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Metal ion doped CdSe quantum dots prepared by hydrothermal synthesis: enhanced photocatalytic activity and stability under visible light

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ABSTRACT

Different kind of metal ion doped CdSe quantum dots (QDs) are synthesized by a simple hydrothermal method. The prepared samples are characterized by powder X-ray diffraction, transmission electron microscopy, UV-vis absorption spectra, and X-ray photoelectron spectra (XPS), while the catalytic activities of photocatalysts are tested by photocatalytic degradation of tetracycline hydrochloride under visible-light irradiation. The results show that the 4 mol% Co-doped CdSe QDs exhibit the best photocatalytic activities under visible-light irradiation. While the solution condition is changed to further evaluate their photocatalytic activities, it can be concluded that the existence of cationic surfactant gives the best result and the degradation efficiency is 85.47%. Moreover, there is almost no loss of photocatalytic activities after four cycles. Experimentally and theoretically, this study shows that the method of metal ions doping will be useful for the improvement of photocatalytic activities and stabilities of CdSe QDs.

Keywords: CdSe; Quantum dots; Doping; Photocatalytic degradation; Tetracycline hydrochloride

1. Introduction

In the past decades, an increasing concern focuses on residues of pharmaceuticals and personal care products in the environment. Therein, antibiotics are greatly concerned due to their extensive use in human and veterinary medicine. Tetracycline hydrochloride belongs to the class of tetracyclines and it is widely used for the treatment of typhoid fever, tetanus, cholera, plague, and so on. But the vast majority of tetracycline hydrochloride cannot be fully absorbed by the body and approximately 40–90% of the antibiotics are discharged into the environment in the parent or metabolized forms [1–6]. Now, the main methods of eliminating antibiotics are physical adsorption and chemical degradation. Photocatalytic oxidation technology has showed a high-efficiency, low-power, no

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secondary pollution and depth, and a thorough oxidizing of various types of organic pollutants and toxic pollutants which are difficult to biodegrade in particular. Therefore, photocatalytic technology, which is widely used to degrade refractory organic matter, is more excellent than biological process for the removal of organic pollutants and toxic pollutants.

Quantum dots (QDs) are nanometer-scale semiconductor crystals and are defined as particles with physical dimensions smaller than the exciton Bohr radius. The QDs are made up of elements from II–VI (e.g. CdSe, CdTe, CdS, ZnSe), III–V (e.g. InP, InAs), or IV–VI (e.g. PbSe) group. In comparison with conventional semiconductor photocatalysts, the QDs have become a hotspot for scholars because of their superior photochemical properties, such as higher quantum yields, photostability, tenability, broad absorption, and narrow emission [7]. CdSe is a conventional II–IV semiconductor with a gap band of 1.7 eV that can play as an excellent photocatalytic material and can be sensitive to visible light [8,9]. For QDs, environment-friendly preparation process plays a significant role in their performance in the years to come, due to the fact that the environmental pollution is getting worse. There are many ways for preparing CdSe QDs, such as chemical bath deposition, microwave method [10,11], hydrothermal method [12–14], and so on. Among all the synthesis methods, hydrothermal method is the most effective on account of low synthesis temperature, simple operation, and less pollution. And, the structure and composition of the synthesized samples can be adjusted by changing the reaction conditions such as ion species and ion concentration [15].

However, the CdSe QDs have also some shortcomings, such as photocorrosion or photodissolution [16–20], which restrict their photocatalytic properties and reduce their stabilities. Hence, it is necessary for us to take steps to overcome their drawbacks. Fortunately, the defects of CdSe QDs can be improved by further modification [21,22] via loading [23,24], doping [15,25], and so on.

Metal ion doping is an important method to improve photocatalytic activity and make photocatalyst more stable. So, metal ion doping is a technique having vast prospective. Metal ion doping causes the surface defects of the photocatalysts; the defects can capture electrons or holes and then restrain the recombination of electrons and holes. Therefore, different metal ion doping is used to modify the photocatalysts to improve their photocatalytic activities [26–28].

In this study, the effect of different metal ion doping concentration and different metal ion on the photocatalytic activity was studied. The 4 mol% Co-doped CdSe QDs have the best photocatalytic activities on degradation of tetracycline hydrochloride under visible-light irradiation. The tentative mechanism of photocatalytic reaction on Co-doped CdSe QDs was also discussed based on our experimental results.

2. Experimental section

2.1. Materials

All chemicals used in the study were of analytical grade without further treatment. Cadmium chloride hemi(pentahydrate), cobalt chloride hexahydrate, zinc chloride, calcium chloride, kalium chloride, iron chloride hexahydrate, tetracycline hydrochloride, sodium dodecyl sulfate, tert-butanol, edetate disodium, sodium hydroxide, and hydrochloric acid were purchased from Shanghai Guoyao Chemical Co. Se power, sodium borohydride, 3-Mercaptopropionic acid, polyethylene glycol 2000, and benzalkonium chloride were purchased from Aladdin.

