Materials Letters 65 (2011) 486–489

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Optical and photocatalytic properties of arginine-stabilized cadmium sulfide quantum dots

Yuming Guo, Lingling Wang, Lin Yang *, Jie Zhang, Lili Jiang, Xiaoming Ma

College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, PR China
Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang 453007, PR China

ARTICLE INFO

Article history:
Received 14 July 2010
Accepted 19 October 2010
Available online xxxx

Keywords:
Nanomaterials
Semiconductors
Cadmium sulfide
Arginine
Photocatalysis

ABSTRACT

Currently, environmental pollution caused by organic compounds leads to severe negative consequences in the human society. Therefore, the removal of these pollutants from aqueous media has become one of the most important issues in environmental science. In the present study, CdS QDs were successfully prepared under aqueous conditions using L-arginine as the stabilizing agent. Optical property determination results reveal that the CdS QDs exhibited strong absorption and photoluminescence in a visible wavelength region. Moreover, the CdS QDs could effectively degrade two organic dyes under visible light irradiation. This suggested that the CdS QDs prepared in this work might be used as the potential photocatalyst to effectively treat the organic pollutants under visible light irradiation.

1. Introduction

Currently, organic pollutants such as dyes and phenolic compounds emitted from various sources have caused severe ecological problems due to their nondegradability and toxicity. Therefore, the removal of these pollutants has become one of the most important issues in environmental science. Photocatalysis is believed to be a superior method to decontaminate these pollutants, in which semiconductors are the most widely used photocatalysts. However, TiO_2, the mostly studied semiconductor photocatalyst, can only be effectively activated by UV light, and thereby its response to solar light is rather poor. Therefore, it is still a critical task to find a suitable semiconductor photocatalyst that can effectively treat the organic pollutants under visible light irradiation.

Colloidal semiconductors, also named as quantum dots (QDs), have attracted considerable attention over the past decades due to their size dependent optical properties. One of the approaches to synthesize QDs is to use biomolecules as stabilizers. From previous reports, amino acids can interact with metal ions to form complexes [1–6]. Consequently, the amino acids might be used as the stabilizers to prepare the QDs. Several studies reported the syntheses of QDs using cysteine and histidine as stabilizers [7–11]. However, hitherto the preparation of QDs using other amino acids and the application of the as-prepared QDs in photocatalysis are seldom reported. Therefore, the preparation of QDs with good properties, e.g. photocatalytic activities, using amino acids as stabilizers attracts considerable interest.

In the present work, L-arginine (Arg) was selected as the stabilizing agent to prepare the CdS QDs under aqueous conditions. The results showed that the CdS QDs exhibited strong absorption and photoluminescence (PL) in the visible wavelength region. Moreover, the CdS QDs could effectively degrade the organic dyes under visible light irradiation. This suggested that the CdS QDs prepared in this work might be used as the potential photocatalyst to effectively treat the organic pollutants under visible light irradiation.

2. Materials and methods

To prepare the CdS QDs, 0.12 mmol Arg and 0.06 mmol $CdCl_2$ were dissolved into 20 mL double distilled water (DD water) and the pH was adjusted to 10.0. Then the solution was incubated at 30 °C for 12 h for the complete interaction between Cd^{2+} and Arg. Subsequently, 20 mL of the thioacetamide (TAA) aqueous solution (6 mM) was added under moderate stirring. This was followed by a reflux for 1 h at 100 °C under moderate stirring. The orange precipitates were collected through the centrifugation, washed and dried at 30 °C in vacuum for 24 h. The size and morphology were determined through high resolution transmission electron microscopy (HR-TEM, JEOL JEL-2010). The X-ray diffraction (XRD) pattern was recorded on DX-2000 diffractometer with Cu Kα radiation (λ = 1.5406 Å). The UV–Visible absorption and PL spectra were recorded on Lambda-17 UV–Vis Spectrophotometer and Cary Eclipse Fluorescence spectrophotometer, respectively. In addition, for

* Corresponding author. Tel.: +86 373 3325999; fax: +86 373 3328507.
E-mail address: yanglin1819@163.com (L. Yang).

0167-577X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2010.10.057

comparison, bulk CdS was prepared under similar conditions without adding Arg.

