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Hydrothermal synthesis of the cauliflower-like CdS microspheres to enhance solar photocatalytic degradation of Oxytetracycline hydrochloride

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ABSTRACT

The Cadmium sulfide (CdS) microsphere photocatalysts with the cauliflower-like morphology have been synthesized by hydrothermal method. The as-prepared photocatalysts have been characterized by powder X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis, UV–vis absorption (UV–vis), and the thermo-gravimetric analysis. The UV–vis measurements show that the CdS microsphere prepared with 2 h have a band gap about 2.13 eV, which is smaller than the reported 2.42 eV, thus the as-prepared photocatalysts can be easily photoexcited and exhibit better photocatalytic performance. The photo-degradation experiments have been performed with CdS photocatalysts prepared with various synthesis conditions. Particularly, the CdS microsphere photocatalysts show the highest degradation ratio (72.78%) of Oxytetracycline hydrochloride under the visible light irradiation.

Keywords: Photocatalytic; CdS; Cauliflower-like; Oxytetracycline hydrochloride

1. Introduction

Antibiotics have been found to pose serious threat to the ecosystem and human health by enhancing the development of antibiotic-resistant bacterium. In order to solve this problem, it is necessary to find an effective method [1–3]. Photocatalytic technology provides a good way for the degradation of antibiotics in aquatic environments. Recently, semiconductor photocatalyst (such as TiO_2 and WO_3) have drawn intense research interest because of their unique structural, optical, and surface properties, which lead to their wide applications in photodegradation of the pollutants in the environment [4–8]. Kah Hon Leong's group has synthesized the nanocrystalline anatase TiO_2, through modified sol-gel method by reacting $TiCl_4$ with benzyl alcohol at room temperature. The TiO_2 samples showed excellent photocatalytic activity for the degradation of 2,4-DCP under natural sunlight irradiation [7]. Diana B. Hernandez-Uresti synthesized WO_3 nanoparticles with hexagonal structures and monoclinic structures were synthesized via a microwave-assisted

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hydrothermal process without the use of any additives in which the reaction time was 30 or 60 min. The photocatalytic activity of WO_3 was evaluated by photo-degraded rhodamine B (RhB), indigo carmine (IC), and tetracycline (TC) under UV–vis irradiation [8]. However, most of the photocatalyst (such as TiO_2, WO_3) could not achieve the excellent photocatalytic performance due to the limit of the UV light irradiation. Therefore, a new type of the visible-light semiconductor nanocrystal photocatalyst with high efficiency is still essential.

Cadmium sulfide (CdS), a well-known visible-light-sensitive material with the band gap of 2.42 eV, have been investigated extensively and could be used in electronics, photovoltaic material, bioselective chromatography, and photochemical catalysis [9–11]. Currently, various CdS nanomaterials with well-defined structures have been extensively explored to realize the combination of respective properties of each component or achieve cooperatively enhanced performances [12–14]. Therefore, the morphology of CdS is a crucial parameter in modifying its properties and nanostructures with novel morphologies are being intensively investigated. Up to now, various kinds of CdS nanocrystals, for example, sphere [15], nanorods [16], nanowires [17], hollow spheres [18], nanoribbons [19], and nanoparticles [20], have been fabricated within the cadmium chalcogenide system.

Recently, a number of methods have been explored to fabricate nanocrystals, such as the solvothermal synthesis [21], thermal evaporation [22], the hydrothermal method [23], and other methods [24,25]. Among these, the hydrothermal method is promising as an avenue for the assembly of CdS nanocrystals with controlled morphologies that have been extensively explored. For example, Li Yuexiang's group have synthesized the CdS nanorods by the hydrothermal method using ethylenediamine as the template agent and coordination agent [26], and Licheng Wang's group have synthesized the flower-like CdS microcrystallites through a convenient hydrothermal process with $NaH_2PO_2{\cdot}H_2O$ in aqueous solution [27]. However, most of the hydrothermal methods are capping-reagent-assisted method which may affect the photocatalytic activity of CdS. Thus, it is desirable to synthesis the cauliflower-like CdS microsphere photocatalysts without the capping-reagent for enhanced photocatalytic activity. To the best of our knowledge, the cauliflower-like CdS microsphere photocatalysts is rarely used in the degradation of Oxytetracycline hydrochloride.

Herein, a facile, simple hydrothermal method was employed to synthesize the uniform CdS microspheres, which is based on the Ostwald ripening [28]. The surface of CdS photocatalysts were rough and displayed monodisperse cauliflower-like morphology. Also, the as-prepared photocatalysts has been characterized by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDS), X-ray diffraction (XRD), UV–vis, and thermo-gravimetric analysis (TGA). The CdS microspheres photocatalysts exhibits excellent photocatalytic activity on the Oxytetracycline hydrochloride under the visible light irradiation.

2. Experimental section

2.1. Materials

Cadmium nitrate tetrahydrate $\{Cd(NO_3)_2{\cdot}4H_2O\}$, sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) were purchased from Aladdin Chemistry Co. Ltd. Ethanol, TC, oxytetracycline hydrochloride, RhB, ciprofloxacin (CIP) were purchased from Shanghai Shunbo Biological Engineering Co. Ltd. All the materials used in the experimental were of analytical grade. The water used in the experiment was double deionized water.