2.2. Samples preparation

The synthesis of metal ion doped CdSe QDs was carried out by a simple hydrothermal method. In the typical synthesis procedure, 0.4 mmol cadmium chloride hemi (pentahydrate) and 0.017 mmol cobalt chloride hexahydrate were dissolved in de-ionized water. 3-mercaptopropionic acid (0.056 ml) was used as a capping agent. Furthermore, 0.75 mmol selenium (Se) was reduced with sodium borohydride and this solution was added to the cadmium chloride hemi (pentahydrate) solution. Finally, the mixture was transferred to 50 ml Teflon-lined autoclave. The autoclave was then placed for 40 min at 160℃ in oven [29]. After being cooled down to room temperature naturally, the products were precipitated through centrifugation, washed thrice by distilled water and absolute alcohol, and dried at 60℃ for 12 h. In order to obtain different products, the experimental parameters, such as the kind of metal ion and the amount of metal ion, had been changed during the synthesis procedure.

2.3. Characterization

The particle size and shape of the samples was investigated by the transmission electron microscopy (TEM). X-ray powder diffraction (XRD) patterns of the prepared samples were analyzed by a Y-2000 diffractometer (D/max 30 kv) using Cu-Kα radiation

(λ = 0.154178 nm). The UV–Vis absorption and fluorescence of the as-prepared QDs was recorded using a double-beam UV–Vis spectrophotometer (Japan Shimadzu UV–Vis 1700) and a fluorometer (Aminco-Bowman Series 2, Thermo Spectronic, Pitsford, NY), respectively. The chemical composition analysis of the samples was made by X-ray photoelectron spectra (XPS) (VG Multiab-2000) using a PHI Quantum 2000 XPS system with a monochromatic Al-Kα source and charge neutralizer. All spectra were calibrated to C 1s pesky at 284.6 eV.

2.4. Photocatalytic experiments

The photocatalytic activity of the QDs was evaluated by the photocatalytic degradation of tetracycline hydrochloride in aqueous solution under visible-light irradiation. A 500 W Xe lamp with a 420 nm cut-off filter was used as the light source to provide visible-light irradiation. In each experiment, 0.05 g of photocatalyst was added to 100 mL tetracycline hydrochloride solution with a concentration of 20 mg/L. Prior to irradiation, the suspensions were magnetically stirred in the dark for 10 min to obtain the saturated absorption of tetracycline hydrochloride onto the catalysts. At irradiation time intervals of every 5 min, the suspensions were collected and then centrifuged (10,000 rpm, 10 min) to remove the photocatalyst particles. The concentrations of the tetracycline hydrochloride were monitored using a UV–Vis spectrophotometer (Japan Shimadzu UV–vis 1700) by checking the absorbance at 357 nm during the photodegradation process. The photocatalytic degradation efficiency (DE) was calculated by the following formula:

$$\mathrm{DE} = [(1 - A_i/A_0)] \times 100\% \qquad (1)$$

where A_0 is the initial absorbency of antibiotic solution that reaches absorbency balance and A_i is the absorbency of reaction solution.

3. Results and discussion

3.1. XRD spectroscopy

XRD pattern is used to investigate the phase structures of the samples, and the typical diffraction patterns are shown in Fig. 1. It is known that CdSe can exist as cubic or hexagonal, or a mixture of both. Comparison of the observed diffraction lines with the standard JCPDS-ICDD data of both cubic and hexagonal structures reveals that the structures of the nanocrystals are matching the cubic modifications better than the hexagonal structure. The diffraction lines appearing for the nanoparticles can be indexed as (111), (220), (311), and (331) belonging to CdSe cubic phase in accordance with (JCPDS-ICDD (19-0191)). However, it is shown in Fig. 1 that the (220) crystal plane diffraction peak is slightly drifted, which is to justify that Co^{2+} is successfully doped into CdSe QDs [30,31].

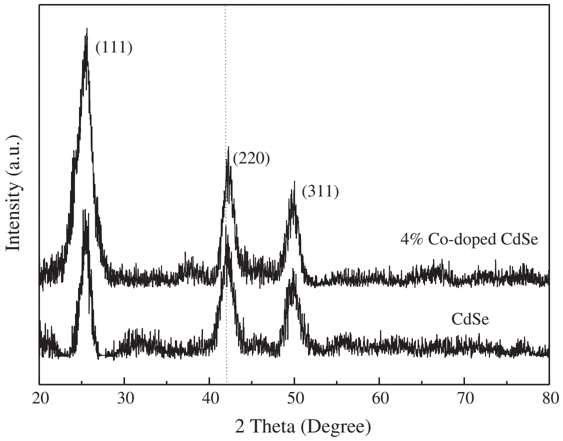

Fig. 1. XRD patterns of all samples.

3.2. TEM images

The structure and morphology of samples is characterized by TEM images. The TEM images of pure CdSe and 4 mol% Co-doped CdSe QDs are shown in Fig. 2. From Fig. 2, it can be clearly seen that pure QDs are spheric particles with uniform particle size distribution. The average particle size comes out to be around 10 nm, and Co ion doping does not change morphology and size significantly.

