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CHARACTERIZATION AND PHOTOCATALYTIC PROPERTIES OF CdS NANOWIRES SYNTHESIZED BY REFLUX-ASSISTED SOLVOTHERMAL METHOD

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CdS nanowires were synthesized by reflux-assisted solvothermal method. The phase and morphologies of as-synthesized CdS samples were investigated by X-ray powder diffraction (XRD), Raman spectrophotometry and transmission electron microscopy (TEM). The results show that the product synthesized by the 160 ^{o}C and 24 h reflux-assisted solvothermal method was hexagonal CdS nanowire with aspect ratio of >300. The photocatalytic reaction of as-synthesized CdS samples was investigated by photodegradation of methyl orange (MO) and rhodamine B (RhB) under visible light irradiation. They were found that CdS nanowires showed photocatalytic degradation of 99.66% for MO and 93.63% for RhB within 60 min under visible light.

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1. Introduction

Organic pollutants from textile, paint, food, plastic, cosmetic and electronic industries are a major source of water pollution because the organic pollutants are non-biodegradable, toxic and harmful to the living organisms. To solve the environmental problem, semiconductor photocatalysts have been very great interesting materials due to complete mineralization, high photodegradation of organic pollutants, low cost, and the requirement of mild temperature and pressure conditions [1-3]. Among semiconductor photocatalysts, CdS as a II–VI semiconductor has high potential in a wide range of applications including optoelectronics, photovoltaics, chemical sensors, photocatalysis, photodetectors and biological sensors [4-6]. It is one of the most efficient visible-light-driven photocatalyst for hydrogen production and organic decomposition because of its narrow band gap of 2.4 eV and its appropriate conduction band edge potential lower than the H_2O/H_2 electrode potential [7-10]. The band gap is appropriate for sunlight absorption and can lead to easy transformation of solar energy into chemical energy under solar radiation [8].

One-dimensional (1D) semiconductors such as nanorods, nanowires and nanotubes show high photocatalytic performance for dye degradation due to their unique electrochemical properties, high surface-to-volume ratio, large specific surface area and more redox active sites on their surfaces [11-13]. Moreover, the dimensional anisotropy and delocalization of electrons along the growth direction can promote the separation rate of photo-generated charge carriers thus make these promising nanostructure candidates for photocatalytic process [11]. For example, $Cs_2V_4O_{11}$ nanowires with extremely high length–diameter ratio show high photocatalytic activity of methylene blue (MB) under visible light irradiation within 60 min [2]. The vertically ordered ZnO

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nanowire arrays on indium tin oxide glass substrate showed high photocatalytic activity and retained high photocatalytic efficiency of methyl orange (MO) [14].

In this research, synthesis and characterization of CdS nanowires with high aspect ratio as visible-light-driven photocatalyst by a reflux-assisted solvothermal method are reported. Phase and morphology of CdS nanowires were investigated by X-ray powder diffraction (XRD), Raman spectrophotometry and transmission electron microscopy (TEM). The photocatalytic performance of CdS nanowires was investigated by photodegradation of methyl orange (MO) and rhodamine B (RhB) under visible light irradiation.

2. Experiment

All chemicals with analytical grade were used without further purification. In a typical experimental procedure, 0.005 mole $Cd(NO_3)_2 \cdot 5H_2O$ and 0.006 mole thiourea were dissolved in 100 ml of ethylenediamine under vigorous stirring at room temperature for 30 min. Then, the solution was transferred to a 250 ml round-bottom flask and was refluxed in oil bath at 60 and 80 °C for 2 h. Then, the solution was loaded in Teflon-lined stainless steel autoclaves and heated in an oven at 120 and 160 ^oC for 12 and 24 h. The precipitates were filtered, washed with distilled water and absolute ethanol, and dried in an oven at 80 ^oC for 24 h for further characterization.

X-ray powder diffraction (XRD) patterns of the products were recorded on a Philips X'Pert MPD X-ray powder diffraction (XRD) with a graphite monochromator and Cu K_α line at a scanning rate of 0.02 deg/s ranging from 10 to 80 deg. Raman spectra of samples were recorded on a HORIBA Jobin Yvon T64000 Raman spectrometer of 50 mW and 514.5 nm wavelength Ar green laser. Transmission electron microscopic (TEM) images, high resolution transmission electron microscopic (HRTEM) images and selected area electron diffraction (SAED) pattern were taken on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV.

The photocatalytic measurement of as-synthesized CdS samples was investigated by photodegradation of methyl orange (MO) and rhodamine B (RhB) as model dyes under visible light illumination. The 0.2 g of as-synthesized CdS samples were added to 200 ml of 20 ppm MO and RhB solutions under vigorous stirring. The solutions were kept in the dark for 30 min. Subsequently, the suspension solutions were exposed to a visible light radiation from Xe lamp at a distance of 15 cm from the upper surface of reaction solution. Approximately 5 ml of suspension solution was collected at different time intervals and centrifuged at a speed of 6000 rpm to remove the residual photocatalyst from the MO and RhB solutions. In the end, the residual contents of MO and RhB were measured by UV-visible spectrophotometer at λ_{max} = 465 nm for MO and λ_{max} = 554 nm for RhB. The degradation was calculated by the following equation

$$\text{Decolorization efficiency (\%)} = \frac{C_o - C_t}{C_o} \text{x100} \quad (1)$$

, where C_o is the initial concentration at 0 min and C_t is the concentration at time t.

