



Facile synthesis of stable cadmium sulfide quantum dots with good photocatalytic activities under stabilization of hydrophobic amino acids

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ARTICLE INFO

Article history:

Received 21 November 2011

Accepted 13 January 2012

Available online 21 January 2012

Keywords:

Cadmium sulfide

Quantum dots

Hydrophobic amino acids

Photocatalysis

ABSTRACT

In the present study, the stable CdS quantum dots were successfully prepared using hydrophobic amino acids methionine and valine as stabilizers through a facile one-pot strategy in aqueous media. The CdS quantum dots exhibited strong absorption and photoluminescence properties in the visible wavelength region. From the results, the CdS quantum dots can effectively photocatalytically degrade the organic dyes through the mediation of the hydroxyl radical under visible light irradiation. More importantly, the CdS quantum dots exhibit good recycling stability during the photocatalytic experiments. This suggested that the as-prepared CdS quantum dots might be used as potential photocatalyst to effectively treat the organic pollutants under visible light irradiation.

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1. Introduction

CdS quantum dots (QDs) have attracted considerable attention over the past decades due to their unique properties and potential applications, such as the photoelectric conversion, light-emitting diodes for flat-panel displays, and lasers [1–3]. However, owing to the ultra-small size and high surface energy, the QDs tend to the serious agglomeration, leading to the significant difficulties in the preparation of the stable QDs. Previously, the CdS QDs were generally prepared using surfactants and polymers as stabilizers [4–6]. However, the introduction of the toxic stabilizers and the complicated procedures significantly limit the applications. Therefore, it is urgent to construct a facile method to prepare the stable and well dispersed QDs. Because of the coordinating interactions between amino acids and metal ions [7,8], the amino acids might be used as stabilizers to prepare the stable QDs [9–12]. However, hitherto the synthesis of the stable CdS QDs using hydrophobic amino acids as stabilizers is seldom reported and attracts our interest.

Currently, QDS are widely used in photocatalytic degradation of the biological nondegradable organic pollutants [1–3,13,14]. However, most of the existing photocatalysts can only exert the functions under UV light irradiation, which seriously limits their applications. Therefore, it is still a great challenge to find an effective photocatalyst to treat the organic pollutants under visible light irradiation.

Herein, using two hydrophobic amino acids methionine (Met) and valine (Val) as stabilizers, the stable CdS QDs were successfully prepared through a facile one-pot method. The CdS QDs exhibited special optical properties in visible wavelength region. Moreover, the CdS QDs showed strong photocatalytic degradation activities for organic dyes under visible light irradiation. This suggested that the as-prepared CdS QDs might be used as photocatalyst to effectively treat the organic pollutants under visible light irradiation.

2. Materials and methods

To prepare the CdS QDs, 0.12 mmol amino acids and 0.06 mmol CdCl₂ were dissolved into 20 mL double distilled water (DD water) and incubated for 12 h at 30 °C. Then, 20 mL thioacetamide aqueous solution (3 mM) was added and refluxed for 1 h at 100 °C. The yellow products were centrifuged, washed, dried in vacuum and denoted as Met-CdS and Val-CdS, respectively. For comparison, the bulk CdS was also prepared in the absence of amino acids. The size and morphology of the samples were determined through transmission electron microscopy (TEM, JEOL JEL-2010). The XRD patterns were recorded on DX-2000 diffractometer with Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The FT-IR spectra were recorded on Bio-Rad FTS-40 infrared spectrometer. The UV-Visible absorption and photoluminescence (PL) spectra were recorded on Lambda-17 UV-vis and Cary Eclipse fluorescence spectrophotometers, respectively.

For photocatalysis experiment, 30 mg CdS QDs were suspended in 24 mL DD water by sonicating. Then 6 mL rhodamine B (RhB) aqueous solution (250 ppm) was added and stirred in the dark for 60 min to establish an adsorption/desorption equilibrium. Then the

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suspension was irradiated by 500 W xenon lamp for photocatalysis under moderate stirring. At specified intervals, the suspension was taken from the reactor and centrifuged. The content of RhB in the supernatant was determined by UV–Vis spectroscopy at 554 nm. For comparison, the photocatalytic activities of the bulk CdS was also determined.

The formation of hydroxyl radical ($\cdot\text{OH}$) on the photo-irradiated CdS QDs' surface was detected *in situ* by fluorimetric assay using terephthalic acid (TPA) as a probe under similar conditions to the photocatalytic experiment except the replacement of RhB with TPA. The photo-irradiated suspension was taken from the reactor and centrifuged. Then the fluorescent intensity of 425 nm excited with 315 nm was detected.

