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Macroscopic urea-functionalized cadmium sulfide material with high visible-light photocatalytic activity for rewritable paper application

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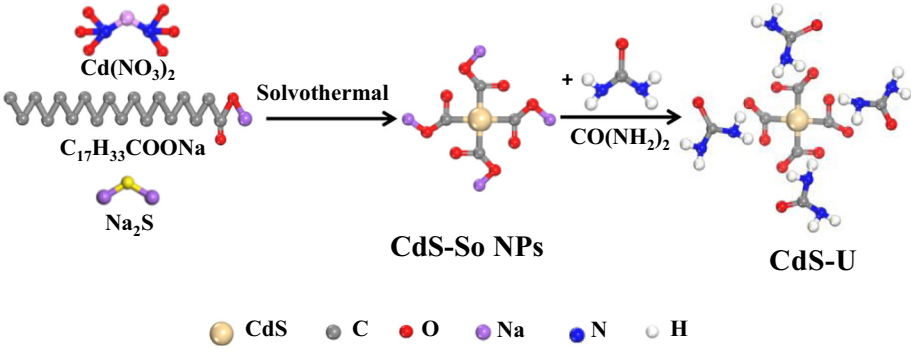
GRAPHICAL ABSTRACT

The CdS-U material exhibits excellent visible light photocatalytic activity and plasticity, making it convenient to produce visible light-responsive rewritable films.



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ABSTRACT

A macroscopic urea-functionalized CdS (CdS-U) is synthesized for the first time. The CdS-U material is formed through the interaction between —NH_2/—NH groups on urea and —COO^- groups on sodium oleate-capped CdS nanoparticles (CdS-So NPs). The CdS-U material exhibites excellent visible light photocatalytic activity and plasticity and has the potential to be produced as rewritable papers. It is convenience to produce a large-scale film by CdS-U. Letters can be written on the CdS-U film and disappear through a dissolution-irradiation process, and then the CdS-U film can be recycled by drying. This novel CdS-U material might be of interest and provide a new chance to advance the application of visible light photocatalyst on rewritable papers.

1. Introduction

Visible-light-responsive photocatalysts have attracted great attention for they can harvest and utilize solar energy to solve energy and environmental problems [1,2]. Among various visible light photocatalysts [3,4], CdS is one of the most promising

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visible-light-responsive photocatalysts with a narrow energy band gap (2.4 eV) [5]. However, CdS suffers from the difficulty in recovery, the photocorrosion, and the limited catalytic activity, which largely restricts the practical application of CdS [6,7].

Recently, a variety of strategies have been employed to overcome these shortcomings, for example, loading with noble metals (such as Ag [8], Au [9] and Pd [10]), integrating with other semiconductors to form specific stack architectures (such as TiO_2/CdS [11], g-C_3N_4/CdS [12], g-C_3N_4/Fe_3O_4/AgI/Bi_2S_3 [13] and CdS-Au-TiO_2 [14]), coupling with magnetic materials (such as Fe_3O_4 [15], Fe_3O_4/ZnO/$CuWO_4$ [16,17], g-C_3N_4/Fe_3O_4/Ag/Ag_2SO_3 [18] and $ZnFe_2O_4$ [19]), and varying the morphology of CdS (such as the nanorods [20], nanotubes [21] and nanosphere [22]). However, papers reported thus far have focused on CdS at the nano level, which suffers from a complicated recovery step and the random aggregation of CdS during the photocatalytic process, and largely limited the practical applications [23]. Therefore, it is of great significance to develop a synthesis method for producing a macroscopic CdS with high visible-light photocatalytic activity for the industrial and practical applications.

As a green chemistry technology, photocatalysis has been widely used in various fields, such as sterilization [24,25], water and air purification [26,27] and water-splitting [28,29]. Besides, light-responsive rewritable paper (RPs), as a potential practical application of photocatalyst, has become prevalent recently [30]. To date, a variety of strategies has been employed in RPs, including light-responsive, pH-responsive and humidity-responsive color switching [31,32]. However, the instability of switchable materials, the toxicity of switchable dyes, the rate of color switching and the complex synthesis routes remarkably limited the practical applications of RPs [33,34].

Herein, we present a simple, economical and environment-friendly method to synthesize a macroscopic urea-functionalized CdS (CdS-U) for the first time. The synthesized CdS-U material not only possesses high visible-light photocatalytic activity but also has the excellent plasticity. It is so convenient for CdS-U to produce visible light-responsive rewritable films. Compared with the light-responsive materials for RPs in previous reports, CdS-U film has the advantage of (i) high absorption efficiency and suitable band position, (ii) convenient information erasion, (iii) long preservation time for information and (iv) relatively low cost [35,36]. The information can be easily written on the surface of CdS-U film using a pen, erased by dissolving RPs in water under visible light irradiation. Then, the dissolved RPs can be recycled by heating.

