Nanometer CdS preparation and its photocatalytic performance under visible light irradiation

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In this paper, CdS nanometer particles are successfully synthesized by hydrothermal method and its photo catalytic performance was evaluated via degradation Ciprofloxacin under visible light irradiation. The morphology, size and structure are characterized by scanning electron microscopy, X-ray diffraction spectroscopy, UV-vis absorption spectrophotometer, respectively. The results show that CdS exhibit excellent photo catalytic performance for degradation Ciprofloxacin with a maximum removal rate of over 95% at 60 min under visible light irradiation due to its higher visible light absorption and comparatively low electron-hole pair recombination. The possible mechanism of the photo catalytic degradation processes is proposed.

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Keywords: CdS, Hydrothermal method, Photodegradation, Visible light irradiation

1. Introduction

In recent years, as a promising new environmental technology, photo catalytic technology has important part in promoting waste purification (decontamination, detoxification and deodorization) and decomposing pollutants [1-7]. With the rise of nanotechnology, it has become pollution control technology and attracted wide attention of many scholars.

The photo catalytic system involves illumination of large band gap semiconductor particles such as TiO_2 and ZnO [8-14]. However, they are difficult to absorb visible light, thus, only make use of 3-5% of the solar energy because of their wide band gap. Therefore, the exploration of efficient visible light photo catalysts is an urgent issue from the viewpoint of using solar energy [15-19].

Antibiotics is a kind of chemical pollutions, and it can inhibit or affect biological functions of others living body at low concentrations. It has played a huge role in in human health and animal and plant pest control because of its discovery and application. However, with its mass production and application, pollution problems have become more serious. Because of complex structure of antibiotics, enriched easily in the environment, antibiotic contamination can induce drug-resistant strains, and cause serious impact on the environment microflora [20]. The main sources of pollution contaminated medical antibiotics, industrial pollution and agricultural antibiotic [21-22].

In this work, we report the photo catalytic degradation of Ciprofloxacin (CPLX) under visible light irradiation by CdS photo catalyst synthesized via a hydrothermal synthesis method. It found that the CdS exhibit much higher performance in the degradation of CPLX under visible light irradiation. The proposed mechanism of this improvement was discussed in detail.

2. Experimental

2.1 Synthesis of CdS photo catalyst

In this study, we use $CdSO_4 \cdot 8/3H_2O$ and CS $(NH_2)_2$ as the precursor. First, 9 mmol $CdSO_4 \cdot 8/3H_2O$ and CS $(NH_2)_2$ dissolved in 10 mL distilled water, respectively. And then, the solution of CS $(NH_2)_2$ join into the cadmium sulfate solution drop by drop, and then join the polyvinylpyrrolidone (PVP) (0.005g) as surfactant. Continue stirring until the solution fully mixed evenly for 2 h at room temperature, and then the mixed solution is loaded into the reactor with Teflon lined, gradually warming up to 160 ^oC and kept for 24 h. The products collect by centrifugation and wash with ethanol and deionized water alternating for several times, put at 50 ^oC in vacuum drying box, drying collected 12 h, and obtain pale yellow solid CdS powder catalyst.

In the experiment, all chemicals were of analysis pure and purchased Sinopharm Chemical Reagent Co., Ltd of China.

2.2 Characterization

The surface morphology and structure of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The X-ray

diffraction spectroscopy (XRD) patterns were collected on a PW3040 X-ray instrument. UV-vis absorption spectra were recorded using a ShimadzuUV-2450 UV-vis spectrophotometer. The FTIR was recorded by a Nicolet Nexus 470 fourier transform infrared spectrometer.

2.3 Photocatalytic experiments

The photo catalytic performance of the as-prepared samples was evaluated through the photo catalytic degradation of CPLX under visible light irradiation. The certain mass samples were dispersed in 100 mL CPLX aqueous solutions. The mixed suspensions were first magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. Under the ambient conditions and stirring, the mixed suspensions were exposed to visible light irradiation produced by a 400 W metal halogen lamp (wavelength: 390-800 nm). At certain time intervals, 3 mL of the mixed suspensions was extracted and centrifugated to remove the photo catalyst. The filtrates were analyzed by recording UV-vis spectra of CPLX using a ShimadzuUV-2450 UV-vis spectrophotometer.

