



Facile one-pot preparation of cadmium sulfide quantum dots with good photocatalytic activities under stabilization of polar amino acids

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ABSTRACT

In the present study, through a facile one-pot strategy, the stable cadmium sulfide (CdS) quantum dots were prepared successfully using two different polar amino acids including aspartate and glutamate as additives. The as-prepared CdS quantum dots exhibited unique absorption and photoluminescence properties in visible light region. From the results, the CdS quantum dots could photocatalytically degrade the rhodamine B efficiently through the mediation of photo-generated hydroxyl radicals under visible light irradiation. Furthermore, it should be noted that the CdS quantum dots exhibited comparatively good recycling stability during the photocatalytic reaction. These results suggest that the as-prepared CdS quantum dots might be used as the potential photocatalysts to treat the organic pollutants efficiently under visible light irradiation.

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1. Introduction

Currently, with the rapid development of the textile industry and the widespread applications of pesticides and herbicides, large amounts of toxic organic pollutants were emitted and caused serious ecological and environmental problems. Therefore, the efficient treatment of organic pollutants with the facile method has become a rigorous task in environmental science. Recently, photocatalysis is considered to be a promising and attractive technique for the treatment of organic pollutants, in which the semiconductors are the most frequently used photocatalysts [1,2]. Unfortunately, as the most studied photocatalyst, TiO₂ can only be activated by the UV irradiation, this significantly limits its practical applications. Consequently, it is still a challenging task to explore the suitable photocatalysts that can efficiently decontaminate the organic pollutants under visible light irradiation.

Cadmium sulfide (CdS), with a large direct band gap of 2.4 eV, has been recognized as one of the most important semiconductors and has been studied extensively during the past decades. Recently, because of the unique photochemical and photophysical properties, CdS quantum dots (QDs) exhibited important applications in various fields, especially the photocatalytic degradation of organic pollutants [3–7]. However, due to the high surface energy and the seriously undesirable agglomeration, it is still a great challenge to prepare the stable QDs through the facile method. From previous studies, amino acids (AAs) could coordinate with

metal ions [8,9]. Consequently, AAs might be used as additives to prepare the stable QDs. In our previous reports, several different AAs were used as additives to prepare the stable CdS QDs, such as arginine, methionine, and valine [10,11]. However, heretofore the polar AAs containing two carboxyl groups and usually negative at physiological pH including aspartate (Asp) and glutamate (Glu) are seldom used as additives to prepare the CdS QDs.

Herein, using two polar AAs including Asp and Glu as additives, the stable CdS QDs were successfully prepared through a facile one-pot method. Through the mediation of the photo-generated hydroxyl radicals ($\cdot\text{OH}$), the as-prepared QDs could photocatalytically degrade the organic dyes efficiently under visible light irradiation. More importantly, the as-prepared CdS QDs exhibited good recycling stability for the degradation of organic dyes, suggesting their potentials in the treatment of the toxic organic pollutants.

2. Materials and methods

The preparation of the stable CdS QDs is based on our previous reports and slightly modified [10,11]. Briefly, AAs and CdCl₂ with the molar ratio of 2:1 were dissolved into double distilled water (DD water) and incubated for 6 h. Then, thioacetamide aqueous solution was added and refluxed for 1 h at 100 °C. The yellow products were collected and denoted as Asp-CdS and Glu-CdS, respectively. For comparison, the bulk CdS was prepared in the absence of AAs. The size and morphology of the QDs were analyzed by high resolution transmission electron microscopy (HRTEM, JEOL JEL-2010). The XRD patterns were recorded on BrukerAXS D8 Advanced diffractometer with Cu K α radiation

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source ($\lambda=1.5406 \text{ \AA}$). The UV–visible absorption and photoluminescence (PL) spectra were recorded on Lambda-17 UV–vis and Cary Eclipse fluorescence spectrophotometers, respectively.

For the photocatalytic activity evaluation, 24 mL of CdS aqueous suspension (1.25 mg/mL) was mixed with 6 mL of rhodamine B (RhB) aqueous solution (250 ppm). The system was stirred in dark for 1 h to establish adsorption/desorption equilibrium. Then the system was exposed to 500 W xenon lamp for photocatalysis reaction under moderate stirring. At regular intervals, the suspension was taken from the vessel 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 and the commercially available TiO_2 (Degussa P25) were also determined.

The formation of $\cdot\text{OH}$ on the photo-irradiated CdS QDs' surface was detected *in situ* by fluorimetric assay using terephthalic acid (TPA) as a fluorescent probe under photocatalytic conditions except the replacement of RhB with TPA [2,12,13]. The photo-irradiated suspension was taken from the vessel and centrifuged. Then the supernatant was excited by 315 nm irradiation and the photoluminescent intensity at 425 nm was detected.