2.2. Synthesis of CdS microspheres

In a typical synthesis, 1.542 g of Cadmium nitrate tetrahydrate $\{Cd(NO_3)_2{\cdot}4H_2O\}$ and 1.248 g of Sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) were dissolved in 30 mL of deionized water and then formed the clear solution. The mixture was continuously stirred for 15 min at room temperature with the flowing N_2, and then the solution was transferred to an autoclave with a Teflon lining and hydrothermally treated at 180℃ for 2 h. After the autoclave cooled to the room temperature, the yellow precipitate was harvested by centrifugation, washed for several times with deionized water and ethanol to remove possible remaining cations and anions, and dried in vacuum at 55℃ for 8 h. Finally, the CdS microsphere photocatalysts were obtained.

2.3. Characterization of the CdS microspheres

The SEM images were examined by the JSM-7001F SEM (JEOL Ltd., Japan). Elemental mapping over the selected regions of the photocatalyst was conducted by EDS. The XRD patterns were obtained using the MO3XHF22 X-ray diffractometer (MAC Science, Japan) equipped with Ni-filtrated Cu Kα radiation (40 kV, 30 mA). The 2θ scanning angle range was 10–80° at the scanning rate of $10^{\circ}\,min^{-1}$. UV–vis diffuse reflectance spectra (UV–vis DRS) of the photocatalyst was obtained by the dry-pressed disk samples using Specord 2450 spectrometer (Shimazu, Japan)

equipped with the integrated sphere accessory for DRS, using $BaSO_4$ as the reflectance sample. TGA was performed for powder samples (about 10 mg) using the Diamond TG/DTA Instruments (Perkin-Elmer, USA) under a nitrogen atmosphere up to 800℃ with the heating rate of 5.0℃ min^{-1}.

2.4. Measurement of photocatalytic activity

The photocatalytic activity of CdS microspheres was investigated by the photodegradation of Oxytetracycline hydrochloride and the experiment was carried out in the GHX-2 photocatalytic reactor with a 500 W xenon lamp. An amount of 0.1 g photocatalyst was suspended in a 100.0 mL aqueous solution with 15 mg/L Oxytetracycline hydrochloride. After 30 min in the dark, with stirring, it reached absorption equilibrium, and then the initial absorbency was determined. In this process, sample analysis was conducted in 10 min interval to measure dark adsorption. Then the lamp was turned on. The temperature of the reactant solution was maintained below 298 K by the flowing of cooling water during the reaction. Also, the experiment continued for 1 h and conducted in 10 min interval. Then, the UV–vis adsorption spectrum of the centrifuged solution was recorded using an UV–vis spectrophotometer. The photocatalytic degradation rate (Dr) was calculated by the Eq. (1):

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

where A_0 is the initial absorbency of Oxytetracycline hydrochloride solution which reached absorption equilibrium and A_i is the absorbency of reaction solution.

3. Results and discussion

3.1. CdS microsphere photocatalysts characterization

The crystal structure and phase purity of the CdS microsphere photocatalysts was characterized by XRD. As shown in Fig. 1 the diffraction peaks of the CdS microsphere photocatalysts prepared with 2 h can be indexed to the cubic phase of CdS (JCPDS No. 65-3414), which is confirmed by the peaks at $2\theta =$ 24.925°, 26.463°, 28.059°, 43.781°, 47.427°, and 51.817°. Any significant characteristic peaks of some impurities such as S, CdO, Cd, and C are not detected in the XRD pattern, confirming the purity of CdS microsphere photocatalysts.

A Raman spectrum is a useful tool for the investigation of the microstructure of crystalline materials.

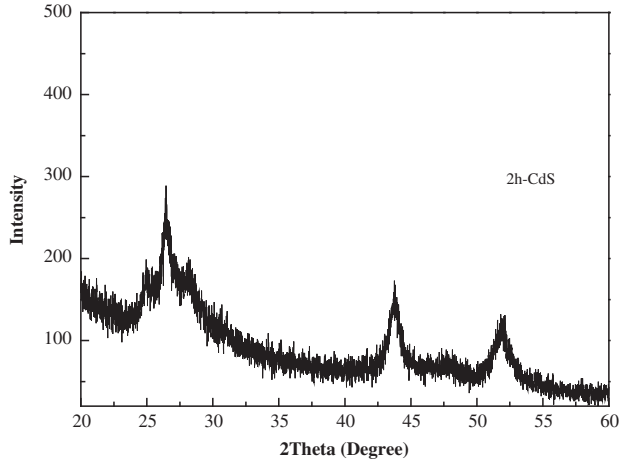

Fig. 1. XRD patterns of CdS microspheres prepared by 2 h.

Fig. 2 shows the spectrum of CdS microspheres, is dominated by 297.9, 598.1, 896.8 cm^{-1}, which corresponds to the longitudinal optical-phonon (LO) modes of the reported cubic CdS [29]. Compared with the mode intensity of CdS microspheres prepared with 1 and 3 h, the ratio of I_{2LO}/I_{1LO} is increasing in 2 h CdS microspheres. Moreover, the ratio of 2-LO to 1-LO mode intensities (I_{2LO}/I_{1LO}) is a parameter used to specify exciton−phonon interaction strength (S) in the semiconductors. The higher ratio indicates the increased crystalline size of CdS [30]. The relatively broad, symmetric, and sharp Raman peaks suggested that CdS microspheres were highly crystalline, which was also consistent with the XRD pattern results and the following SEM picture.