3. Results and discussion

Fig. 1a presents the XRD patterns of the CdS QDs. From the figure, the Met-CdS and Val-CdS exhibit similar XRD patterns, in which three peaks with 2θ values of 26.8° , 44.1° and 52.1° correspond to the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic CdS phase (JCPDF 75–0581), respectively. The broadness of the peaks can be attributed to the

small sizes of the QDs. Fig. 1b–e presents the size and morphologies of the CdS QDs. From the results, the Met-CdS and Val-CdS exhibit similar spherical morphology but different sizes. From the results shown in Fig. 1d–e, the QDs exhibit narrow particle size distributions. The mean diameter of the Met-CdS is 6.45 nm, smaller than that of the Val-CdS (7.22 nm).

Fig. 2a presents the FT-IR spectra of the bulk CdS and CdS QDs. Compared with the spectrum of the bulk CdS, the stretching bending band of the carbonyl group of amino acids at $1550\text{--}1580\text{ cm}^{-1}$ can be found in the spectra of the QDs. However, the intensities decrease obviously. From these results, there is a trace amount of amino acids in the CdS QDs. Furthermore, there are certain interactions between the QDs and the carbonyl groups of the amino acids. It might be these interactions that may contribute to the stability and dispersity of the CdS QDs.

The optical properties of the CdS QDs, including the UV–visible absorption and PL spectra, were determined and the results are shown in Fig. 2b–c. From Fig. 2b, the CdS QDs exhibit broad absorption band from 200 to 600 nm, indicating the effective photo absorption properties. From the results shown in Fig. 2c, when excited with wavelength 202 nm, the CdS QDs exhibit a strong green