In order to further confirm the $\cdot\text{OH}$ mediation effect on the photocatalytic degradation of RhB, additional Vitamin C aqueous solution was introduced into the photocatalytic reaction suspension to perform the photocatalytic degradation of RhB under the photocatalytic conditions.

3. Results and discussion

Fig. 1a shows the XRD patterns of the CdS QDs. From the figure, the Asp-CdS and Glu-CdS exhibit similar XRD patterns. The three peaks at 26.77° , 44.06° and 52.13° are assigned to (111), (220) and (311) planes of the cubic CdS phase (JCPDF 75-0581), respectively. The broadness of the diffraction peaks can be attributed to the small sizes of the QDs. Fig. 1b and c presents the TEM images of the CdS QDs. From the figure, both the Asp-CdS and Glu-CdS exhibit the spherical morphology. From Fig. 1d and e, the QDs exhibit narrow particle size distributions. The mean diameter of the Asp-CdS is 5.25 nm, slightly smaller than that of the Glu-CdS (5.54 nm).

The optical properties of the CdS QDs including the UV–visible absorption and PL spectra were determined and the results are shown in Fig. 2a and b. From Fig. 2a, the CdS QDs exhibit the very broad absorption bands from 200 to 550 nm, indicating the relatively strong photo absorption properties. In addition, from the PL spectra of the AAs-QDs shown in Fig. 2b, the CdS QDs exhibit strong green emission near 528 nm when excited by 202 nm irradiation, which can be attributed to the recombination of the charge carriers within the surface states [14].

On account of the good photo absorption properties, the photocatalytic activities of the CdS QDs on the degradation of RhB under visible light irradiation were evaluated. From the results (Fig. 3a), after exposed to visible light for 110 min, the photodegradation efficiencies of the Asp-CdS and Glu-CdS on RhB are 98.98% and 99.04%, respectively, much high than those of the bulk CdS (15.68%) and the commercial P25 (3.11%), also better than our previous results [10,11]. Furthermore, the recycling properties of the CdS QDs for the photocatalytic reaction were evaluated. From the results (Fig. 3b and c), the photocatalytic activities of the AAs-QDs do not show apparent loss after five cycles of the photocatalytic reaction, revealing their excellent recycling stability. These suggest that the CdS QDs can be reused for many times to degrade the organic pollutants under visible light irradiation, exhibiting the important potentials for practical and long-term applications.

From previous studies, the active oxygen species such as $\cdot\text{OH}$ played critical roles in the photocatalytic degradation of organic

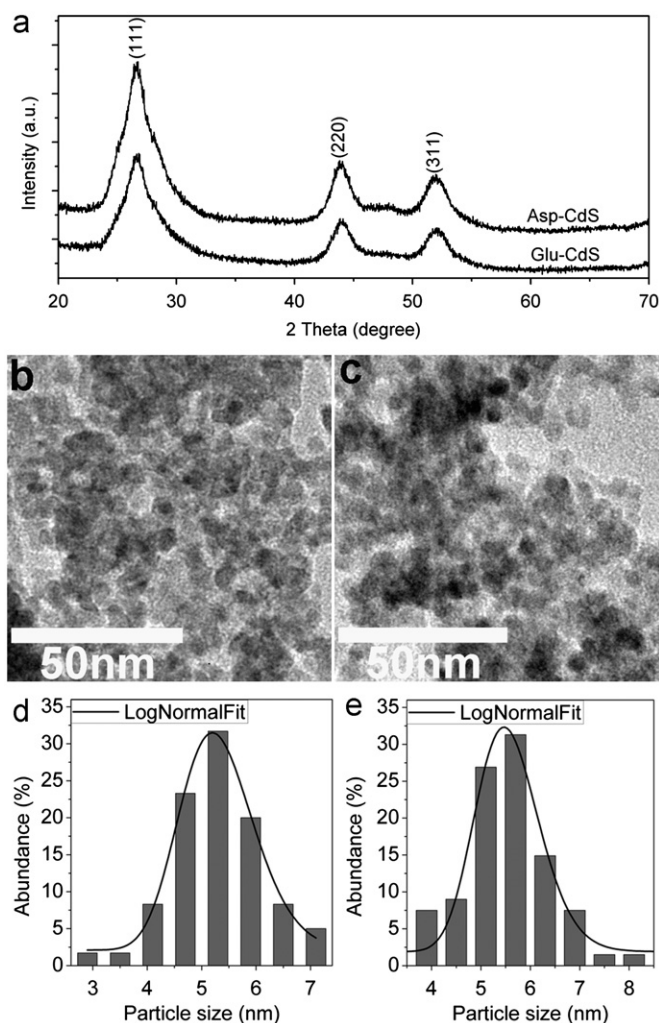
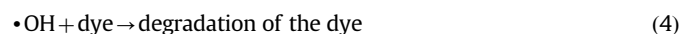
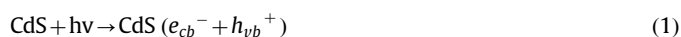