3.3. UV–Vis spectroscopy

As is well acknowledged, the photocatalytic activity of a photocatalyst is determined by the light absorption ability. The spectra of pure CdSe and Co-doped CdSe QDs are displayed in Fig. 3(A). It is obvious that the absorption edge of Co-doped CdSe QDs is wider than the pure CdSe QDs and shifts toward higher wavelength. Moreover, the intensity of absorption is enhanced. It contributes to the capability of photoresponse and improves the performance of photocatalytic. The UV–vis absorption spectroscopy of different metal ions doping CdSe QDs are shown in Fig. 3(B) and the wavelength of the absorption edge are similar, but the absorption intensity of Co-doped CdSe QDs is much stronger than the other.

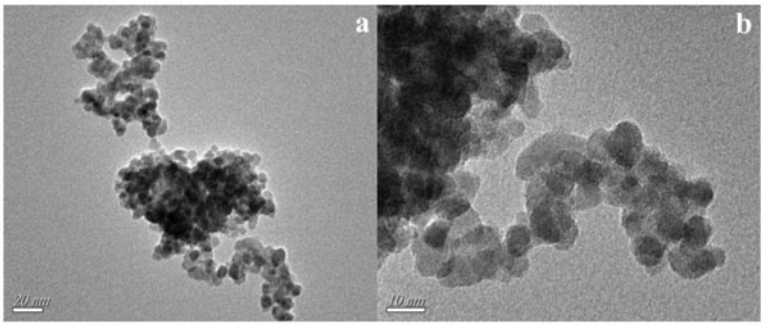

Fig. 2. TEM images of all samples: (a) CdSe, and (b) 4 mol% Co-doped CdSe.

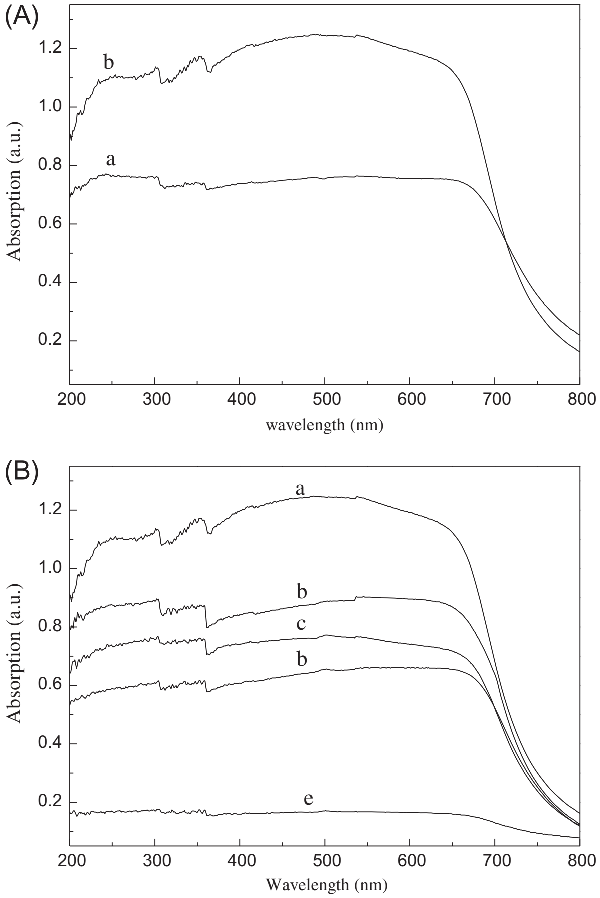

Fig. 3. (A) UV-Vis diffuse reflection spectra of all samples: (a) CdSe and (b) 4 mol% Co-doped CdSe and (B) UV-Vis diffuse reflection spectra of metal ions doped CdSe: (a) Co, (b) Zn, (c) K, (d) Ca, and (e) Fe.

In summary, the doping of Co ion can enhance visible-light absorption ability of CdSe QDs and can contribute to the fast separation of electron–hole pairs. Then, the catalytic activities of CdSe QDs are enhanced.

3.4. XPS spectroscopy

X-ray photoelectron spectroscopy, also called electron spectroscopy for chemical analysis, is widely used both in basic research and in analysis of materials, particularly in surface analysis. The XPS spectrum of Co-doped CdSe QDs is shown in Fig. 4(A) and high-resolution XPS spectra of Cd 2d, Se 3d, and Co 2p are displayed in Fig. 4((B)–(D)), respectively. There are two peaks at binding energies 404.9 and 411.6 eV, which can be assigned to Cd $3d_{3/2}$ and Cd $3d_{5/2}$, respectively, indicative of Cd^{2+}, and the Se 3d peak located at 53.67 eV indicates Se^{2-}. In addition, the Co 2p XPS spectra of the spinel cobaltite consists of two main lines with the Co $2p_{3/2}$ at a binding energy of 781.91 eV and the Co $2p_{1/2}$ at 795.48 eV with the spin-orbit splitting of 13.57 eV. Therefore, the presence of Co clusters could be ruled out entirely. What is more, the presence of two satellite peaks at the higher binding energy side of the Co 2p core-level further indicated that the electronic state of Co^{2+} ions was in high-spin arrangement [32–34].