3. Results and discussion

The typical XRD patterns of the as-synthesized CdS samples prepared by reflux method and reflux-assisted solvothermal method are shown in Fig. 1. All diffraction peaks of samples can be indexed to the (100), (002), (101), (110), (103) and (112) planes of pure hexagonal CdS phase, according to the JCPDS No. 41-1049 [15]. The diffraction peaks of impurities were not detected in these XRD patterns of all samples, indicating that the products were highly pure single phase. They can be seen that the XRD patterns of CdS sample synthesized by reflux method at 60 °C for 2 h show low intensity and boarding diffraction peaks, suggesting that the crystallinity of CdS sample is very poor. They became a little improve when the temperature was 80 °C. When the solvothermal process was also used, the diffraction peaks of as-synthesized CdS samples show

stronger diffraction intensity with the increasing temperature and prolonged reaction time, implying that the crystalline degree of the samples was improved [1, 4, 13]. In conclusion, the crystallinity of CdS samples has been greatly influenced by temperature and time of solvothermal reaction.

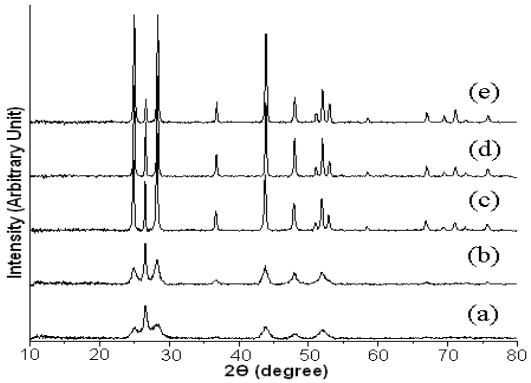


Fig. 1. XRD patterns of the as-synthesized CdS products synthesized by reflux at (a) 60 °C and (b) 80 °C for 2 h, and reflux-assisted solvothermal method at (c) 120 °C for 12 h, (d) 160 °C for 12 h and (e) 160 °C for 24 h.

Raman spectra of CdS nanowires prepared by reflux-assisted solvothermal method at 120 °C for 12 h, 160 °C for 12 h and 160 °C for 24 h are shown in Fig. 2. The hexagonal wurtzite CdS belongs to C^4_{6v} space group. The Raman active modes are $1A_1 + 1E_1 + 2E_2$ (E_2^H and E_2^L) and the $2B_2$ modes are silent. Wurtzite CdS is noncentrosymmetric, thus both A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) components [16-18]. The Raman peaks of the as-obtained CdS nanowires at 298, 592 and 884 cm^{-1} attributed to the fundamental first order, second order, third order longitudinal optical modes [5, 6, 16-18]. The increase in intensity of Raman peaks shows the improvement of crystallinity and reduction in defect density of CdS sample [5, 6, 16-18]. Therefore, CdS nanowires prepared by reflux-assisted solvothermal method at 160 °C for 24 h showed the highest crystallinity, corresponding to the XRD results.

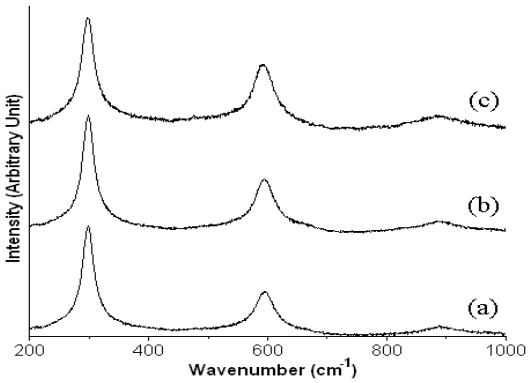


Fig. 2. Raman spectra of CdS nanowires synthesized by reflux-assisted solvothermal method at (a) 120 °C for 12 h, (b) 160 °C for 12 h and (c) 160 °C for 24 h.