Fig. 1. (a) XRD patterns of the CdS QDs. (b) TEM images of the Asp-CdS and (c) Glu-CdS QDs. (d) Particle size distributions of the Asp-CdS and (e) Glu-CdS QDs.

pollutants [10,11]. Therefore, using TPA as fluorescent probe, the photo-generated $\cdot\text{OH}$ formed on the photo-illuminated QDs' surface was measured to evaluate the degradation mechanism of RhB. From Fig. 3d, with the prolongation of the irradiation time, the PL intensities increase gradually, indicating the consecutive formation of $\cdot\text{OH}$ during the irradiation. Based on the results, the photocatalytic degradation mechanism of RhB is proposed. Firstly, the photons with the energy higher than that of the QDs' band gap are absorbed onto the QDs' surface. This results in the excitation of the electrons from valence band (vb) to conduction band (cb), which can produce the holes (h_{vb}^+) at the valence band edge and the electrons (e_{cb}^-) in the conduction band of the QDs (Eq. (1)). Subsequently, h_{vb}^+ and e_{cb}^- can react with water or hydroxyl groups and generate the highly reactive $\cdot\text{OH}$ (Eqs. (2) and (3)). Finally, $\cdot\text{OH}$ can react with RhB molecules absorbed on the QDs' surface to exert the degradation reaction (Eq. (4)).



Additionally, this photodegradation mechanism was further confirmed with the aid of Vitamin C, an important $\cdot\text{OH}$ scavenger.

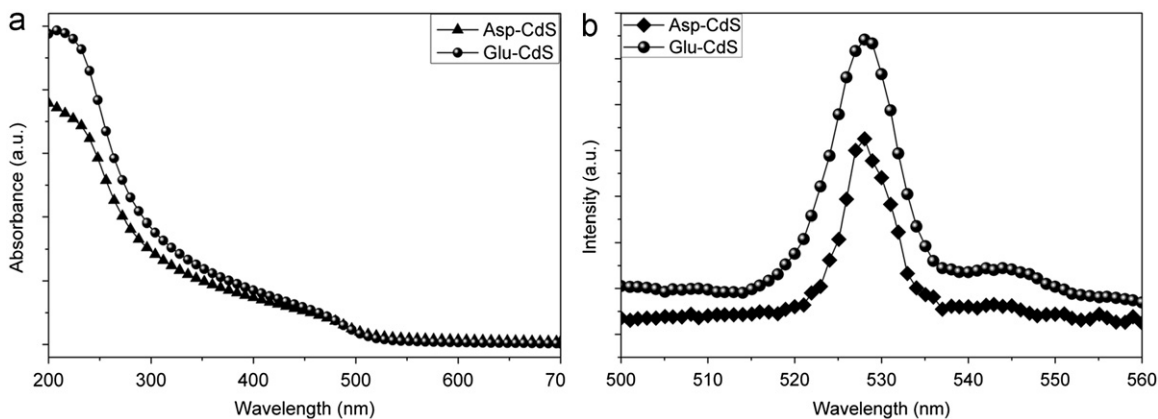


Fig. 2. (a) UV-vis and (b) PL spectra of the CdS QDs.