3. Results and discussion

Fig. 1 shows the FESEM image of the as-prepared CdS photocatalyst. The sample displays the particle structure and the particles are monodisperse with diameters about 50 nm. The morphology of the prepared photo catalysts was spherical. Further, the Brunauer-Emmett-Teller (BET) specific surface area and pore structure of CdS were investigated using nitrogen adsorption-desorption measurements. The results lie in Table 1.

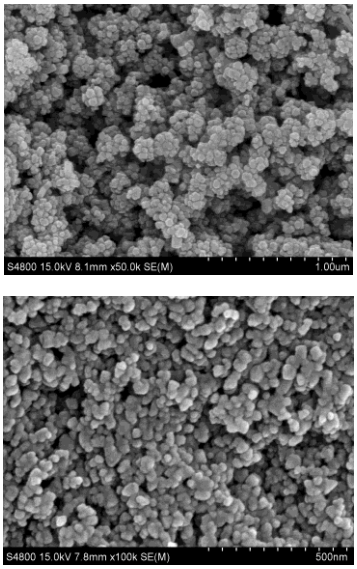

Fig. 1. The FESEM of the as-prepared CdS photocatalyst

Table 1. The determination results of SBET to as-prepared CdS

BET	L	Vtotal
44.17 m^2/g	34.1 Å	$1.37\times10^{-4} m^3/g$

The result shows that the SBET can reach to 45 m^2/g, and the higher area can supply more surface active sites and make the transport of charges easier, exhibiting better photo catalytic performance.

The as-prepared CdS is verified by X-ray diffraction (XRD) spectra, as shown in Fig. 2. CdS nanospheres exhibit a (002) diffraction peak at 26° and a (100) peak at 44.5°. The XRD analysis further shows that the main diffraction peaks of CdS particle correspond to those of cubic phase CdS (JCPDS 80-0019).

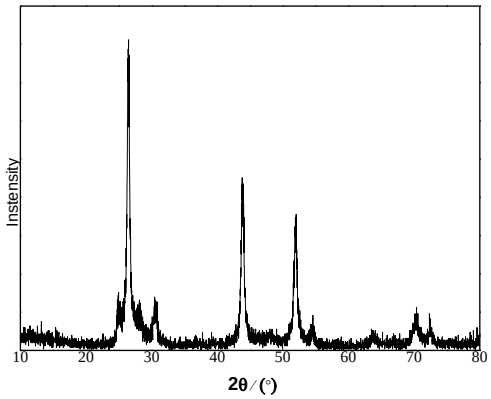

Fig. 2. The XRD spectra of as-prepared CdS photocatalyst

The UV-vis absorption spectra of CdS sample is shown in Fig. 3. The sharp characteristic absorption peak located at 495 nm. That belongs to the range of visible light. That is to say, the potocatalyst can generate more photo-generated electrons and holes pairs under visible light irradiation.