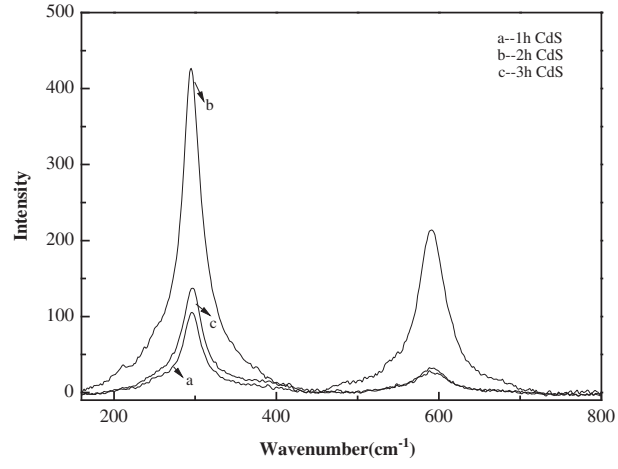

Fig. 2. Raman spectra for various CdS samples prepared by different time.

The UV–vis absorption spectra of CdS microsphere photocatalysts were shown in Fig. 3. It was obviously seen that the absorption spectrum of CdS microsphere photocatalysts (Fig. 3) was very broad and featureless in the whole spectrum region. Also, the absorption peak of CdS microspheres prepared with different time (Fig. 3) were shown in the visible-light region. The band gap of the materials can be estimated using the formula (Eq. (2)): $Eg = 1{,}240/\lambda g$ (2), where Eg is the band gap energy and λg is the wavelength of the absorption edge [31]. The absorption edge for CdS microspheres prepared with 2 and 3 h was about 580 nm, corresponding to the band gap of 2.13 eV, which was smaller than that reported in previous literature (CdS, 2.42 eV) [32]. While for the CdS microspheres prepared with 1 h the absorption edge shifted to around 540 nm, a blue shift was observed clearly, thus can be attributed to the size quantization effects. The decrease in grain size leads to the wider energy gap and a blue shift [31]. At last, the near-vertical absorption edge shows the narrow band gap and uniform size of CdS microsphere photocatalysts prepared with 2 h which is demonstrated by the SEM picture (Fig. 5(a)) [33].

Furthermore, TGA of the CdS microsphere photocatalysts (Fig. 4(a and b)) prepared with 2 h displays the mass change when the samples were exposed to the heat treatment. Fig. 4 shows the plot of the TGA data (a) and the DSC data (b). From the TGA curve, two prominent major weight losses could be observed. The first weight loss of 3.25% occurred at the range of 50–140˚C. The corresponding DSC curve shows an exothermic peak at 56.8˚C which is related to the decomposition of water. The second weight loss of 8.57% in TGA between 687 and 746˚C has been

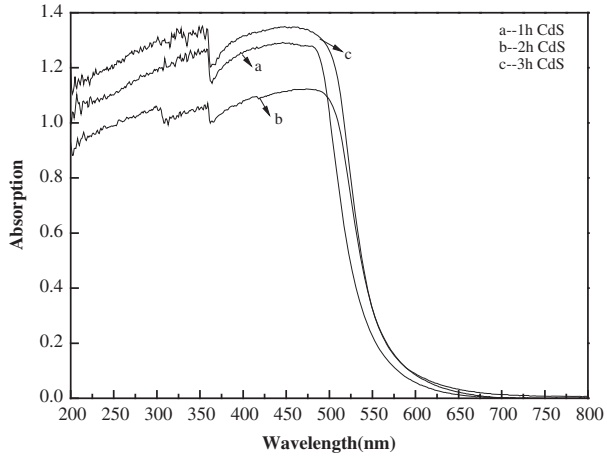

Fig. 3. DRS for various CdS microspheres prepared with different time.

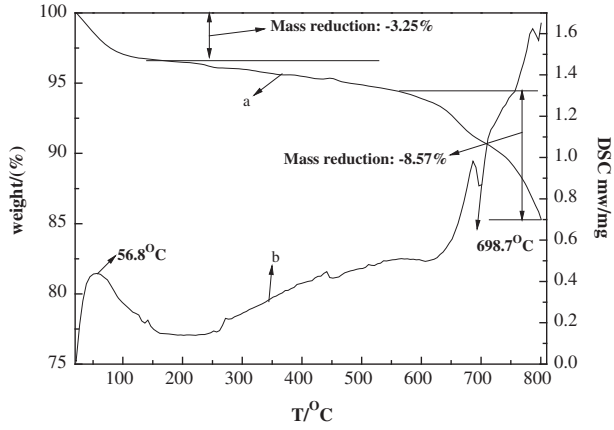

Fig. 4. TG-DSC curves for CdS samples.

reported mainly because of the change from cubic to hexagonal phase in inert gas atmosphere, which is corresponding to the absorption of DSC peak at 698.7˚C that may be attributed to the chemical transformation or the physical change, such as the phase change of CdS or the decomposition of CdS [34]. From the Fig. 4, only about 10% of the CdS microspheres photocatalysts have lost during the calcinations process confirming the thermal stability of the CdS microspheres photocatalysts.

