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Effect of calcination on the photocatalytic performance of CdS under visible light irradiation

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ABSTRACT

The photocatalytic activity of cadmium sulfide (CdS) under visible light irradiation was evaluated by degrading methylene blue (MB). Upon calcination in air/O_2 atmosphere, the photocatalytic activity of CdS was enhanced by eliminating the trap energy levels. Meanwhile, the effect of cadmium oxide (CdO) on the photocatalytic activity of CdS was also studied by in situ forming CdO on the surface of CdS. CdO blocked the light absorption of CdS, which decreased the photocatalytic activity of CdS.

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1. Introduction

The presence of organic pollutants in water, air and soil has already been a great environmental problem to human being. People are seeking appropriate ways to eliminate these contaminants. As a kind of non-biological technology to degrade/mineralize most of the organic pollutants, photocatalysis has received an enormous amount of research interest [1–7].

Different kinds of photocatalysts, such as TiO_2, doped TiO_2, ZnO, etc., have been developed toward various types of contaminants [8–11]. Among these photocatalysts, hexagonal CdS as one of the most important II–VI group semiconductors has received much more attention in utilizing solar energy due to its band gap (2.4 eV) matching well with the solar spectrum [12–16]. For improving the photocatalytic activity of CdS, the processes in the photocatalytic reaction, including the generation, separation, recombination and migration of the photogenerated electrons and holes, should be comprehensively investigated [17,18]. Electron–hole recombination is actually a vital factor which decreases the photocatalytic activity of CdS. The recombination centers present in the material include structural defects and shallow impurity energy levels which can be regarded as the trap energy levels. In this paper, hexagonal CdS was directly treated by a simple calcination method in air/O_2 atmosphere to eliminate the trap energy levels and the photocatalytic activity for degrading methylene blue (MB) was enhanced. At the same time, the effect of CdO on the photocatalytic activity of CdS was also studied by in situ forming CdO on the surface of CdS. CdO decreased the photocatalytic activity of CdS through blocking the light absorption of CdS.

2. Experimental

2.1. Photocatalyst treatment

CdS powder (A.R. Beijing Shuanghuan Weiye Reagent Co., Ltd.) was ground thoroughly with a small amount of ethanol in an agate mortar. The powder was calcined at 400 °C for 15–300 min in air or O_2 or Ar atmosphere and then cooled to room temperature.

2.2. Characterization

The surface morphology of the samples was obtained by using a scanning electron microscope (SEM, XL30 S-FEG, FEI). X-ray diffraction (XRD) patterns of the samples were collected by using a rotating-anode diffractometer with Cu K_a radiation (M18X-AHF, Mac Science). Diffuse reflection spectra were measured on a UV–vis spectrophotometer (UV-2550, Shimadzu). Fluorescence spectra were recorded on a spectrometer (SPEX 1403). Chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB-5, VG).

2.3. Photocatalytic performance

The photocatalytic activities of the samples were evaluated by the degradation of MB under visible light irradiation. The irradiation source was a 500 W halogen lamp (Institute of Electric Light Source, Beijing), which was fixed inside a cylindrical pyrex vessel and cooled by a circulating water jacket (pyrex). A long-pass glass filter was used to cut off the light with wavelength below 420 nm. The radial flux was measured with a radiant power/energy meter (70260, Oriel) and the average light intensity was 30 mW cm^{-2}. In a typical procedure, 45 mg of the sample and 90 mL of 3×10^{-5} M MB solution were used for the photocatalytic test. Prior to irradiation, the solutions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. During irradiation, 3 mL of turbid solution was taken from the reaction solution at certain time intervals and