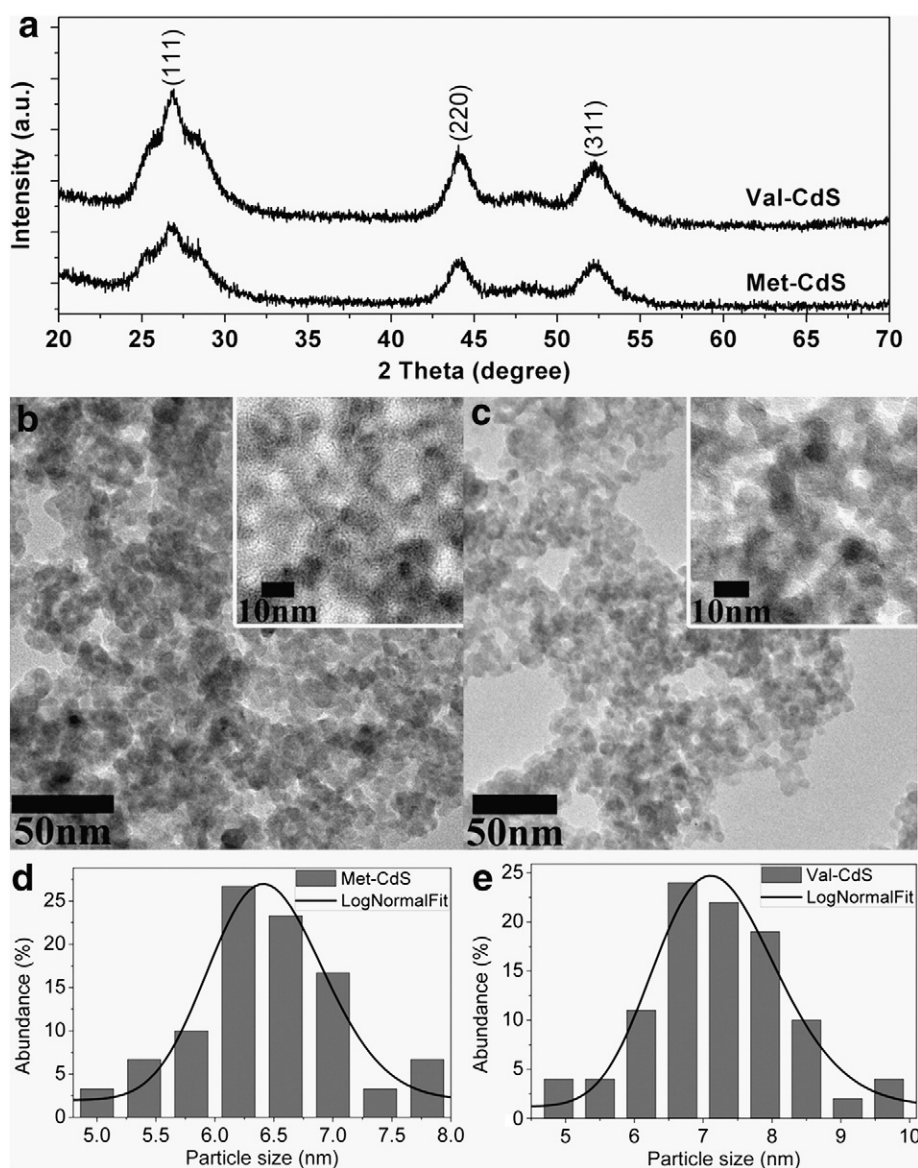


Fig. 1. (a) XRD patterns of the CdS QDs. (b) TEM images of the Met-CdS and (c) Val-CdS QDs. Inset: Magnified images. (d) Particle size distribution of Met-CdS and (e) Val-CdS QDs.

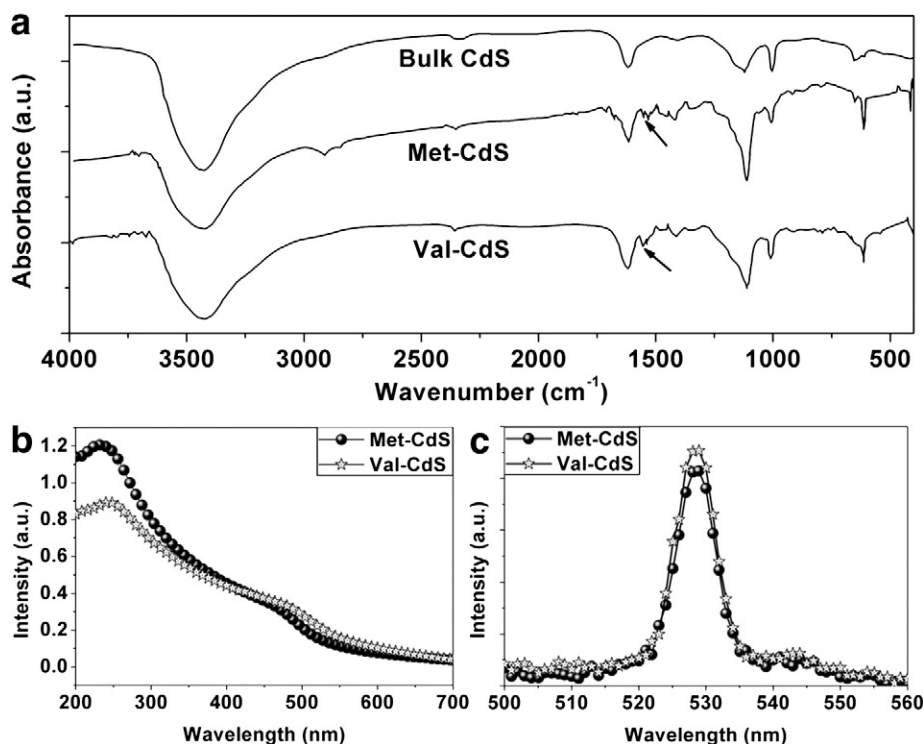


Fig. 2. (a) FT-IR spectra of the bulk CdS, Met-CdS, and Val-CdS. (b) UV-vis and (c) PL spectra of the CdS QDs.

emission near 528 nm with the quantum yield up to 20%, which can be attributed to the recombination of the charge carriers within surface states.

Because of the photo absorption properties, the photocatalytic activities of the CdS QDs to degrade RhB under visible light irradiation were studied. From the results (Fig. 3a), after 110 min visible light irradiation, the photodegradation efficiencies of the Met-CdS and Val-CdS on RhB are 84.9% and 89.7%, respectively, much higher than

those of the bulk CdS (15.7%) and the sample prepared by conventional methods (22.71%).