The SEM image shows the morphology and chemical composition of CdS microsphere photocatalysts prepared with 2 h (Fig. 5(a–c)), and it can be seen clearly that CdS microspheres are quite uniform with the diameter about 1.5 μm (Fig. S1 in the supplemental files) and display the cauliflower-like morphology. From the high-magnification of CdS photocatalysts (Fig. 5(b and c)), it can be seen that the surface of the CdS microsphere photocatalysts were rough. Energy-dispersive X-ray spectrometry (EDS) was also used to determine the local chemical composition of the product. From the Fig. 5(d), the distributions of Cd and S have been shown in the picture. There are no elements other than Cd and S (the peak of C is likely attributed to the absorption of CO_2 because of samples exposure to the atmosphere or the conductive adhesive which was used to fix the CdS during the EDS experiment) present in the sample. At last, the uniform CdS microsphere photocatalysts with the highly crystalline has been synthesized with the good morphology.

3.2. Photocatalytic activity of CdS microsphere photocatalysts

In order to explore the effect of photodegradation of targets, the TC, Oxytetracycline hydrochloride, CIP, and RhB were chose as the photodegradation targets

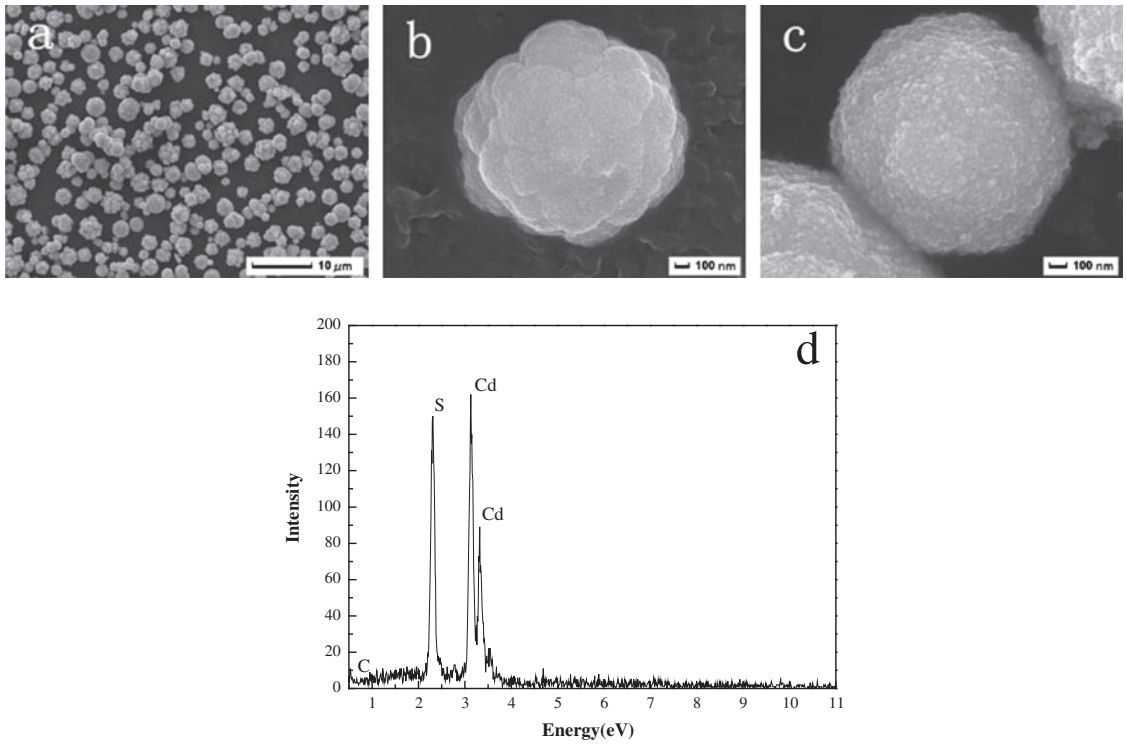

Fig. 5. SEM images of CdS microspheres (a) low magnification of CdS microspheres, (b and c) high magnification of CdS microspheres, and (d) EDS analysis of CdS microspheres.

and all the concentration of targets are 15 mg/L. Fig. 6 illustrates the degradation ratio of CdS microsphere photocatalysts with different targets. In this stage, only 0.05 g CdS microsphere photocatalysts was added into the photocatalytic system. As shown in the Fig. 6, the degradation ratio of Oxytetracycline hydrochloride reaches to 53.5%. The results indicated that different pollutants could be degraded by the CdS microsphere photocatalysts, but the degradation ratio of Oxytetracycline hydrochloride was higher than other targets. So the Oxytetracycline hydrochloride was chosen as the major targets in the next experiment.

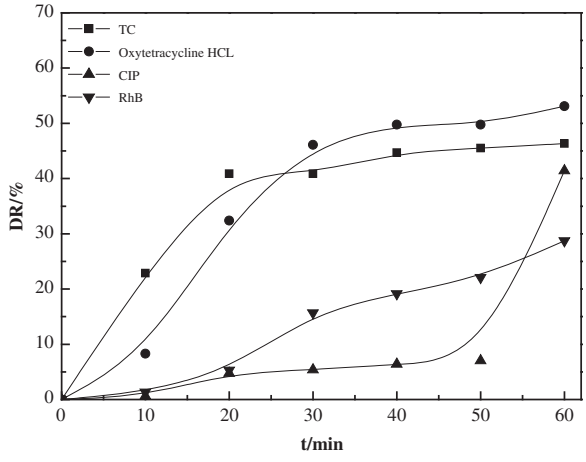

Fig. 6. The influence of different pollutants for the photocatalytic activity of CdS microsphere photocatalysts.