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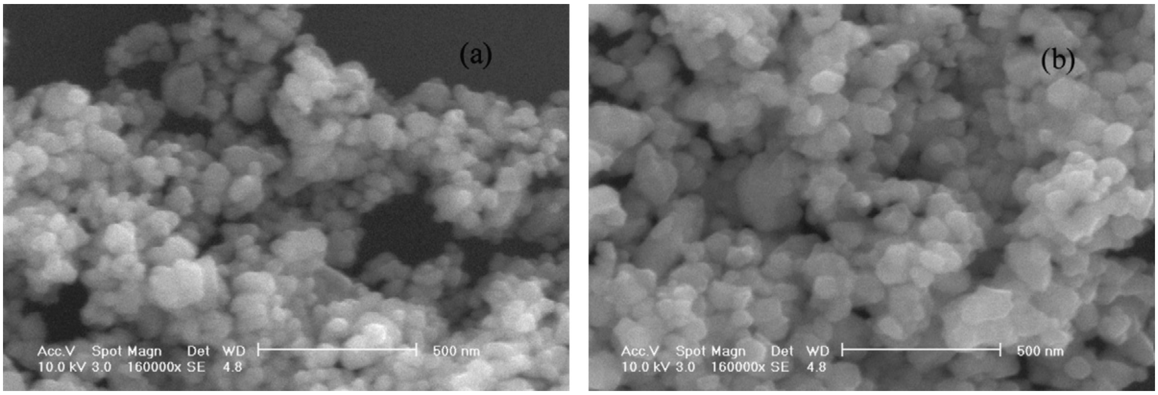

Fig. 1. SEM micrographs of CdS: (a) without calcination and (b) calcined at 400 °C for 45 min in air atmosphere.

then centrifuged to remove the catalysts. The concentration of MB was determined by measuring the absorbance of the clear solution with a UV–vis spectrophotometer (UV-2550, Shimadzu).

3. Results and discussion

It can be seen from Fig. 1 that the CdS particles aggregate and the mean size grows from 55 nm to 97 nm upon calcination, but the morphology almost does not change. The phases of the samples were first characterized by XRD. As shown in Fig. 2, for samples calcined in air atmosphere, when the calcination time is shorter than 45 min, all the diffraction peaks of the samples correspond to the hexagonal phase of CdS (Greenockite, JCPDS 41-1049); whereas additional reflections corresponding to the CdO (JCPDS 01-1049) are observed when the calcination time prolongs to 45 min. These CdO peaks are obviously stronger when the sample is calcined at 400 °C for 45 min in O_2 atmosphere.

Considering the XPS technique reflects the surface characteristics of materials, herein, XPS has been used to further confirm the existence of CdO. Fig. 3 presents the XPS spectra of CdS sample calcined at 400 °C for 45 min in air atmosphere. The binding energies of Cd $3d_{5/2}$, Cd $3d_{3/2}$, S $2p_{3/2}$ and S $2p_{1/2}$ are 405.6 eV, 412.3 eV, 161.9 eV and 162.4 eV, respectively, close to the reported values in literature [19]. The peak at 530.6 eV matches well with the literature value for oxygen in CdO [20], indicating the formation of CdO on the surface of CdS. According to the peak areas of Cd $3d_{5/2}$, S $2p_{3/2}$ and O 1s, the surface atomic ratio of (S + O)/Cd is estimated to be 0.9691:1 while that of O/Cd is 0.8121:1. It is well known that some of sulfur evaporates at temperatures higher than 375 °C [21], and the surface atomic ratio of S/Cd will be non-stoichiometric, which correlates with the formation of CdO. It is thus deduced that, for the CdS samples calcined for a short time (below 45 min), the quantity of formed CdO on the CdS surface is below the detection limit of XRD, leading to no diffraction peaks of CdO in XRD.