2. Experiment

2.1. Chemicals

Sodium oleate (So), NaOH, Na_2S, and urea were purchased from Sinopharm chemical reagent Co. Ltd. $Cd(NO_3)_2{\cdot}4H_2O$, ethanol and methylene blue (MB) were received from Aladdin industrial Inc. All of the used chemicals were analytical grade without further purification.

2.2. Preparation and characterization of CdS-U

The sodium oleate-capped CdS nanoparticles (CdS-So NPs) were prepared by a solvothermal method. Firstly, 15 mmol of $Cd(NO_3)_2{\cdot}4H_2O$ and 2.5 mmol of sodium oleate were added to a beaker containing 80 mL of ethanol under vigorous stirring. Then 30 mmol of thioacetamide was added into the mixture. After stirring for 2 h, the solution pH was adjusted to 5.0 using 1 M NaOH solution. The obtained mixture was placed in a Teflon-lined autoclave and kept at 120 °C for 24 h. Finally, a yellow precipitate was obtained and collected by centrifugation, washed with distilled water and ethanol for several times, and dried in an oven at 60 °C overnight.

The macroscopic CdS-U was prepared as follows: 0.4 g CdS-So NPs and 20 g urea were mixed thoroughly in 50 mL of distilled water, and then the suspension was mixed for 20 min. After that, the mixture stirred at 75 °C to remove excess water and the CdS-U was obtained. To obtain these complicated patterns, the CdS-U solution was placed into a metallic mold and then dried at 75 °C to remove excess water.

The CdS-U film was prepared by recrystallization of CdS-U. Firstly, CdS-U was dispersed in distilled water. Secondly, the mixture was heated to 75 °C and then an appropriate amount of the CdS-U solution was cast onto a 5×6.5 cm^2 glass plate. Finally, an orange CdS-U film was formed immediately at room temperature.

2.3. Adsorption and photocatalytic degradation of MB

For the adsorption experiments, 10 mg of photocatalyst samples were added into a flask containing 50 mL of 20 mg/L MB solution and the flask was shaken at 25 °C. At different contact time, aliquots of MB solution were withdrawn and filtered through a 0.22 μm membrane. The adsorption capacity of MB at the time of t was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where q_t is the adsorption amount at the time t (mg/g), C_0 is the initial concentration of MB (mg/L), C_t is the concentration of MB at time of the t (mg/L). W is the mass of the adsorbent (g), and V is the volume of the solution (L).

The photocatalytic activities of CdS, CdS-So NPs and CdS-U were tested under visible light irradiation using a 500 W xenon lamp. Briefly, 0.02 g of photocatalyst was added into 50 ml of MB solution (10 mg/l). The mixture solution was stirring for 0.5 h in the dark to reach the adsorption-desorption equilibrium before turning on the lamp. 1 ml of suspension was withdrawn at given intervals and then filtered to remove photocatalyst particles. The concentrations of MB in the filtrate were detected by the UV–vis spectrophotometer at the wavelength of 664 nm.

2.4. Analysis

Powder X-ray diffraction (XRD) patterns were obtained from a Bruker D8 Advanced diffraction-meter with Cu Kα radiation. The Fourier transform infrared (FT-IR) experiment was carried out on a Nexus 870 spectrometer. Transmission electron microscopy (TEM) images were acquired using JEOL JEM 2100 microscopy at an acceleration voltage of 200 kV. Field-emission scanning electron microscopy (SEM) images were acquired using Hitachi SE-4800. X-ray photoelectron spectra (XPS) was obtained on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu$ = 1253.6 eV). UV–vis diffuse reflectance spectra (DRS) were taken on a Hitachi U-3010 UV–vis spectrometer. The released Cd^{2+} contents were determined by inductively coupled plasma (ICP) at Optima 5300DV.

3. Results and discussion

3.1. Morphology and chemical structure of macroscopic CdS-U

A general scheme for the synthesis of CdS-U is illustrated in Scheme 1. Sodium oleate (So) is a strong chelating reagent, which can strongly couple with CdS to form rod-like micelles on the surface of CdS in aqueous phase [37,38]. The obtained mixture was sodium oleate-capped CdS nanoparticles (CdS-So NPs) with many