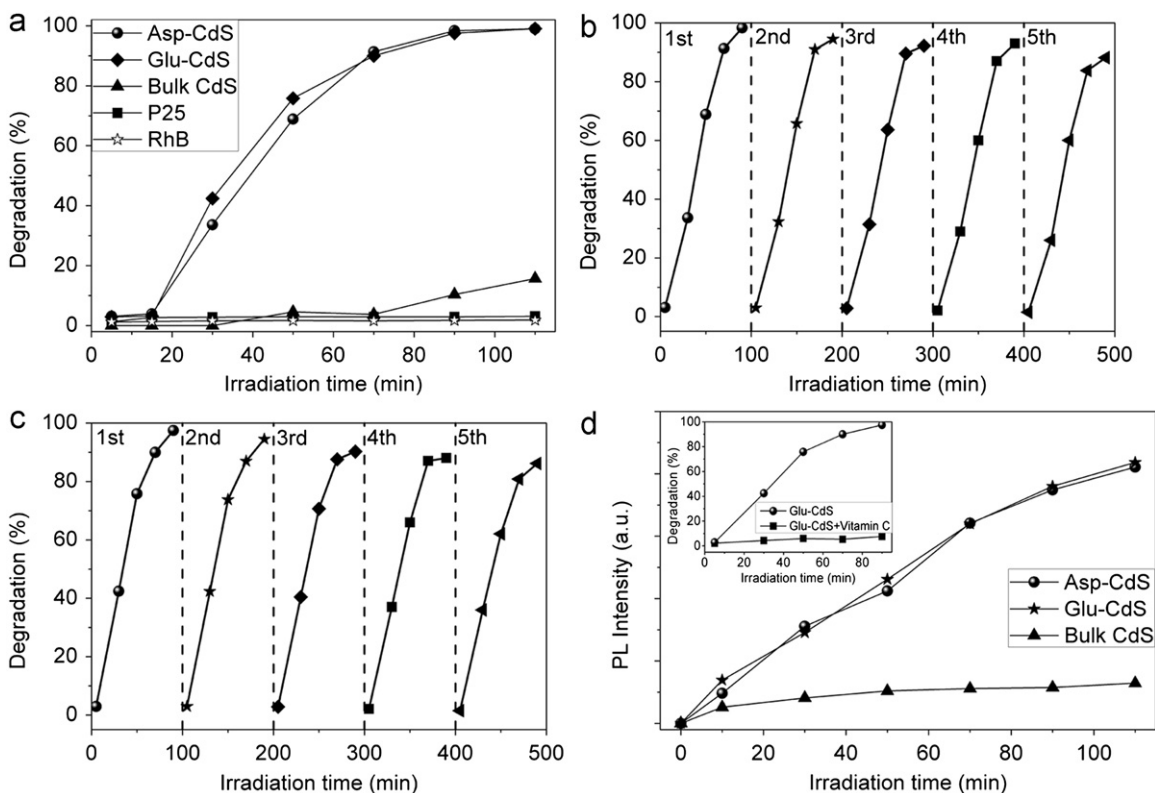


Fig. 3. (a) Photocatalytic degradation of RhB in the presence of the CdS QDs. (b) The recycling of the Asp-CdS and (c) Glu-CdS on the photocatalytic degradation of RhB. (d) The PL intensities at 426 nm against irradiation time for TPA on the CdS QDs. Inset: the photodegradation of RhB in the presence of Glu-QDs and Glu-QDs+Vitamin C.

From the result shown in the inset of Fig. 3d, the photocatalytic degradation of RhB in the presence of the mixture of Vitamin C and Glu-QDs decreases significantly, which can be attributed to the scavenging of photo-generated $\cdot\text{OH}$ by Vitamin C. This further confirms that the photocatalytic degradation of RhB by the QDs is really mediated by the photo-generated $\cdot\text{OH}$.

4. Conclusions

In summary, the stable CdS QDs were successfully prepared using polar AAs Asp and Glu as additives. Through the mediation of photo-generated $\cdot\text{OH}$, the CdS QDs exhibited strong photocatalytic activities and good recycling stability to degrade the organic dyes under visible light irradiation, suggesting the potential application in the efficient treatment of the organic pollutants under visible light irradiation.

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References

- [1] Fan Y, Deng M, Chen G, Zhang Q, Luo Y, Li D, et al. *J Alloys Compd* 2011;509:1477–81.
- [2] Yu X, Yu J, Cheng B, Huang B. *Chem-Eur J* 2009;15:6731–9.

- [3] Guo Y, Wang J, Tao Z, Dong F, Wang K, Ma X, et al. *CrystEngComm* 2012;14:1185–8.
- [4] Guo Y, Wang J, Yang L, Zhang J, Jiang K, Li W, et al. *CrystEngComm* 2011;13:5045–8.
- [5] Hu Y, Liu Y, Qian H, Li Z, Chen J. *Langmuir* 2010;26:18570–5.
- [6] Rajendran V, König A, Rabe KS, Niemeyer CM. *Small* 2010;6:2035–40.
- [7] Zhang F, Wong SS. *Chem Mater* 2009;21:4541–54.
- [8] Chin J, Lee SS, Lee KJ, Park S, Kim DH. *Nature* 1999;401:254–7.
- [9] Davis AV, O'Halloran TV. *Nat Chem Biol* 2008;4:148–51.
- [10] Guo Y, Jiang L, Wang L, Shi X, Fang Q, Yang L, et al. *Mater Lett* 2012;74:26–9.
- [11] Guo Y, Wang L, Yang L, Zhang J, Jiang L, Ma X. *Mater Lett* 2011;65:486–9.
- [12] Yu J, Wang W, Cheng B, Su B-L. *J Phys Chem C* 2009;113:6743–50.
- [13] Zhao W, Sun Y, Castellano FN. *J Am Chem Soc* 2008;130:12566–7.
- [14] Di X, Kansal SK, Deng W. *Sep Purif Technol* 2009;68:61–4.