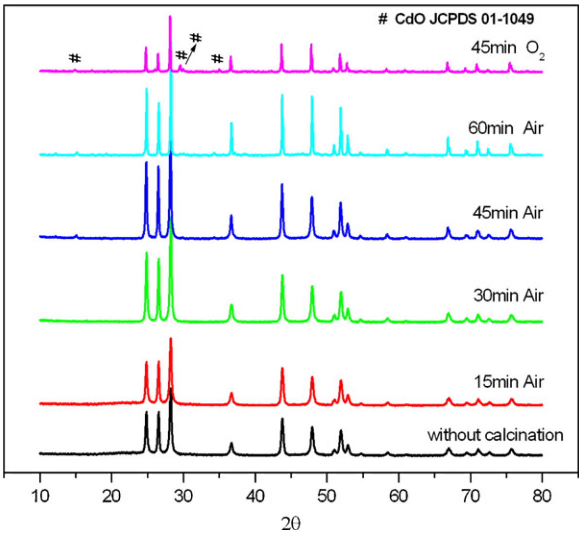

Fig. 2. XRD patterns of CdS calcined at 400 °C.

Fig. 4(a) shows the diffuse reflection spectra of CdS calcined at 400 °C in air atmosphere. With increasing the calcination time, the color of the samples changes from yellow to pale-yellow and the absorption curve becomes sharper. Correspondingly, the absorption band edges of CdS with calcination time of 0, 15, 30, 45, 60 and 300 min are 523, 519, 514.3, 514, 513.9 and 512.9 nm, respectively. The absorption band edges do not distinctly change with increasing the calcination time from 30 to 300 min, at the same time, the amount of CdO is increasing. Due to the similar band gap size of CdO and CdS, CdO has little effect on the absorption band edges of CdS. The blue shift of the absorption edge can be attributed to the elimination of trap energy levels, i.e., structural defects and shallow impurity energy levels, and the decrease of the band tail states [16,22,23]. High quality particles with a low density of trap states generally have weak trap emission and strong band edge emission, while low quality samples have more trap emission and weak band edge emission [24]. Fig. 4(b) shows the fluorescence spectra of CdS calcined at 400 °C in air atmosphere. The peaks at 507 nm and 680 nm are assigned to the band edge emission and the trap emission, respectively [25]. With increasing the calcination time, the band edge emission becomes stronger while the trap emission becomes weaker. Hence the calcination treatment decreases the trap states.

Investigations on the degradation of MB under visible light irradiation were carried out with different CdS samples. Under irradiation with photon energy equal to or higher than the band gap of CdS, the photogenerated electrons on the conduction band are scavenged by the molecular oxygen (present in the solution) to yield a series of active oxygen species which degrade the MB molecules [26,27]. Fig. 5 presents the effect of calcination time on the photodegradation efficiency of CdS. For the untreated CdS sample, only 48% MB (5.78×10^{-6} mol g^{-1} h^{-1}) can be photodegraded within 5 h irradiation. First, upon calcination in air atmosphere, the photodegradation efficiency and the stability of the photocatalytic activity are improved (Fig. 5(a)), which can be further improved by using sacrificial reagent to prevent the photocorrosion. According to a series of photodegradation results, the optimal calcination time in air atmosphere is 45 min and about 90% MB (1.08×10^{-5} mol g^{-1} h^{-1}) is degraded after 5 h irradiation, with the efficiency improved by 87.5%. Generally, there are two parameters influencing the photodegradation efficiency: one is the generation of charge carriers, the other is the separation of photogenerated

