these findings that the carbon species generated during hydrothermal carbonization of glucose likely hampers the release of S^{2-} ions and reduces the deposition rate of CdS, thus leading to the formation of dominant cubic CdS crystals [36]. Notably, the typical diffraction peaks attributed to