For photocatalytic activity determination, 25 mg of the CdS QDs was suspended in 25 mL of a 50 ppm organic dye aqueous solution by sonicating for 30 min. Before the photocatalytic experiment, the suspension was stirred in the dark for 60 min to establish an adsorption/desorption equilibrium. Afterwards, the suspension was exposed to an irradiation of 500 W xenon lamp for photocatalysis under moderate stirring. At specified time intervals, 5 mL of the suspension was taken from the reactor and centrifuged to separate the catalyst. The content of the organic dyes in the supernatant was monitored by UV–Visible absorption spectroscopy at 664 nm for methylene blue (MB) and 554 nm for rhodamine B (RhB). As the comparison, the photocatalytic activities of bulk CdS and commercial P25 were also determined under same conditions.

3. Results and discussion

Fig. 1(a–b) presents the size and morphology of the as-prepared CdS QDs. From the figures, the QDs exhibit spherical morphology and good dispersivity. The size distribution of the QDs was analyzed and the result is presented in Fig. 1(c). From the figure, the QDs exhibit a narrow particle size distribution, and the average diameter is 7.44 nm. Fig. 1(d) shows the XRD spectrum of the QDs. The three peaks with 2θ values of 27.549°, 44.686° and 53.039° correspond to the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic CdS phase (JCPDF 42-1411), respectively. No obvious diffraction peaks from other impurities are observed. The broadness of the peaks is attributed to the small dimensions of the QDs.

Fig. 2(a) presents the FT-IR spectra of pure Arg and the CdS QDs. Compared with the spectra of pure Arg, the out-of-plane bending band of NH_2 at 1682 cm^{-1}, the stretching bending band of CO at 1562 cm^{-1}, and the bending band of OH at 1330 cm^{-1} in Arg appear at 1651, 1574 and 1372 cm^{-1} in QDs, respectively [12]. However, the intensities of all the three bands decrease obviously. From these results, on the one hand, there is a trace amount of Arg in the QDs. On the other hand, there are certain interactions between the QDs and the functional groups of the Arg, including NH_2, CO, and OH. It is these interactions that may contribute to the formation and stability of the QDs. The optical properties of the QDs, including UV–Visible absorption and PL spectra, were determined and the results are shown in Fig. 2(b–c). From Fig. 2(b), the QDs exhibit a broad absorption band from 200 to 500 nm, indicating the effective photo absorption property. From Fig. 2(c), a strong green emission near 528 nm is observed excited with wavelength 202 nm, which is surface-defect emission and can be attributed to the surface states, such as sulfur vacancies and/or sulfur dangling bonds [13].

To examine the photocatalytic efficiency of the CdS QDs, the photodegradation of MB and RhB under visible light irradiation at room temperature was conducted. The results are shown in Fig. 3(a–b). From Fig. 3(a), after 90 min irradiation, the photodegradation efficiency of the QDs on MB can reach 91.6%. However, the bulk CdS and commercial P25 just slightly induce the photodegradation of MB. This suggests that the QDs can effectively induce the photocatalytic degradation of MB. In order to confirm the photocatalytic efficiency of the QDs, the photodegradation of RhB in the presence of the QDs was also determined and the result is shown in Fig. 3b. From the data, the photocatalytic efficiency of