From the reports, the active oxygen species such as •OH and superoxide are the key active intermediates in the photocatalytic degradation. Therefore, with the aid of TPA, the •OH formed on the photo-illuminated QDs' surface was detected to determine the degradation mechanism of RhB. From the results (Fig. 3b), with the increase of the irradiation time, the PL intensities increase gradually, indicating

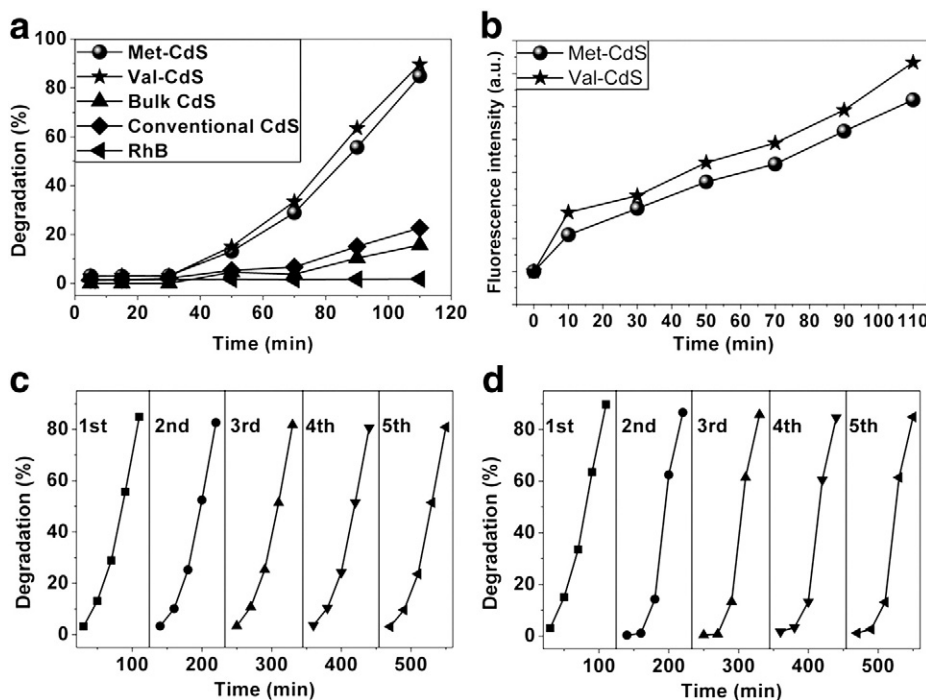
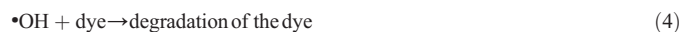


Fig. 3. (a) Photocatalytic degradation of RhB in the presence of the CdS QDs. (b) The PL intensities at 426 nm against irradiation time for TPA on the CdS QDs. (c) The recycling of the Met-CdS and (d) Val-CdS on the photocatalytic degradation of RhB.

the continuous formation of •OH during the irradiation. Moreover, the PL intensities of the two CdS QDs are different, revealing the different •OH production efficiency. The •OH production efficiency of the Val-CdS is higher than that of the Met-CdS, consistent with the photocatalytic activities. Based on the results, the photocatalytic degradation mechanism of the RhB is proposed. Firstly, the photons possessing the energy higher than that of the QDs' band gap are firstly absorbed on the QDs' surface. This will promote the electrons from the valence band (*vb*) to the conduction band (*cb*), generating the positive hole (h_{vb}^+) at the valence band edge and the electron (e_{cb}^-) in the conduction band of the QDs (Eq. (1)). Secondly, h_{vb}^+ and e_{cb}^- can react with water or hydroxyl groups and transform into •OH (Eqs. (2), (3)). Finally, •OH can react with RhB absorbed on the QDs' surface to exert the degradation (Eq. (4)).



Furthermore, the recycling of the CdS QDs on the photocatalytic degradation of RhB was determined. From the results (Fig. 3c–d), after five cycles of the photocatalytic reaction, the photocatalytic activities did not show significant loss. These reveal that the CdS QDs can be reused for several times to degrade the organic pollutants under visible light irradiation without great decrease in photocatalytic activity, exhibiting the prospects for practical and long-term applications.

4. Conclusions

In summary, the stable CdS QDs with good optical properties were successfully prepared using Met and Val as the stabilizing agents. Through the mediation of the hydroxyl radicals, the CdS QDs showed strong photocatalytic activities and good recycling stability to degrade the organic dyes under visible light irradiation, suggesting the potential application in the effectively treatment of the organic pollutants under visible light irradiation.

Acknowledgements

This work was financially supported by the National Science Foundation of China (21171051) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1061) and the Innovation Fund for Outstanding Scholar of Henan Province (114200510004) and Henan Key Proposed Program for Basic and Frontier Research (112102210005, 112300410095) and the Natural Science Foundation of Henan Educational Committee (2010A150013) and the Henan Normal University College Students Innovation Experiment Program.

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