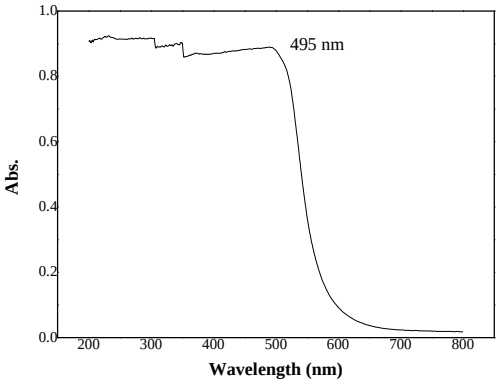

Fig. 3. The UV-vis absorption spcctra of as-prepared CdS photocatalyst

Photo catalytic degradation of CPLX by CdS was performed under visible light irradiation. Fig. 4 shows the UV-vis absorbance of CPLX at the varied irradiation time under visible light irradiation using CdS. It is observed that the UV-vis absorption peak of CPLX, related to the concentration of CPLX in the solution, becomes weak with the increase in the irradiation time. Fig. 5 displays the time-dependent degradation rates of CPLX by CdS of different weight (0, 25, 50, 75, 100 mg) under visible light irradiation. The normalized temporal concentration changes (C/C_0) of CPLX during the photo catalytic process are proportional to the normalized maximum absorbance (A/A_0), which can be derived from the change in the CPLX absorption profile at a given time interval. It is observed that the concentration of CPLX is hardly reduced under visible light irradiation in the absence of the photo catalyst. When the mass of CdS reach to 75 mg, the degradation rate of CPLX can reach to over 95%.

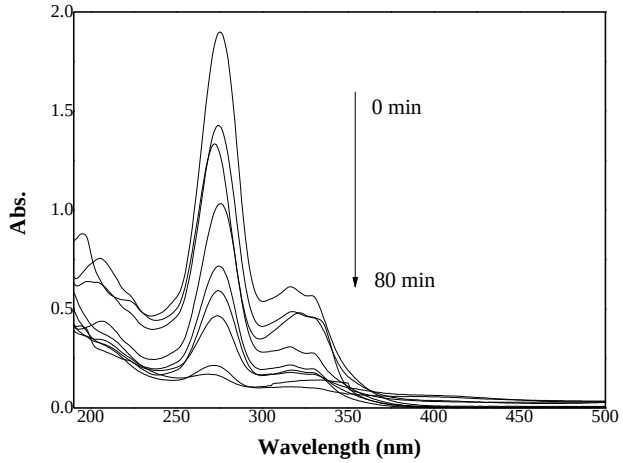

Fig. 4. UV-vis absorption of CPLX with the variation of irradiation time under visible light

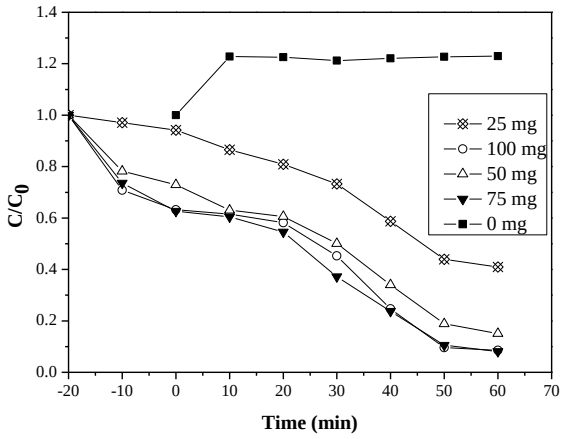

Fig. 5. Photocatalytic degradation of CPLX by CdS with different mass under visible light irradiation.

When CdS is introduced, the degradation rate is increased to 61% for CdS-25 mg and reaches a maximum value of 95% for CdS-75/100 mg at 60 min. This enhancement should be ascribed to the increase in visible light absorption and the reduction of the electron-hole pair recombination in CdS with the mass increase of CdS. However, when the CdS content is further increasing, the photocatalytic rate invariableness. The authors consider that 75 mg of CdS is the supposed optimized quantity of CdS leading to the maximum degradation rate using a single value of 100 mg over this supposed optimized quantity of CdS. It is necessary to have about the same number of experimental points around (at the left and at the right) of an extreme point.

This phenomenon should be due to the following possible reasons: (i) excessive CdS can cover the active sites on the surface of CdS to decrease the amount of absorbed CPLX on the surface of CdS; (ii) more CdS can act as a kind of recombination center and promote the recombination of electron-hole pairs in the process of the photo catalysis. However, the self-sensitized degradation of the antibiotics should play a critical role in the improvement of photo catalytic performance under visible light irradiation.

