



Cadmium sulfide with tunable morphologies: Preparation and visible-light driven photocatalytic performance



Zhi Fang^a, Liqin Zhang^a, Tao Yang^a, Lei Su^b, Kuo-Chih Chou^a, Xinmei Hou^{a,*}

^a State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

^b Research Center for Bioengineering and Sensing Technology, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Keywords:

CdS
Tunable morphologies
Formation mechanism
PC performance

ABSTRACT

Wurtzite cadmium sulfide (CdS) with four kinds of morphologies including dendrites, flowers, multipods and spheres, were tunably prepared using a facile and simple hydrothermal route with an assistance of N,N-dimethylformamide (DMF). The formation mechanism of CdS with different morphologies was discussed based on the phase and microstructure characterization by X-ray diffraction (XRD) and field emission scanning electronic microscopy (FE-SEM) with energy dispersive spectrometer (EDS). The effect of morphology on the photoelectrochemical (PEC) performance was investigated using linear sweep voltammetry (LSV), photocurrent versus irradiation time curve (I-t) and electrochemical impedance spectroscopy (EIS). The results show that the dendrite-like CdS exhibits the highest photocurrent density with 0.748 mA/cm² at 0.253 V. The photodegradation of Rhodamine B (RhB) further proves the dendrite-like CdS possesses excellent photocatalytic (PC) performance, which could be mainly attributed to the unique hyperbranched structure, larger surface area and smaller crystal size.

1. Introduction

Organic pollutants (OP), coming from industrial, agricultural production and human activities, lead to water pollution. It is still a severe problem and does harm to the living being [1]. Physical adsorption [2], biodegradation [3], ultrafiltration [4] and photodegradation [5–7] have been widely used to remove OP from wastewater in industrial applications. Photodegradation using semiconductor photocatalysts is a great attractive pathway to oxidize OP into harmless products (H₂O and CO₂) under solar light irradiation [8]. Since the first report of TiO₂ electrode as a photocatalyst was published in 1972 [9], photocatalysis has been widely applied on the degradation of OP. However, TiO₂ only responds to the ultraviolet (UV) accounting for about 4% of the solar energy as a result of its wide band gap of 3.2 eV [10]. More attentions have been paid to develop the visible-light-responsive photocatalysts.

Cadmium sulfide (CdS), as one of important visible-light-driven photocatalysts with a narrow band gap of 2.4 eV, can efficiently absorb visible light [11–13]. As a result, CdS has an excellent PC performance and has been extensively investigated. However, the main defects still remain such as a high recombination rate of photoexcited electron-hole pairs [14] and its photocorrosion [15]. In order to obtain high energy

conversion efficiency and stability, countless efforts have been devoted. For instance, Tada *et al.* [16] prepared a CdS-Au-TiO₂ heterojunction by adjusting the band structure to prevent electron-hole pairs from recombining and photocorrosion. Simon *et al.* [17] decorated CdS nanorods with Ni as a co-catalyst to catch photoelectron and built a redox couple (•OH/–OH) to consume photohole. Besides the adjustment of band structure, the size and shape of materials play an equally important role in their performance. Various kinds of nanostructures such as nanoparticle [18] nanowires [19,20], nanorod [21,22], nanoflowers [23,24], nanotrees [25] and so on have been synthesized using the solvothermal method [26]. In addition, Yu *et al.* [27] synthesized porous CdS nanosheet-assembled flowers using an ion-exchange method. Tian *et al.* [28] prepared sea-urchin shaped Bi₂S₃/CdS photocatalyst using one-pot growth hydrothermal method. Chen *et al.* [29] have studied essentially CdS with different morphologies. The formation mechanism has been also analyzed in detail. However, the influence of different morphologies on the PC performance of CdS is seldom systematically compared.

In this study, CdS with different morphologies including dendrites, flowers, multipods and spheres were tunably synthesized using N,N-dimethylformamide (DMF) assisted hydrothermal route [29]. The morphologies ranging from one dimensional (1D) to three dimensional

* Corresponding author.

E-mail address: houxinmeiustb@ustb.edu.cn (X. Hou).

(3D) nanostructures were controllably prepared by varying the content of DMF. Based on this, the effect of different morphologies on PC performance of CdS was systematically investigated. By comparison, CdS with dendrite-like morphology possesses the best PC performance and photodegradation efficiency, which could draw more attention to be developed into excellent photocatalysts.

2. Experimental section

2.1. Tunable preparation of CdS with different morphologies

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ as cadmium source, thiourea as sulfur source and DMF were all purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.. They were analytical reagents and used without further treatment. In a typical procedure, 1 mmol of CdCl_2 and 1 mmol of thiourea were dissolved in 10 mL of deionized water. Then different amount of DMF ranging from 0 to 70 mL were added into the above solution under magnetic stirring. After that, the deionized water was added into the solution until the total volume reached up to 80 mL. Then the above mixture was transferred into a 100 mL-Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 200 °C for 12 h. Finally the solution was cooled to room temperature. The product was centrifugation, washed three times using deionized water and ethanol and finally dried in an oven at 60 °C for 12 h. At last, the yellow precipitate was collected for the following experiment.

2.2. Phase and morphology characterization

The phase was characterized using a X-ray diffraction (XRD; M21XVHF22, Mac Science Co, Ltd., Yokohama, Japan) with Cu $\text{K}\alpha$ (20 kW, $\lambda=1.54056 \text{ \AA}$) radiation over a 2θ range from 10 to 90°. The morphologies of the products were observed on a field emission scanning electron microscope (SEM; JSM-6701F, JEOL, Tokyo, Japan). Element analysis was conducted by energy-dispersive spectra (EDS) on a JEOL JSM-6701F SEM.