3.5. Photoluminescence spectroscopy

Fluorescence spectroscopy is a kind of emission spectrum caused by electron–hole recombination. The fluorescence emission spectra of the samples are displayed in Fig. 5. The effect of different metal ion on fluorescence intensity of samples is shown in Fig. 5(A). From Fig. 5(A), it is observed that the emission wavelength is 538 nm and there is no obvious change with different metal ion doping. Meanwhile, the emission intensity of Co-doped CdSe QDs drastically decreased. In Fig. 5(B), it is obtained that the fluorescence intensity decreases by increasing the proportion of Co ion. Due to the doping of Co ions, the recombination of electron–hole pairs is suppressed which may result in decreasing the fluorescent

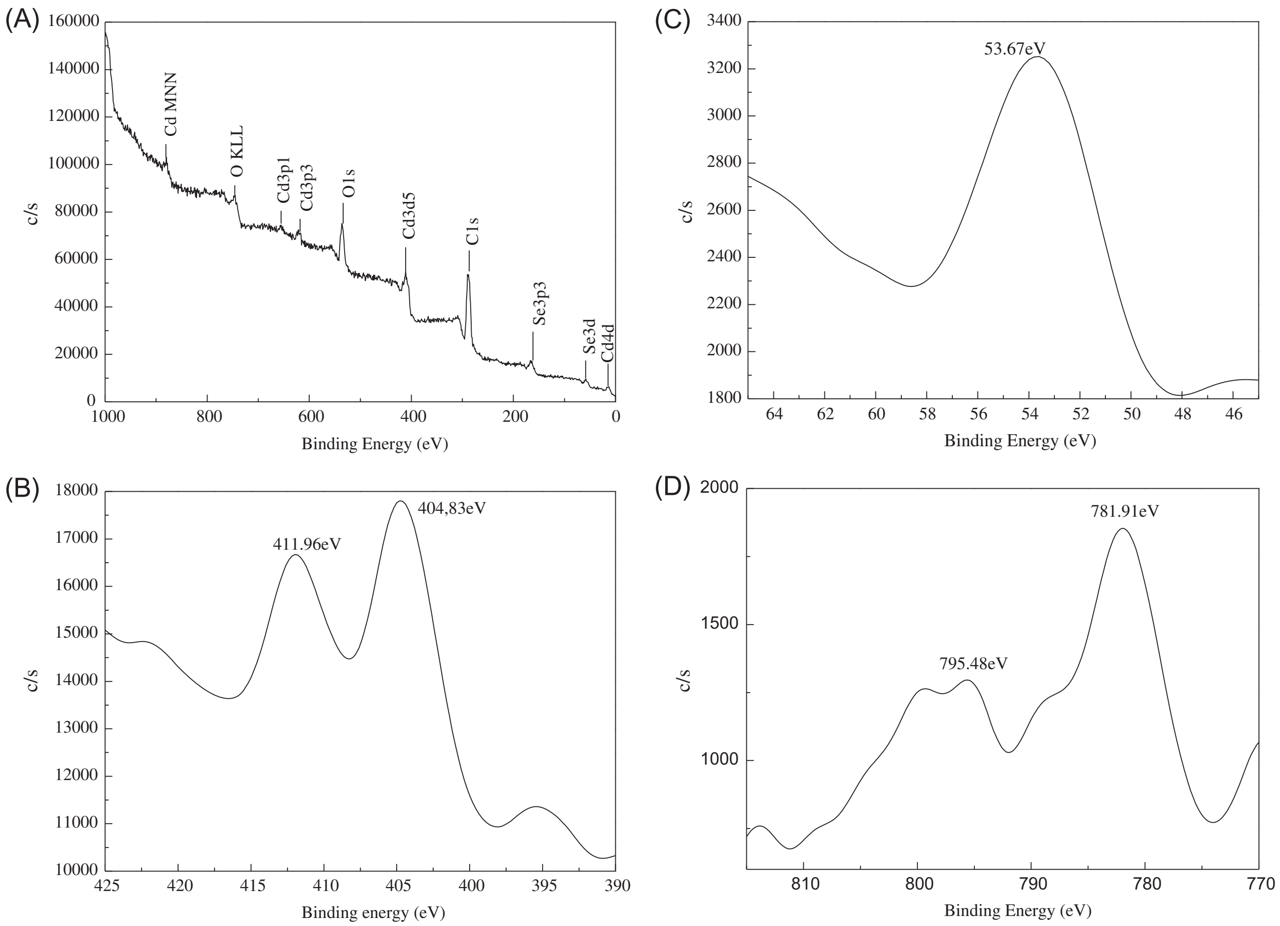

Fig. 4. XPS images of all samples: (A) CdSe, (B) Cd 3d, (C) Se 3d, and (D) Co 2p in 4 mol% Co-doped CdSe.

strength of samples and it is beneficial to improve the photocatalytic activity.