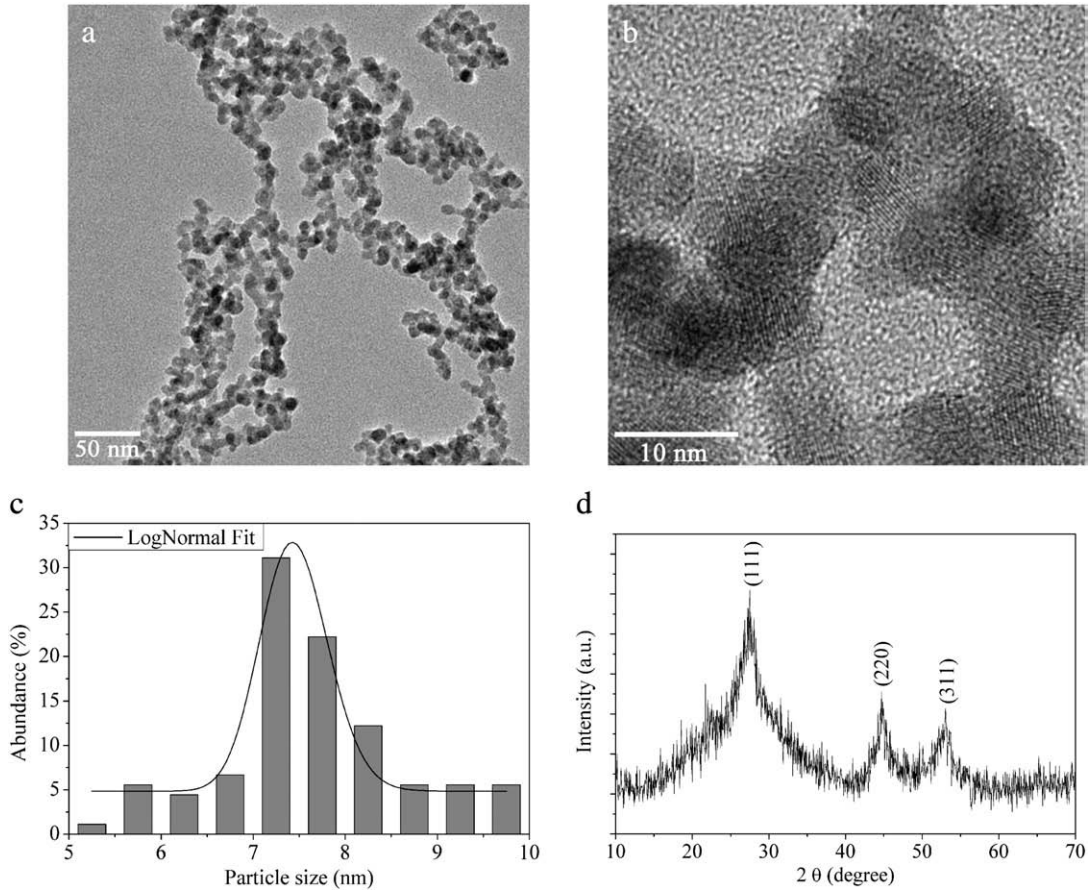

Fig. 1. (a) Low and (b) high magnified TEM images of the CdS QDs; (c) particle size distribution of the CdS QDs; (d) XRD patterns of the CdS QDs.