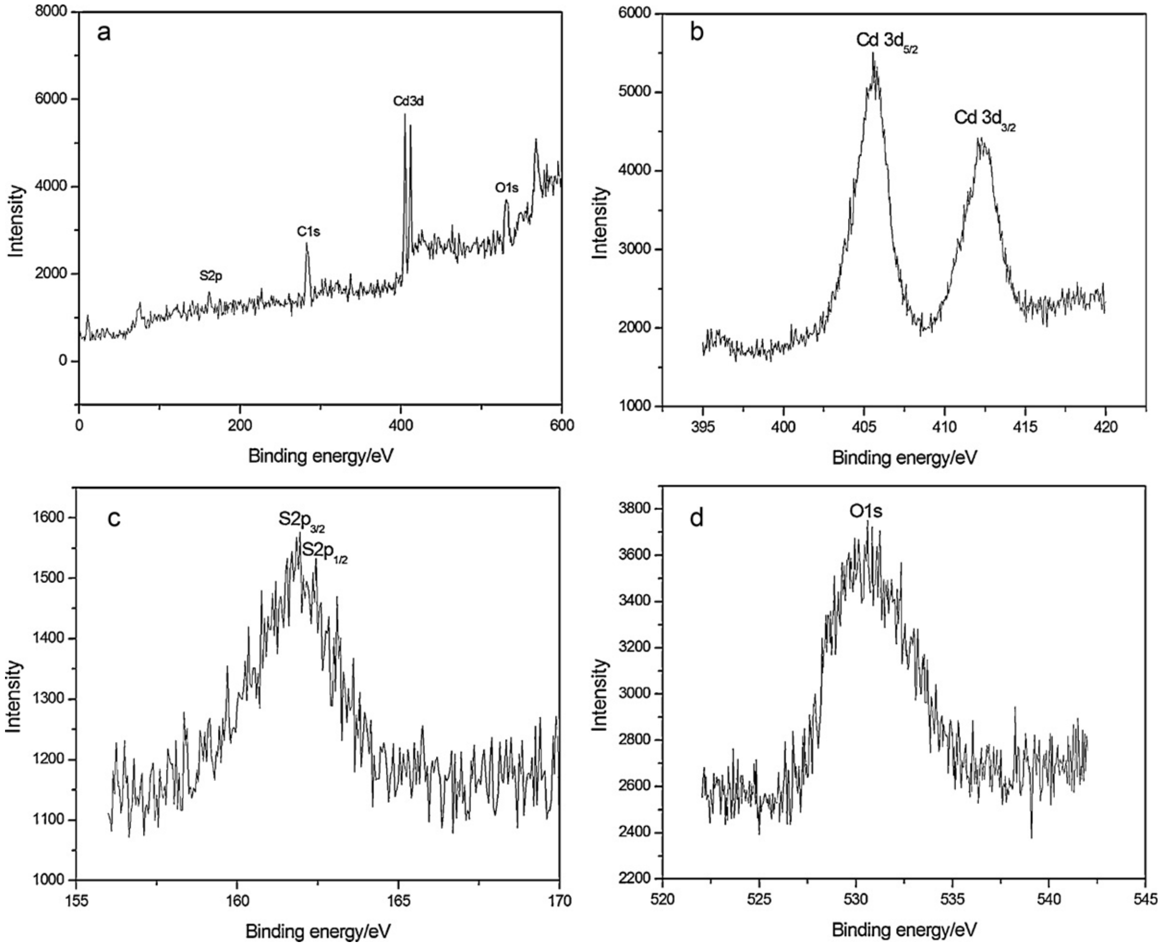

Fig. 3. XPS spectra of CdS calcined at 400 °C for 45 min in air atmosphere.

electrons and holes. Trap energy levels are often regarded as the recombination centers for the photogenerated electrons and holes. As seen in Fig. 4, the trap energy levels can be eliminated by the calcination treatment, facilitating the photogenerated charge carriers separation and hence increasing the degradation efficiency. As confirmed in Fig. 2 and Fig. 3, CdO is formed on the surface of CdS. According to the band structures of CdS and CdO, the conduction band minimum and the valence band maximum of CdO are more positive than the counterparts of CdS [28,29]. After CdS and CdO absorb the photons, electrons are excited from the VB to CB, leaving holes in the VB. Then the electrons in the CB of CdO transfer to the VB of CdS and recombine with the holes. CdO exhibits a band gap in the interval 2.2–2.4 eV [22] and may block the light absorption of CdS, reducing the generation of charge carriers and the photodegradation efficiency. When the calcination time is shorter than 45 min, the elimination of trap energy level is deficient and the separation of photogenerated charge carriers is not sufficient. At the same time, the small amount of formed CdO has little effect on blocking the