Fig. 6 shows the scheme of the photo catalytic degradation ciprofloxacin under visible light. Light-induced electrons/holes pair formation in the surface of CdS semiconductor particles. Meanwhile, the adsorbed O_2 is reduced to $\cdot O_2^-$, which can further degrade ciprofloxacin and the surface hydroxyl group translates into hydroxyl radical ·OH. The high oxidative potential of holes can lead to direct and indirect oxidation of ciprofloxacin. After ciprofloxacin was degradation, the active sites left on the surface of catalyst and the conditions provided for adsorption ciprofloxacin again, then degradation and again. This maybe ascribe the following reasons: (i) CdS can absorb visible light and exhibit excellent photo catalytic performance; (ii) CdS can act as a kind of recombination center instead of providing an electron pathway and promote the recombination of electron-hole pairs.

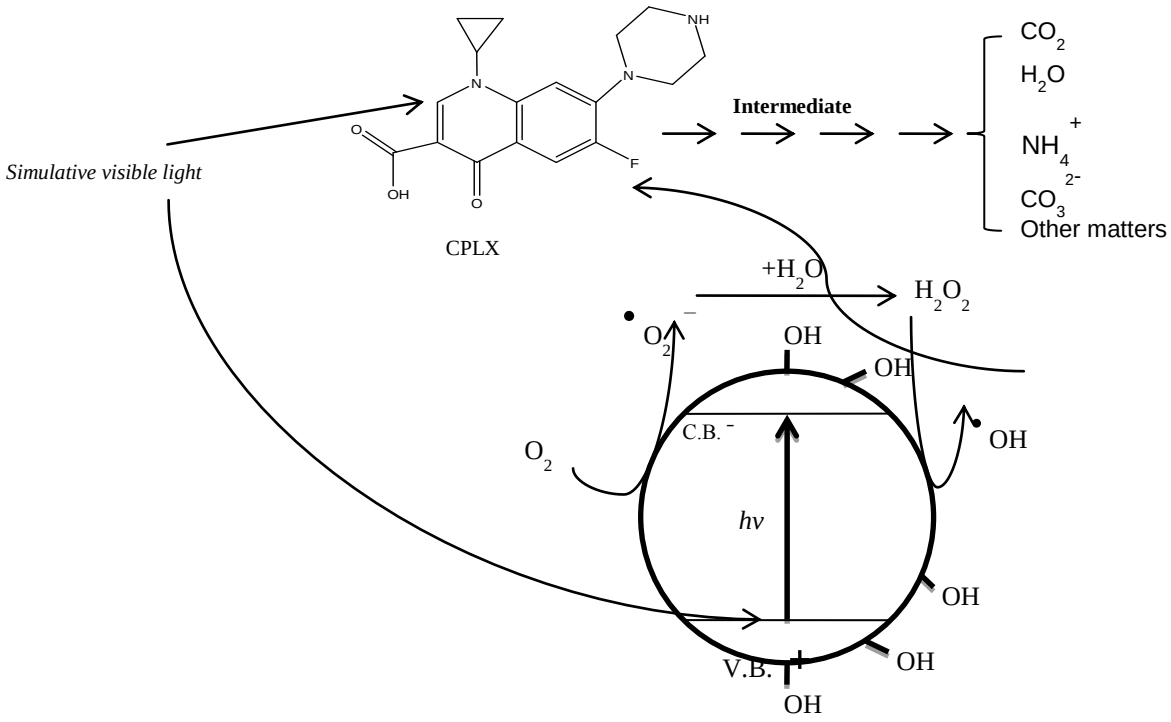

Fig. 6. The schematic diagram of the photocatalytic degradation CPLX with as-prepared CdS under visible light irradiation

4. Conclusions

CdS nanometer particles were successfully synthesized via hydrothermo method, and the photo catalytic performances were investigated. The results of photo catalytic experiments indicated that (1) the CdS particles exhibit an excellent photo catalytic performance; (2) the photo catalytic performance of CdS is dependent on the CdS precursor concentration during preparation and the using 75 mg CdS photo catalyst achieves a highest reduction rate of 95% for 60 min and (3) the enhanced photo catalytic performance is ascribed to the increase of visible light absorption and the reduction concentration of the CPLX.

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