3.6. Photocatalytic experiments

3.6.1. Photocatalytic activity of Co-CdSe QDs

In order to evaluate the potential applicabilities of Co-doped CdSe QDs, the photocatalytic activities of these samples were compared by the degradation of tetracycline hydrochloride under visible-light irradiation. Fig. 6 shows that only a weak capability is detected when the catalysts are free or when the light is off. Experimental results show that the catalysts have reached the adsorption equilibrium in 10 min, and in the light conditions, the tetracycline hydrochloride does not decompose without catalysts. In addition, a conspicuously high photocatalytic activity is seen in the presence of Co-doped CdSe QDs and the DE is 77.09% under visible light, when the concentration of tetracycline hydrochloride is 20 mg/L.

3.6.2. Photocatalytic activity effect of initial concentration of tetracycline hydrochloride

In the beginning of experiment, the concentration of tetracycline hydrochloride with 20 mg/L was chosen as the basis of the experiment. As can be seen from Fig. 7, 20 mg/L tetracycline hydrochloride has the best removal effect and the DE has reached 77.09% in 30 min. This result may be well because when the concentration of tetracycline hydrochloride is lower than 20 mg/L, the photocatalyst cannot completely contact with the contamination molecules, and the DE of photocatalyst does not reach the acme. When the concentration of tetracycline hydrochloride is higher than 20 mg/L, the solution cannot react completely. Therefore, the DE is low.

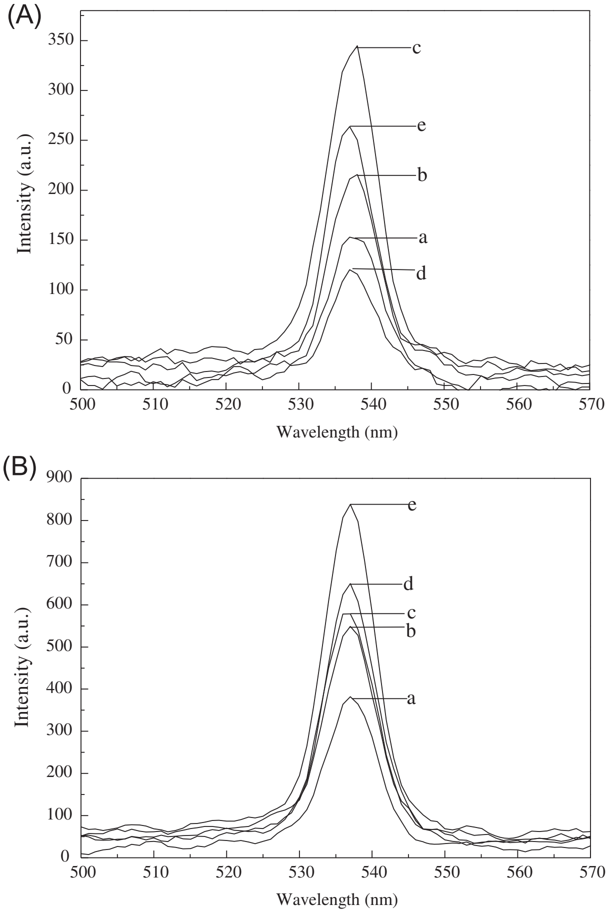

Fig. 5. (A) Fluorescence spectra of metal ions doped CdSe: (a) K, (b) Ca, (c) Fe, (d) Co, and (e) Zn and (B) fluorescence spectra of Co-doped CdSe: (a) 4 mol%, (b) 4.5 mol%, (c) 5 mol%, (d) 5.5 mol%, and (e) 6 mol%.

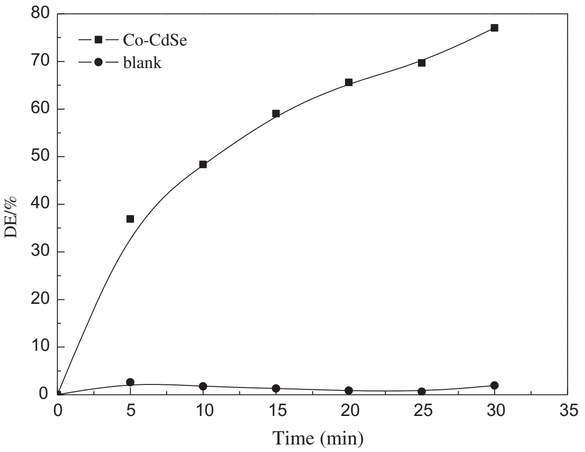

Fig. 6. Photocatalytic activity comparison in different conditions.