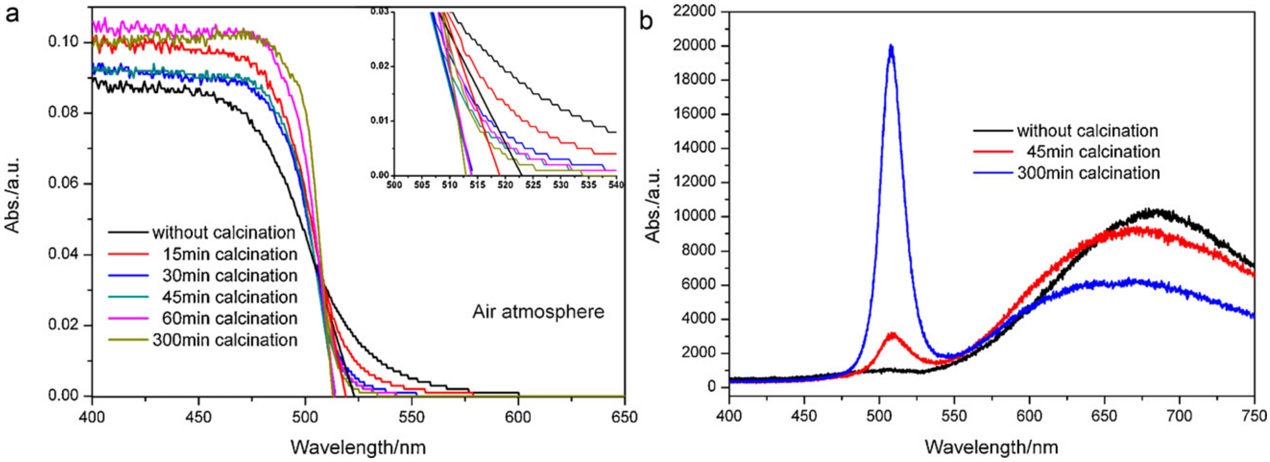

Fig. 4. (a) Diffuse reflection spectra of CdS calcined at 400 °C in air atmosphere. Inset is the enlarged diffuse reflection spectra between 505 and 540 nm. (b) Fluorescence spectra of CdS calcined at 400 °C in air atmosphere. Excitation wavelength: 325 nm.