2.3. PEC measurement

The working electrode was prepared by mixing CdS power, polyvinylidene fluoride (PVDF) with the mass ratio of 8:2 in N-methyl-2-pyrrolidone (NMP) and the stable slurry was coated on a titanium sheet with the coating mass of $\sim 0.1 \text{ mg}$ ($1 \times 1 \text{ cm}^2$) [30]. The Ti sheet was pretreated as follows. The working surface of Ti sheet was polished with 200 cw abrasive paper to remove oxide layer. The opposite surface was covered by insulating tape to prevent from contacting with electrolyte. Then the Ti sheet was ultrasonic washed successively using acetone and ethanol for 10 min. Finally it was cleaned using deionized water and dried as substrate. PVDF acts as the binder to combine photocatalyst with Ti substrate closely in favour of the transmission of photoelectron. NMP acts as solvent and dispersant to form stable and uniform slurry. While NMP does not change the electrochemical performance because it tends to volatilize when being heated. Finally, the electrode was heated at 90 °C for 6 h to evaporate the solvent for the later electrochemical detection as the working electrode.

Photoelectrochemical experiment was performed using a three-electrode setup connected to a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., China). In this setup, Ag/AgCl (saturated KCl) and a platinum plate were used as the reference electrode and the counter electrode respectively. 0.25 mol/L Na_2S and 0.35 mol/L Na_2SO_3 aqueous solutions were used as the electrolyte to maintain the stability of sulfide electrode. A 300 W Xe lamp (PLS-SXE300UV) was utilized to simulate sunlight whose luminous intensity on electrode surface was set at 100 mW/cm^2 . Linear sweep voltammetry (LSV) was recorded both in the dark and under light illumination from -0.6 to -0.2 V . The photocurrent versus irradiation time curve (I-t) was measured at different voltage under light (20 s) and dark (20 s)

alternately. Electrochemical impedance spectroscopy (EIS) was carried out by applying the AC voltage amplitude of 5 mV at 0 V within a frequency range of $0.01-10^5 \text{ Hz}$ in 0.5 mol/L KCl containing equimolar $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (0.005/0.005 mol/L) solution.

2.4. PC performance

The PC performance of as-obtained sample was evaluated by measuring the photodegradation of Rhodamine B (RhB) under 300 W without UV-cut Xe lamp irradiation. In each experiment, 5 mg of CdS catalyst was initially added into 10 mL 4 mg/L RhB solution. Then the mixture was magnetically stirred in dark for 30 min to achieve the adsorption/desorption equilibrium between RhB and catalysts. The Xe lamp was 20 cm above the reactor and the suspensions were magnetically stirred with Xe lamp irradiation. At 5 min intervals, 4 mL suspension was taken, centrifuged and the absorption spectrum changes of RhB were measured at 553 nm to measure the RhB photodegradation. The light was cut off when sampling and the suspension sample was returned to the reactor after the detection.

3. Result and discussion

3.1. Preparation of CdS

Fig. 1 shows the morphological evolution of CdS with addition of different DMF amount ranging from 0 to 70 mL. The other reaction conditions such as the ratio of Cd to S and the reaction time are optimized to be as follows: the molar ratio of Cd/S is 1:1, the morphology of the products is uniform and 12 h is selected as the optimal reaction time. XRD analysis (Fig. 2) indicates that the obtained products are hexagonal CdS (JCPDS card no. 41-1049). As revealed by Fig. 1, when pure H_2O is used as solvent in the absence of DMF, dendrite-like morphology (abbreviated as D-CdS, Fig. 1a and b) is obtained which consists of a trunk with the length of 10 μm and two rows of primary branches with the length of less than 5 μm . Compared with the previous reported results [31], the dendrites obtained in this study just consist of two rows of branches instead of 3-fold symmetric rows of branches. In addition, two rows of branches are separated by 120° and all the branches in the same row are parallel to each other growing at $\sim 30^\circ$ with reference to the trunk. The spine-like structures are possibly the third row of branch which is restricted by the other two rows of branches. In addition, it is clearly observed in this study that there are secondary branches growing on the primary branches. While the dendrites reported in the literature do not have the secondary branches [29]. When 1 mL DMF is added into the hydrothermal reaction system, the flower-like structure consisting of several petals is created to form the flowering shrubs (F-CdS, Fig. 1c and d). Every petal of the flower-like structure consists of trunk and branches which is almost the same as the dendrite-like one. Therefore, the synthesis mechanism of F-CdS is similar to that of D-CdS. When the amount of DMF increases to 20 mL, the F-CdS disappears and instead the multipod-like structure (M-CdS, Fig. 1e and f) with multiple conical arms is obtained. At the same time, there are many wrinkles stacking layer by layer. The cross section of wrinkle is hexagon because the preferential growth direction along the [0001] zone axis of CdS is hexagonal crystal nucleus [29]. When the amount of DMF increases from 40 to 70 mL, spherical particles are produced and aggregated together as shown in Fig. 1g and h.

3.2. Formation mechanism

From the aforementioned experimental results, the reaction mechanism of CdS with different morphologies could be deduced as shown in Fig. 3. Thiourea acts as not only the sulfur source but also a complexing agent to form relatively stable complexes ($[\text{Cd}(\text{Thiourea})_2]^{2+}$). With temperature increasing, the complex ions

Download English Version:

<https://daneshyari.com/en/article/5450004>

Download Persian Version:

<https://daneshyari.com/article/5450004>

[Daneshyari.com](https://daneshyari.com)