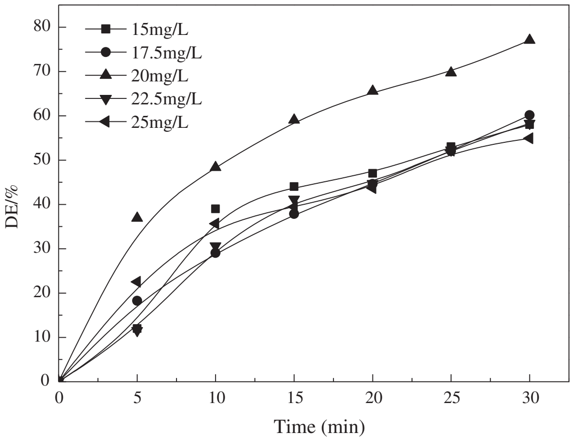

Fig. 7. The influence of different initial concentration of tetracycline hydrochloride.

3.6.3. Photocatalytic activity effect of CdSe QDs prepared with different metal ions

In Fig. 8, the effect of different metal ion doping on the photocatalytic degradation of tetracycline hydrochloride is carried out at an initial concentration of 20 mg/L. It can be observed that Co ion doping can improve the photocatalytic capabilities of CdSe QDs, and its influence is significantly more than other metal ion. The absorption intensity of Co-doped CdSe QDs is much stronger than others and Co-doped CdSe QDs display a weaker absorption of fluorescence spectra, which demonstrates that recombination rate of electrons and holes is lower. So, Co-doped CdSe QDs display higher photocatalytic activities.

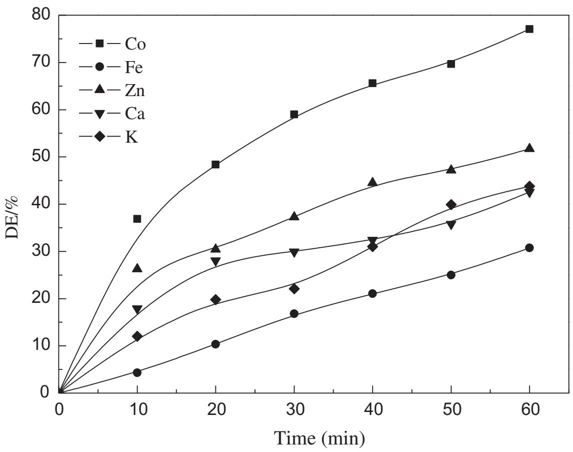

Fig. 8. The influence of CdSe QDs prepared with doping different metal ions.

3.6.4. Photocatalytic activity effect of Co-CdSe QDs prepared with different cobalt ions doping concentration

This study also examined the influence of Co ion doping concentration on the photocatalytic activity. From Fig. 9, it is found that 4 mol% Co-doped CdSe QDs have the best photocatalytic activities for degradation of tetracycline hydrochloride and the DE is 77.09% within 30 min. Through the analysis of fluorescence spectra, 4 mol% Co-doped CdSe QDs have the weakest fluorescence activity compared with other samples. As a result, when cobalt ion doping concentration is 4%, the recombination rate of the holes and electrons is reduced further. So, 4 mol% Co-doped CdSe QDs exhibit the highest photocatalytic activities.

3.6.5. Photocatalytic activity effect of pH

As shown in Fig. 10, it can be concluded that when pH value of the tetracycline hydrochloride solution is 4, it possesses the best photocatalytic activity for the degradation of tetracycline hydrochloride under visible-light irradiation. Furthermore, as shown in our study, the tendency of photocatalytic activity effect of pH has significant variation. In the acidic solution at pH 4, the DE is more than 70%, after adjusting the pH to 7, the DE is about 10% less than before. Finally, DE drops sharply as soon as the solution turns into a strong alkaline solution.

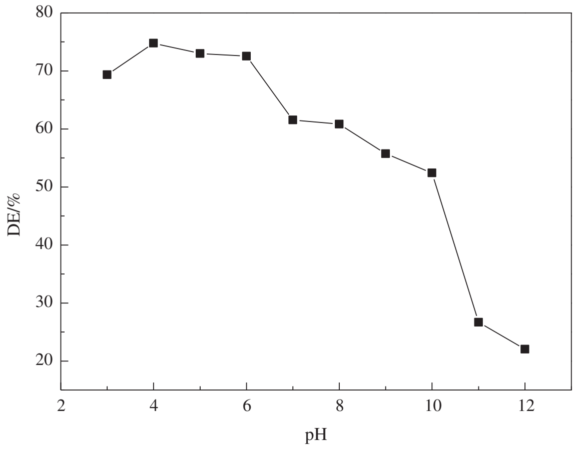

Fig. 10. The influence of pH value of tetracycline hydrochloride.