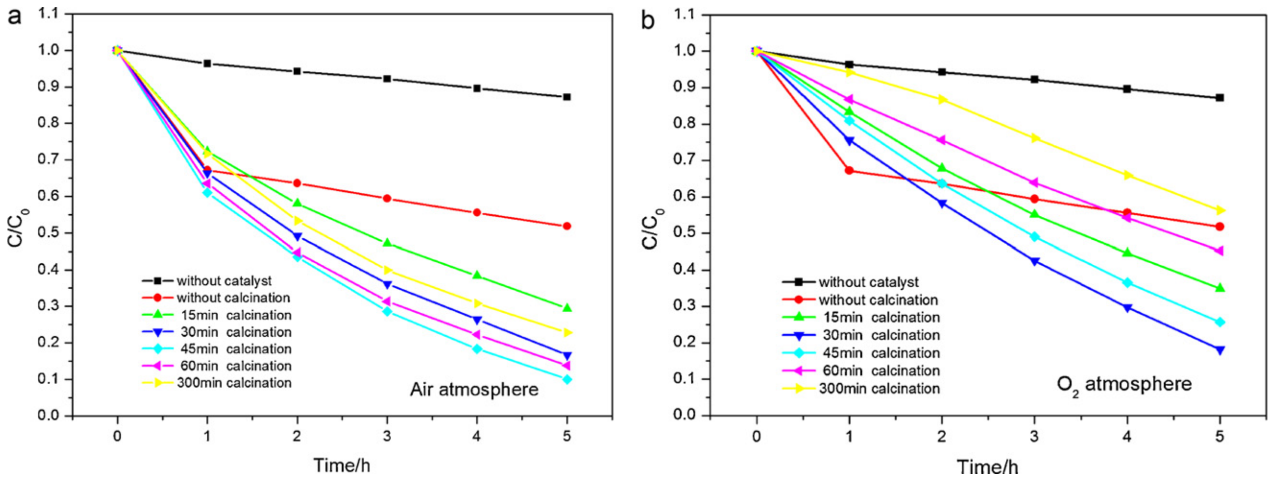

Fig. 5. Photodegradation efficiency of CdS calcined at 400 °C in air and O_2 atmosphere: (a) in air and (b) in O_2.

light absorption of CdS. As the calcination time is increased, the separation efficiency is enhanced. When the calcination time is longer than 45 min, more CdO is formed and the blocking the light absorption by CdO takes effect, thus reducing the generation of charge carriers by CdS. Proper generation and separation of charge carriers is obtained with 45 min calcination treatment. When CdS is calcined in O_2 atmosphere, the formation of CdO will easily take place and the optimal time is 30 min, with the efficiency improved by 69.7% (Fig. 5(b)). When the calcination time in O_2 atmosphere prolongs to 300 min, the block effect of CdO is obvious and the photodegradation efficiency is even lower than that of CdS without calcination treatment after 5 h irradiation. By a close examination of Fig. 5(a) and (b), for the CdS with the same calcination time, the photodegradation efficiency of CdS calcined in air atmosphere is better than that of CdS calcined in O_2 atmosphere, which further confirms the block effect of CdO.

As seen from Fig. 6, the photodegradation efficiency of CdO is almost unchanged upon calcination and about 98% MB (1.18×10^{-5} mol g^{-1} h^{-1}) is degraded by CdS calcined at 400 °C for 45 min in Ar atmosphere. Due to the poor photocatalytic performance, the main effect of CdO is blocking the light absorption of CdS. By comparing the photodegradation efficiencies of CdS calcined in Ar and air atmosphere, it is further confirmed that the enhanced photodegradation efficiency can be attributed to the elimination of the trap energy levels through calcination treatment.

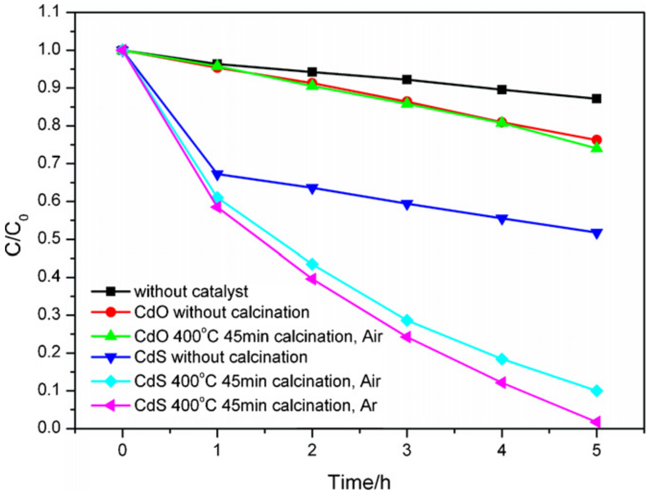

Fig. 6. Photocatalytic degradation of MB by CdO and CdS.

4. Conclusions

By a facile calcination treatment, the photodegradation efficiency of CdS was enhanced. The optimal calcination time in air and O_2 atmosphere was 45 min and 30 min, respectively. Correspondingly, the efficiencies were improved by 87.5% and 69.7%. Upon calcination, the trap energy levels were eliminated, benefiting the separation of photogenerated charge carriers and resulting in the enhanced photocatalytic activity. With increasing calcination time, the formed CdO blocks the light absorption of CdS, reducing the generation of charge carriers and the photodegradation efficiency.

Acknowledgments

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