To investigate the degradation ratio effect of Oxytetracycline hydrochloride with CdS prepared by different time, 0.05 g CdS microsphere photocatalysts prepared with different time was used in this experiment with the 15 mg/L Oxytetracycline hydrochloride. Fig. 7 shows the photocatalytic activity of CdS microsphere photocatalysts prepared with different time. As we know, the reaction time is a significant factor in the chemical reaction which could affect the crystallinity, morphology, and property of CdS microsphere, and the shorter or longer may result in the microspheres reunion which could destroy the integral structure [28]. From the Fig. 7, the degradation ratio of Oxytetracycline hydrochloride exhibits the following trend: 2 h CdS > 3 h CdS > 1.5 h CdS > 1 h CdS. Interestingly, the degradation efficiency of CdS microsphere prepared with 3 h is closely related to the 2 h, which indicates that CdS prepared with 2 h is the most suitable time for the CdS microsphere photocatalysts growing. The CdS microsphere prepared with 2 h has good crystallinity and photocatalytic performance, and

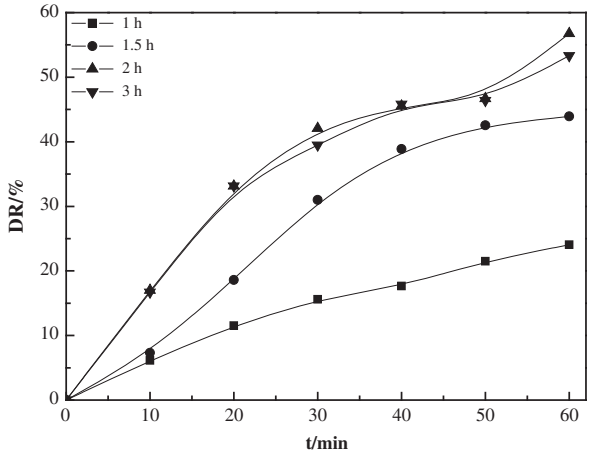

Fig. 7. The influence of CdS microsphere photocatalysts prepared by different time in the photoactivity.

then 2 h was selected as an optimal reaction time for the following investigations.

In the previous experiment, the concentration of Oxytetracycline hydrochloride with 15 mg/L was chosen as a basis of the experiment but it may not be the best reaction concentration. Fig. 8 indicates that the concentration of 15 mg/L Oxytetracycline hydrochloride have the best degradation ratio and the degradation ratio reaches to 56.32% in 60 min. When the concentration is lower than 15 mg/L, such as 10 mg/L, the degradation ratio only reaches 44%, mainly because the CdS microspheres photocatalysts cannot contact Oxytetracycline hydrochloride completely then the photodegradation ratio didn't reach the acme. When the concentration is higher than 15 mg/L, the degradation ratio is also lower than 15 mg/L. The possible reason is that the amount of CdS microsphere photocatalysts made the solution not to react completely. Another possibility is due to the super abundant Oxytetracycline hydrochloride which was absorbed on the surface of photocatalyst. Therefore, the degradation ratio is low. At last, the higher concentration is not a good choice; only 15 mg/L is the optimal concentration in this experiment.

During the previous experiment, only 0.05 g of photocatalysts was used in the experiment corresponding to the 50% degradation ratio of Oxytetracycline hydrochloride which is so weak. The dosage of photocatalyst in the photocatalytic degradation reaction is very important which affects the degradation ratio directly [35]. In order to investigate the influence of the dosage of CdS microsphere photocatalysts, different dosage of photocatalysts were used in the experiment. It worth noting that 0.1 g CdS microsphere photocatalysts show enhanced activities than others (Fig. 9). It may be due to if the visible light was stable, then the photo-electronic was constant in a constant time. So the amount of photocatalyst there was a best value, which can make exposure photon energy get the most fully utilized. When the dosage of the photocatalyst was less than the best value, the photo-electronic and photo-hole was rare. The photons utilization rate was low, so the degradation rate was very low. But with the increase of photocatalyst until more than the best value, not only improve the degradation rate, on the contrary make the solution become turbid, decrease in transmissivity, and lead to the decrease in degradation rate. Fig. 10 displays the photodegradation behaviors of Oxytetracycline hydrochloride with CdS microsphere photocatalysts under visible light illumination, respectively.

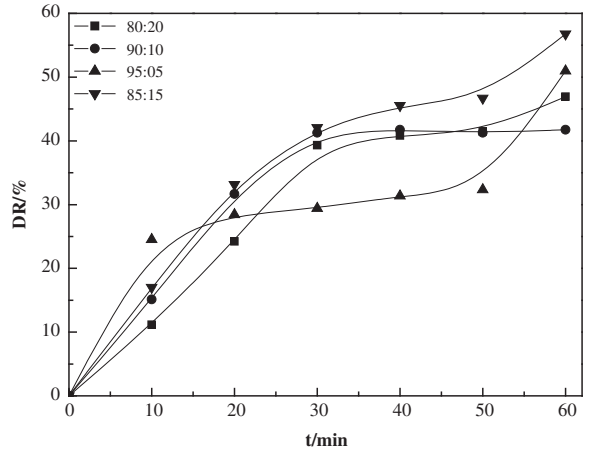

Fig. 8. The influence of the concentration of Oxytetracycline hydrochloride in the photoactivity.