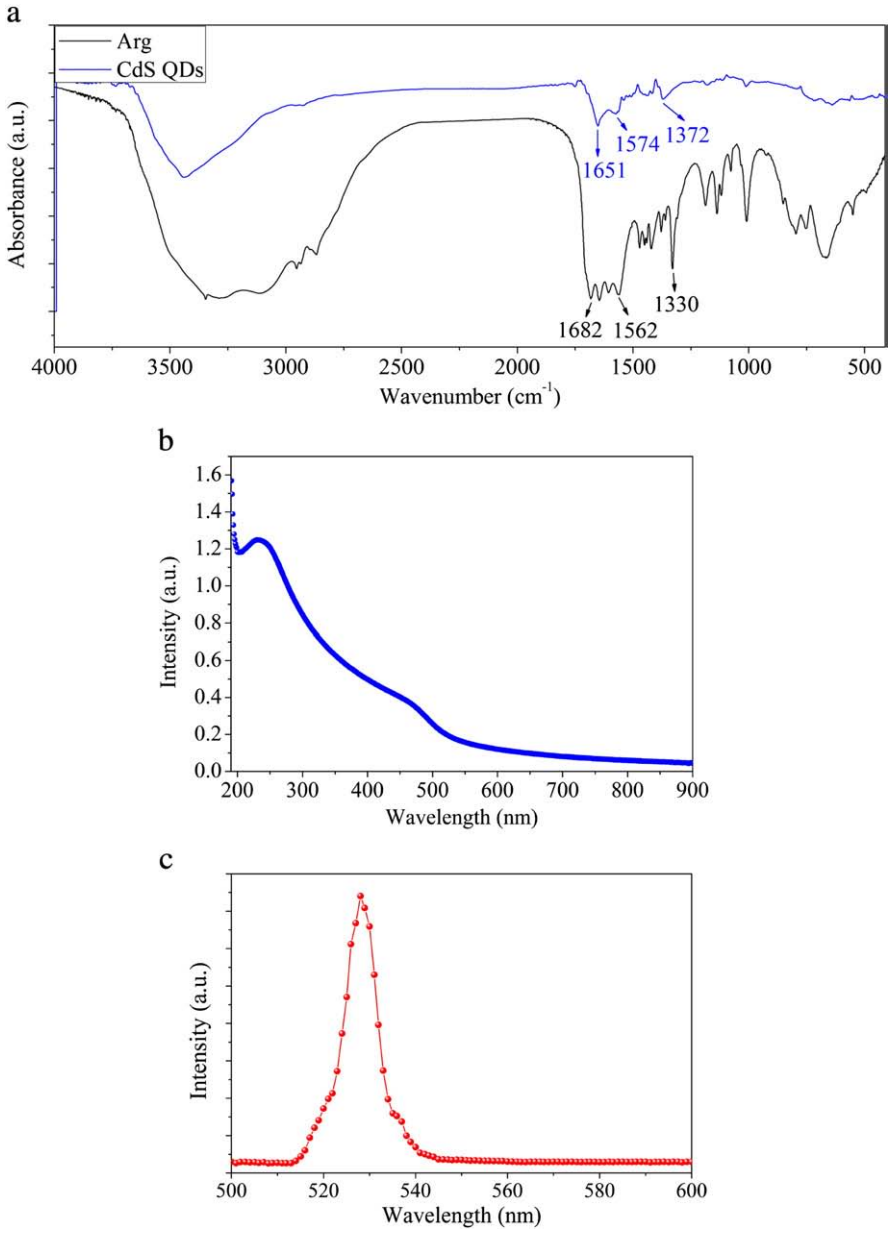

Fig. 2. (a) FT-IR spectra of pure Arg and the CdS QDs; (b) UV–Visible absorption spectrum of the CdS QDs; (c) PL spectrum of the CdS QDs under 202 nm excitation.

the QDs is significantly stronger than those of bulk CdS and P25. These results reveal that the QDs can effectively induce the photodegradation of organic dyes and can be used as the potential photocatalyst to treat the organic dyes. The photocatalytic mechanism is proposed as follows. When CdS QDs are irradiated with the visible light, electrons of the valence band can be excited to the conduction band to give the electron-hole pair on the surface of the QDs (Eq. (1)). The high oxidative potential of the hole (h^+_{VB}) in the QDs permits the direct oxidation of the dyes to reactive intermediates (Eq. (2)).

$$CdS + h\nu \rightarrow CdS(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{oxidation of the dye} \quad (2)$$

In addition, the hydroxyl radical may be also responsible for the degradation of the dyes. It is either formed by the decomposition of water induced by the hole (Eq. (3)) or by the reaction of the hole with OH^- (Eq. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant which leads to the degradation of the organic dyes.

$$h^+_{VB} + H_2O \rightarrow H^+ + \bullet OH \quad (3)$$

$$h^+_{VB} + OH^- \rightarrow \bullet OH \quad (4)$$

$$\bullet OH + \text{dye} \rightarrow \text{degradation of the dye} \quad (5)$$

4. Conclusions

In summary, the CdS QDs were successfully prepared under aqueous conditions using Arg as the stabilizing agent. It is found that Arg plays an important role in the formation of the QDs. The CdS QDs