3.6.6. Photocatalytic activity effect of different concentrations of photocatalyst

The dose of the photocatalyst plays a significant role in the photocatalytic degradation reaction and the concentration of photocatalyst affects the DE directly. In this work, photocatalytic degradation experiment was realized by photocatalyst from 0.01 to 0.09 g, the concentration of tetracycline hydrochloride was 20 mg/L, and the other condition was the same. The dependence of photocatalyst concentrations on the DE is shown in Fig. 11. As can be seen from the graph, the dose of photocatalyst with 0.05 g is the best condition. It may be due to the fact that if the visible light is stable, the photo-electronic is constant at a constant time. So the amount of photocatalyst is the best value, which can make the exposed photon energy to be most fully utilized. When the dose of the photocatalyst is less than the best value, the photo-electronic and photo-hole are rare as well as the photon utilization rate is low, so the DE is very low. But with the increase of photocatalyst until more than the best

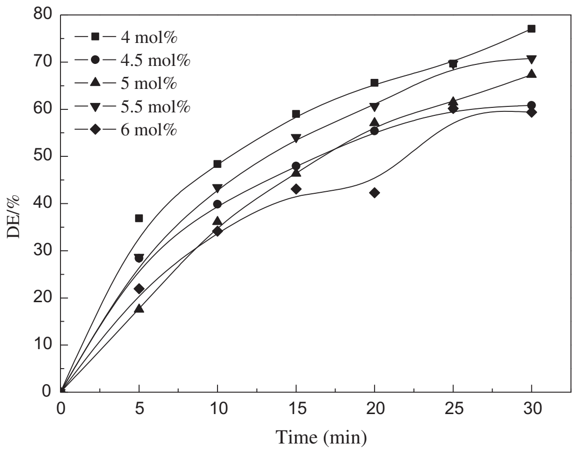

Fig. 9. The influence of Co-CdSe QDs prepared with different cobalt ions doping concentration.

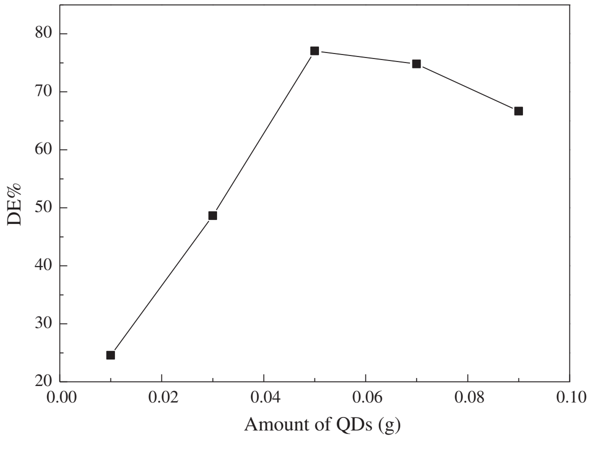

Fig. 11. The influence of different concentration of the photocatalyst.

value, not only improve the DE, on the contrary make the solution become turbid, transmissivity decrease, and lead to the DE to decrease.

3.6.7. Photocatalytic activity effect of different solution conditions

The influence of different surfactants on the catalytic performance was investigated in the following experiment. As shown in Fig. 12, by adding benzalkonium chloride, which is a kind of cationic surfactant, to the solution, the best DE is achieved. Comparing electrons with holes, holes play a dominant role in photodegradation and when the cationic surfactant ionizes in the water, a large number of electrons are adsorbed onto the surface of the surfactants. Then, a large number of holes would be released as free holes and participate in visible-light catalytic reaction, improving the photocatalytic performance of catalyst. Furthermore, to a certain extent, the presence of the cationic surfactant can effectively inhibit the recombination of electrons and holes as well as promote the activity of the catalyst.

3.6.8. Mechanism of photocatalysis

The mechanism of the photocatalysis has been only described by the following experiment. EDTA-2Na and tert-butanol were taken, respectively, as the holes scavengers and the hydroxyl radicals capture agents. It is displayed in Fig. 13 that EDTA-2Na can cause the inhibition of degradation which is little larger than tert-butanol, which justifies that holes play a dominant role in photodegradation in this system.

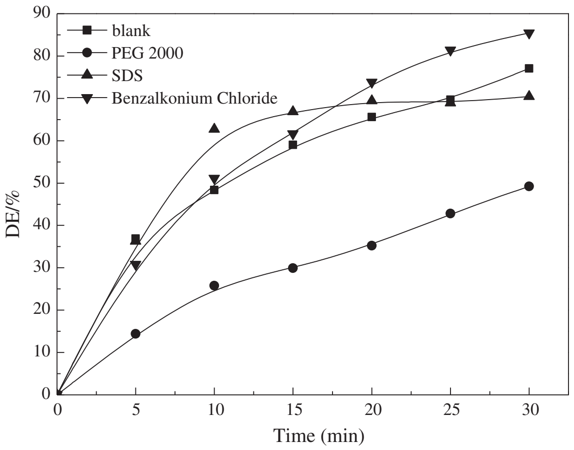

Fig. 12. The influence of solution conditions.