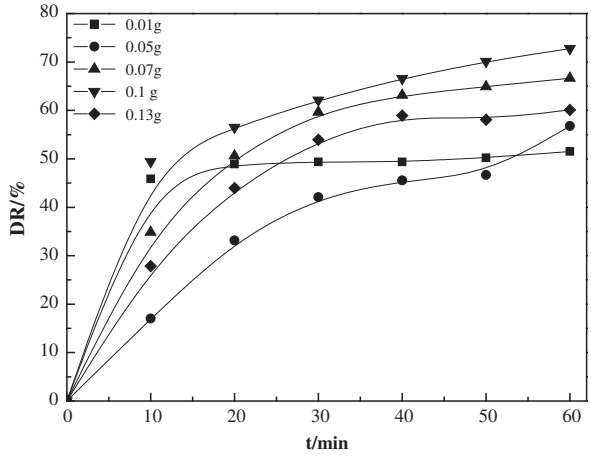

Fig. 9. The influence of the dosage of CdS microsphere photocatalysts in the photoactivity.

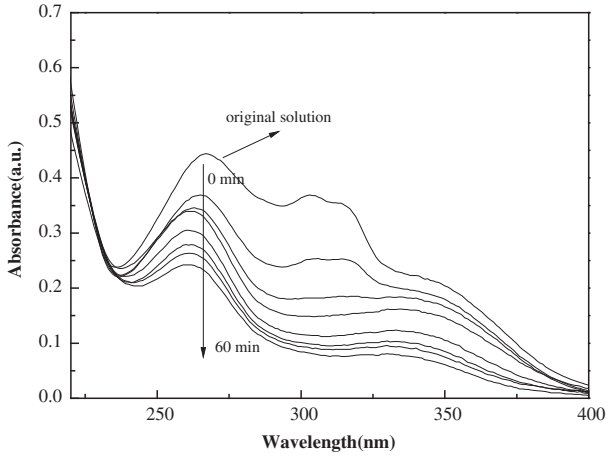

Fig. 10. The photodegradation behaviors images of Oxytetracycline hydrochloride catalyzed by CdS microsphere photocatalysts.

It is significant to authenticate the solution condition in the photocatalytic reaction process for comprehending the photocatalytic mechanism. Both the neutral and alkaline conditions favored targets removal and almost 70% removal of Oxytetracycline hydrochloride was realized in photocatalytic degradation process at 60 min, as illustrated in Fig. 11. Interestingly, the removal of Oxytetracycline hydrochloride achieved only 2% in acidic solution within the same period. One possible explanation is that the photocatalytic transformation of Oxytetracycline hydrochloride is effected by the hydroxyl radical oxidation. In the direct photolysis system, hydroxyl radicals ($OH^{\bullet}$) and hydrated electrons (e^{-}_{aq}) can be formed when water is irradiated with visible light (as shown in Eqs. (3)–(6)).

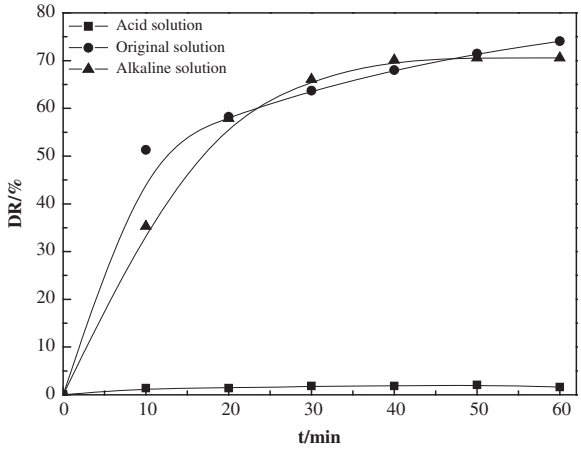

Fig. 11. The influence of the condition of solution in the photoactivity.