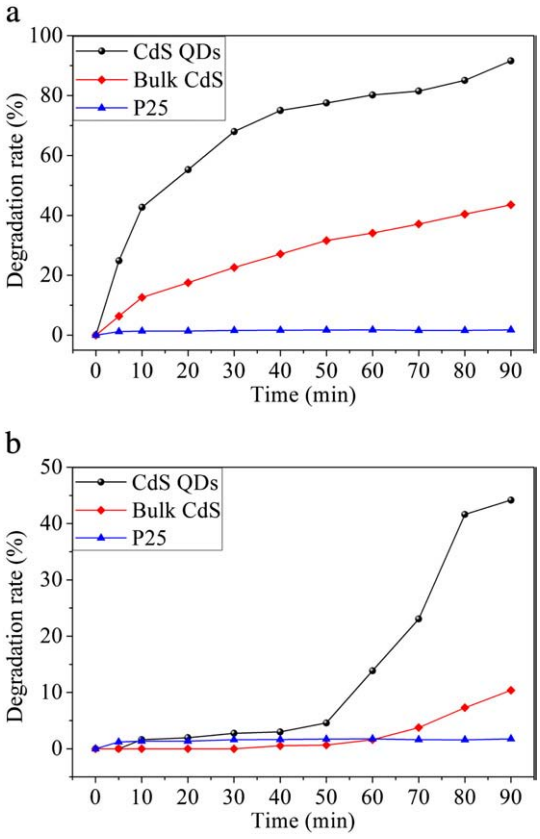

Fig. 3. Photodegradation rate of (a) MB and (b) RhB in the presence of the CdS QDs monitored by UV–Visible absorption.

exhibited strong absorption and photoluminescence. Moreover, the CdS QDs could effectively degrade two organic dyes under visible light irradiation. This suggested that the CdS QDs prepared in this work might be used as the potential photocatalyst to effectively treat the organic pollutants under visible light irradiation.

Acknowledgements

This work was financially supported by the National Key Basic Research and Development Program of China (Grant No. 2009CB626610), the National Science Foundation of China (Grant No. 20771036) and the Natural Science Foundation of He'nan Educational Committee (Grant No. 2010A150013).

References

[1] Clem Gruen L. Interaction of amino acids with silver(I) ions. Biochim Biophys Acta BBA Protein Structure 1975;386:270–4.
[2] Stillman M, Shaw F, Suzuki K. Metallothioneins: Synthesis, Structure and Properties of Metallothioneins, Phytochelatins and Metal-Thiolate Complexes. New York: John Wiley & Sons; 1992.
[3] David B-O, Gerald C, Nagaraja R, Nick B, Edward L. Characterization of the Co^{2+} and Ni^{2+} binding amino-acid residues of the N-terminus of human albumin. Eur J Biochem 2001;268:42–8.
[4] Slocik JM, Moore JT, Wright DW. Monoclonal antibody recognition of histidine-rich peptide encapsulated nanoclusters. Nano Lett 2002;2:169–73.
[5] Chin J, Lee SS, Lee KJ, Park S, Kim DH. A metal complex that binds [alpha]-amino acids with high and predictable stereospecificity. Nature 1999;401:254–7.
[6] Davis AV, O'Halloran TV. A place for thioether chemistry in cellular copper ion recognition and trafficking. Nat Chem Biol 2008;4:148–51.
[7] Cao X, Li CM, Bao H, Bao Q, Dong H. Fabrication of strongly fluorescent quantum dot-polymer composite in aqueous solution. Chem Mater 2007;19:3773–9.
[8] Chanu TI, Negi DPS. Synthesis of histidine-stabilized cadmium sulfide quantum dots: study of their fluorescence behaviour in the presence of adenine and guanine. Chem Phys Lett 2010;491:75–9.
[9] Chatterjee A, Priyam A, Bhattacharya SC, Saha A. pH dependent interaction of biofunctionalized CdS nanoparticles with nucleobases and nucleotides: a fluorimetric study. J Lumin 2007;126:764–70.
[10] Oluwafemi SO, Revaprasadu N, Ramirez AJ. A novel one-pot route for the synthesis of water-soluble cadmium selenide nanoparticles. J Cryst Growth 2008;310:3230–4.
[11] Park Y-S, Dmytruk A, Dmitruk I, Kasuya A, Takeda M, Ohuchi N, et al. Size-selective growth and stabilization of small CdSe nanoparticles in aqueous solution. ACS Nano 2009;4:121–8.
[12] Kumar S, Bai S. Spectroscopic studies of L-arginine molecule. Indian J Pure Appl Phys 2010;48:251–5.
[13] Di X, Kansal SK, Deng W. Preparation, characterization and photocatalytic activity of flowerlike cadmium sulfide nanostructure. Sep Purif Technol 2009;68:61–4.