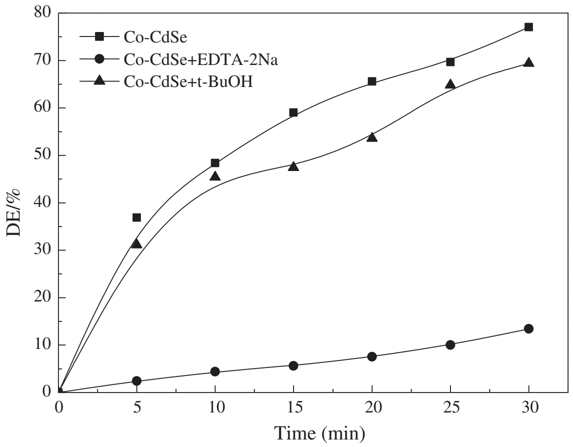

Fig. 13. Photocatalytic degradation of tetracycline hydrochloride under visible-light irradiation with (a) Co-CdSe, (b) Co-CdSe+EDTA-2Na, and (c) Co-CdSe+t-BuOH.

3.6.9. Degradation kinetics of tetracycline hydrochloride

To investigate the kinetics of photocatalytic degradation of tetracycline hydrochloride with the 4 mol% Co-doped CdSe QDs, photocatalytic tests were carried out with CdSe and 4 mol% Co-doped CdSe. The pseudo-first-order equation is introduced to describe the experimental data as follows:

$$\text{In}\frac{C_0}{C_t} = kt \qquad (2)$$

where k (min^{-1}) is the pseudo-first-order rate constant; C_0 and C_t are the initial and final concentrations of tetracycline hydrochloride.

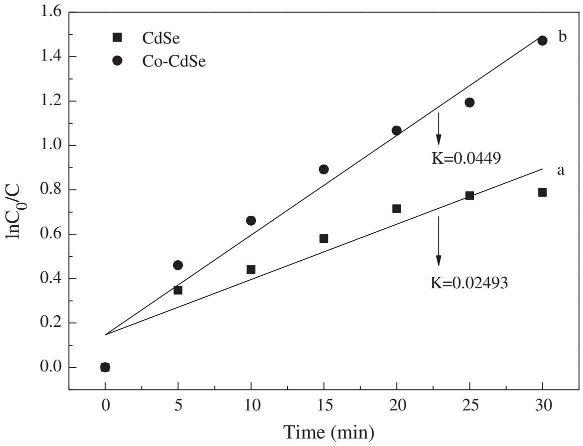

Fig. 14. The degradation rate constant of (a) CdSe and (b) 4 mol% Co-CdSe.

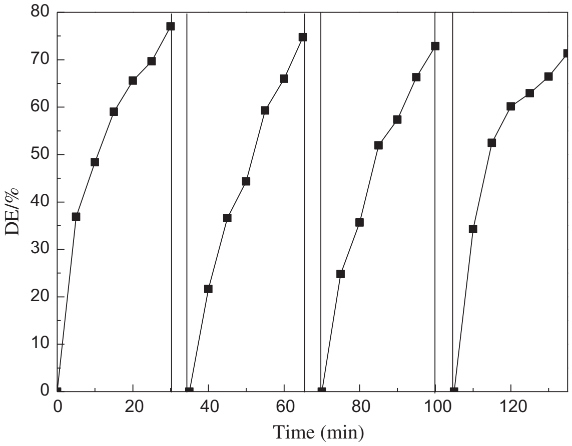

Fig. 15. Cycling runs in photocatalytic degradation of tetracycline hydrochloride in the presence of 4 mol% Co-CdSe under visible-light irradiation.

Fig. 14 shows the degradation kinetics curves of tetracycline hydrochloride over 4 mol% Co-doped CdSe QDs during irradiation time. The result shows that the degradation of tetracycline hydrochloride follows the pseudo-first-order kinetic model at the tested concentration range. It could be found that the rate constant of 4 mol% Co-doped CdSe QDs for degradation is 0.0449 at the tetracycline hydrochloride concentration of 20 mg/L, but the rate constant of CdSe is 0.0249. Therefore, degradation rate of tetracycline hydrochloride increases twice as the cobalt ions doping.

3.7. Repeated experiments

In order to examine the stabilities of catalysts, a recycling experiment is shown in Fig. 15. The 4 mol% Co-doped CdSe QDs photocatalysts were collected by centrifugation, washed with ethanol, and dried for a new photoreaction cycle. As shown in Fig. 15, the photocatalytic properties of 4 mol% Co-doped CdSe QDs remain unchanged after four cycles and it indicates that 4 mol% Co-doped CdSe QDs have excellent stabilities and reusabilities.

4. Conclusion

In summary, Co-CdSe QDs were successfully prepared via a simple hydrothermal method in alkaline condition. The 4 mol% Co-doped CdSe QDs showed the best photocatalytic activity for the degradation of tetracycline hydrochloride under visible-light irradiation. And the photocatalysts were better when there was cationic surfactant in the solution and its DE could reach 85.47%. Furthermore, the Co-doped CdSe QDs have pre-eminent stabilities because the photocatalytic activities of samples still remain efficient after four cycle test.

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