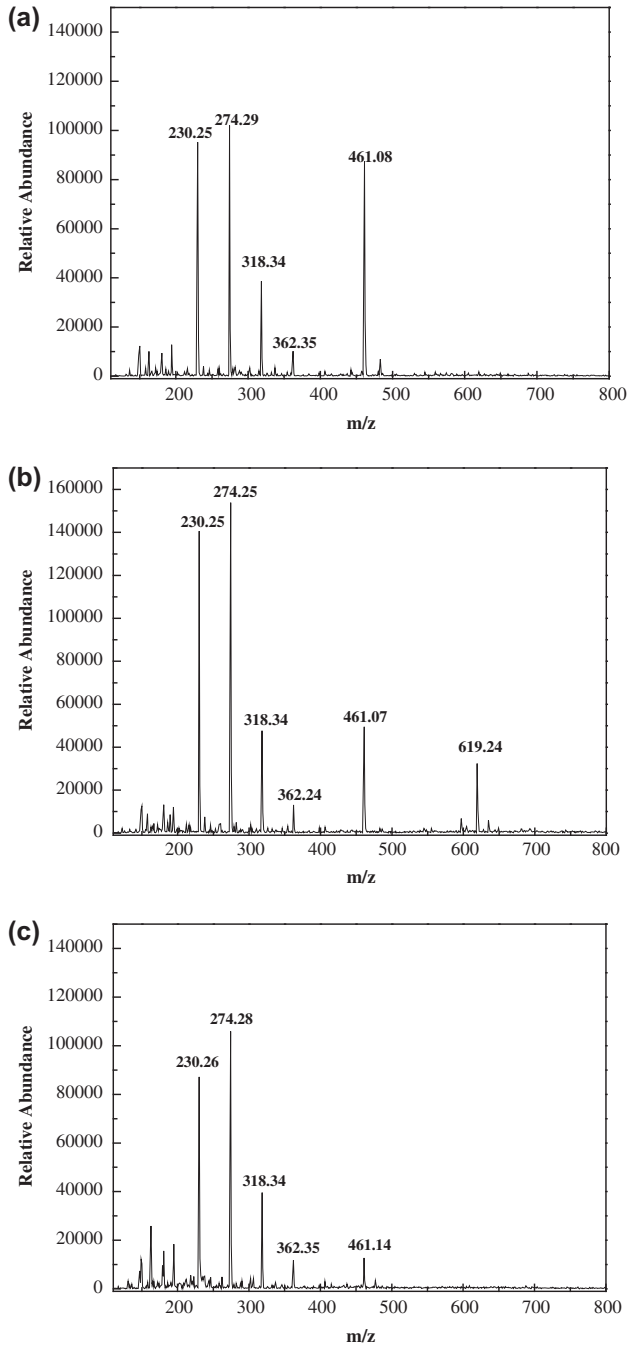

Fig. 12. MS chromatograms and m/z degraded Oxytetracycline hydrochloride: (a) Oxytetracycline hydrochloride, (b) degradation of Oxytetracycline hydrochloride in 30 min, and (c) degradation of Oxytetracycline hydrochloride in 60 min.

$$CdS + hv \rightarrow CdS\,(h^{+} + e^{-}_{aq}) \quad (3)$$

$$e^{-}_{aq} + O_2 \rightarrow O_2^{\bullet -} \quad (4)$$

$$OH^- + h^+ \rightarrow OH^\bullet \quad (5)$$

$$\text{Oxytetracycline hydrochloride} + OH^\bullet + O_2^{\bullet -} \rightarrow \text{inorganic molecules} \quad (6)$$

The alkaline solution can provide higher concentration of hydroxyl ions to react with holes (h^+) to form hydroxyl radicals [36]. However, the amount of holes (h^+) produced by CdS determines the improvement of degradation ratio that is not obvious.The low concentration of hydroxyl ions in acidic condition may inhibit the photodegradation ratio of Oxytetracycline hydrochloride.

In order to demonstrate the various degradation products in the photocatalytic system, MS was employed to identify the intermediates precisely, and the results shown in Fig. 12. From Fig. 12, it can be seen that a sharply prominent ion with m/z = 461 was the Oxytetracycline molecular ion which the HCl had dissolved and the peaks of other major byproducts were found. From the analysis of MS, the hydroxyl radical ($OH^\bullet$) as the oxidized species, attacked the Oxytetracycline and substituted the H of Oxytetracycline. The following sequence was generated by successive ions attacked and their fragmentations upon successive collision-induced dissociation: m/z = 496 → 461 (loss of HCl) → m/z = 362 (loss of OH, CH_3, and $CONH_2$) → m/z = 318 (loss of N, CH_2, and CH_3) → m/z = 274 (loss of CH, C, and OH) → m/z = 230 (loss of CH, C, and CH) [37]. The process of the degradation and intermediates were shown in Fig. 13. At last, the intermediate products would be degraded to the small inorganic molecular material.

According to the obtained results, it is not very clear that if the other visible light photocatalysts could be used for the degradation of Oxytetracycline hydrochloride. In order to know the other visible light photocatalysts for the degradation ratio of Oxytetracycline hydrochloride, the TiO_2, normal CdS, $ZnFe_2O_4$, WO_3, and Fe_3O_4 have been used in the degradation of Oxytetracycline hydrochloride. Fig. 14 shows, the degradation ratio for Oxytetracycline hydrochloride which follows the following trend: CdS microsphere photocatalysts > TiO_2 > WO_3 > normal CdS > Fe_3O_4 > $ZnFe_2O_4$. The results illustrate that CdS microsphere photocatalysts possess the best photodegradation ratio. The results could be attributed to the following reasons. Not only CdS has the excellent properties such as the narrow band gap, but also the cauliflower-like morphology may affect the degradation process. Unlike the normal CdS and other photocatalysts which is amorphous, the CdS microsphere photocatalysts have the cauliflower-like morphology which makes the surface to look rough and increase the

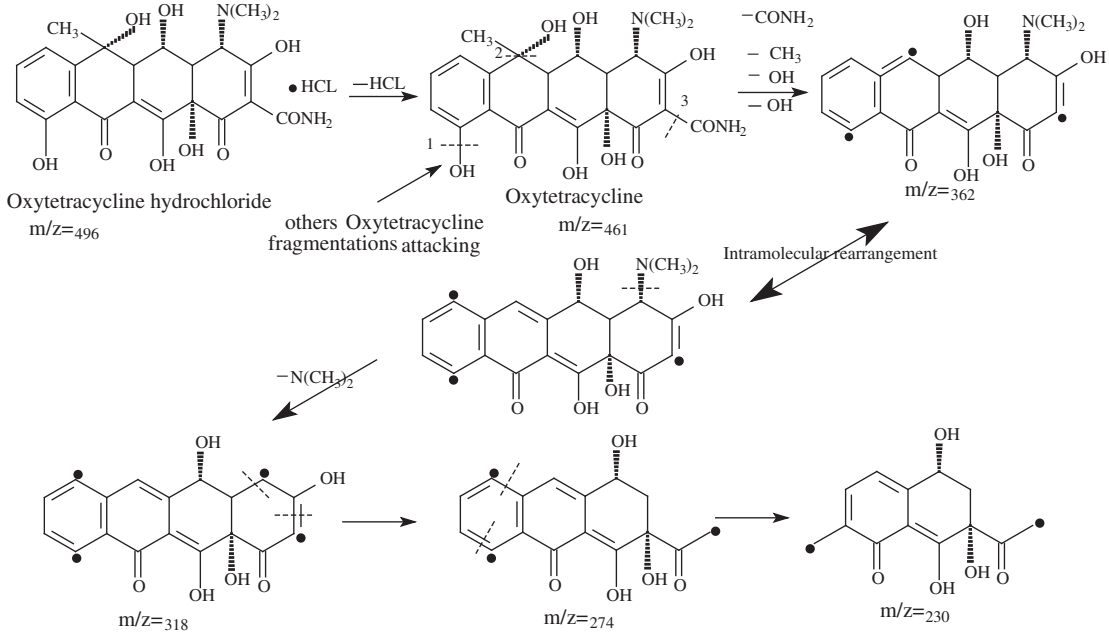

Fig. 13. The process of degradation Oxytetracycline hydrochloride ($C_{22}H_{24}N_2O_9$·HCl) with CdS microspheres photocatalyst.

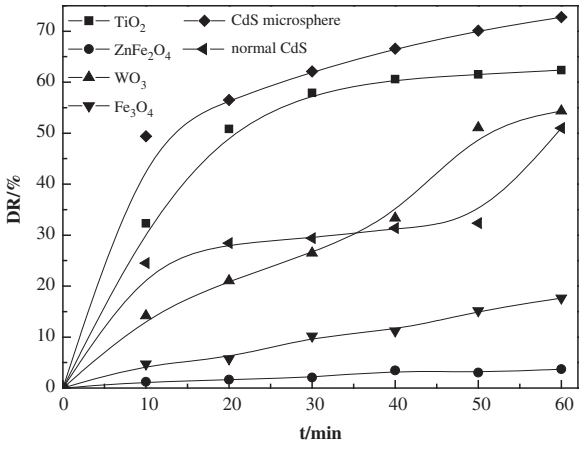

Fig. 14. Photocatalytic degradation of Oxytetracycline hydrochloride with different photocatalysts.

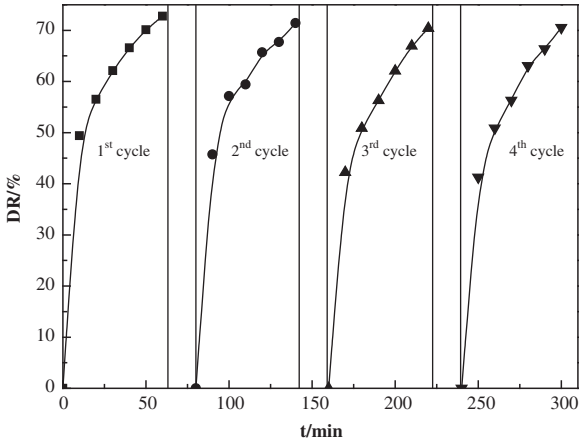

Fig. 15. Recyclability evaluation for CdS microsphere photocatalysts: four reaction cycles for photo-degradation of Oxytetracycline hydrochloride under visible light irradiation.

specific surface area with Oxytetracycline hydrochloride molecules, thus the degradation ratio is improved [38].

At last, the recycled photocatalytic experiment has been taken to evaluate the recyclability of CdS microsphere photocatalysts. CdS microsphere photocatalysts were recycled and reused successively for four times for the photodegradation of Oxytetracycline hydrochloride under the same experimental condition. Fig. 15 displays the degradation ratio of Oxytetracycline hydrochloride in the recycled photocatalytic experiment. No significant loss of degradation ratio is observed after four successively recycled experiments, indicating that the CdS microsphere photocatalysts exhibit good stability in the recycled photocatalytic experiment.

4. Conclusion

In this paper, a fast and convenient hydrothermal synthetic method for the preparation of CdS microsphere photocatalysts has been proposed. The as-prepared CdS microsphere photocatalysts displays uniform size. Based on the data of UV–vis absorption analysis, the band gap of CdS microsphere photocatalysts is 2.13 eV which is smaller than the reported 2.42 eV. Narrower the band gap is, the more photoexcited the electrons are, and higher the photocatalytic activity is. The photocatalytic degradation of different photodegradation targets has been explored and the optimal conditions have been discussed. The optimal photodegradation ratio of Oxytetracycline hydrochloride is 72.78% in 60 min under visible-light irradiation.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2014.932708.

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