Figs. 3 and 4 show TEM images HRTEM images and SAED pattern of CdS samples prepared by reflux method and reflux-assisted solvothermal method. They can be seen that the CdS sample synthesized by reflux method at 60 °C for 2 h contains uniform nanoparticles with size of 10-20 nm. When the reaction temperature was increased to 80 °C, CdS nanorods were produced. TEM images of the samples prepared by reflux-assisted solvothermal method at 120 °C for 12 h, 160 °C for 12 h and 160 °C for 24 h contain the well-defined and uniform nanowires with

different aspect ratios. The aspect ratio of CdS nanowires increase with the increase of temperature and prolonged reaction time. The aspect ratios of CdS nanowires prepared by reflux-assisted solvothermal method at 120 ^{o}C for 12 h, 160 ^{o}C for 12 h and 160 ^{o}C for 24 h are 25, 150-200 and >300, respectively. Thus the CdS nanowires with the highest aspect ratio have been successfully synthesized by reflux-assisted solvothermal method at 160 ^{o}C for 24 h. The HRTEM images of CdS nanowires synthesized by the 160 ^{o}C and 24 h reflux-assisted solvothermal method show interplanar space of 0.3585 nm of single CdS nanowire with the plane aligned along the growth direction of CdS nanowire. The value corresponds to the interplanar space of the (100) plane of wurtzite CdS nanowire, certifying that the CdS nanowires grew along the [001] direction [5, 10, 19, 20]. The selected area electron diffraction (SAED) pattern of single CdS nanowire indicates that the as-obtained CdS nanowires have single-crystalline property, specified as the (110), (112) and (002) planes of hexagonal CdS nanowires.

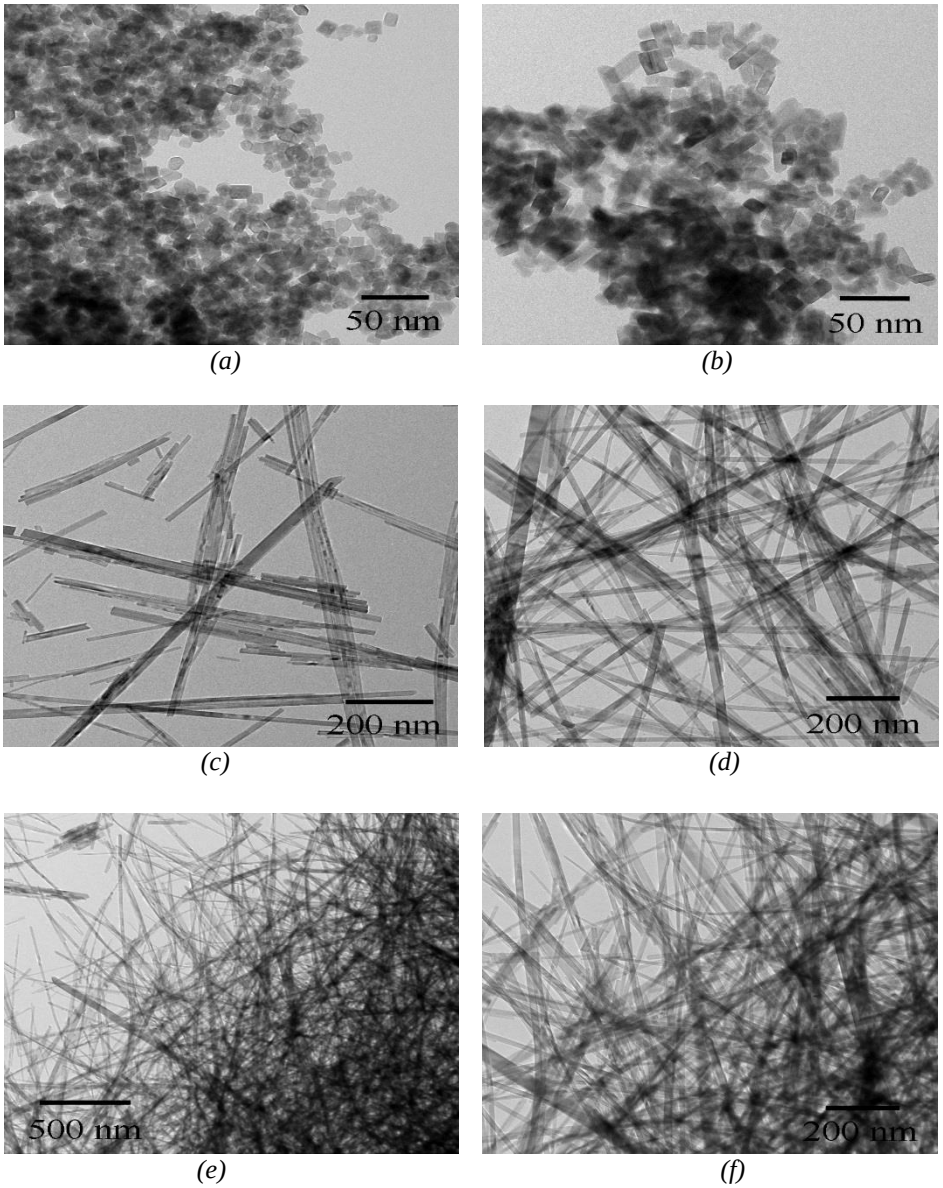


Fig. 3. TEM images of the as-synthesized CdS products synthesized by reflux at (a) 60 ^{o}C and (b) 80 ^{o}C for 2 h, and reflux-assisted solvothermal method at (c) 120 ^{o}C for 12 h, (d) 160 ^{o}C for 12 h and (e, f) 160 ^{o}C for 24 h.

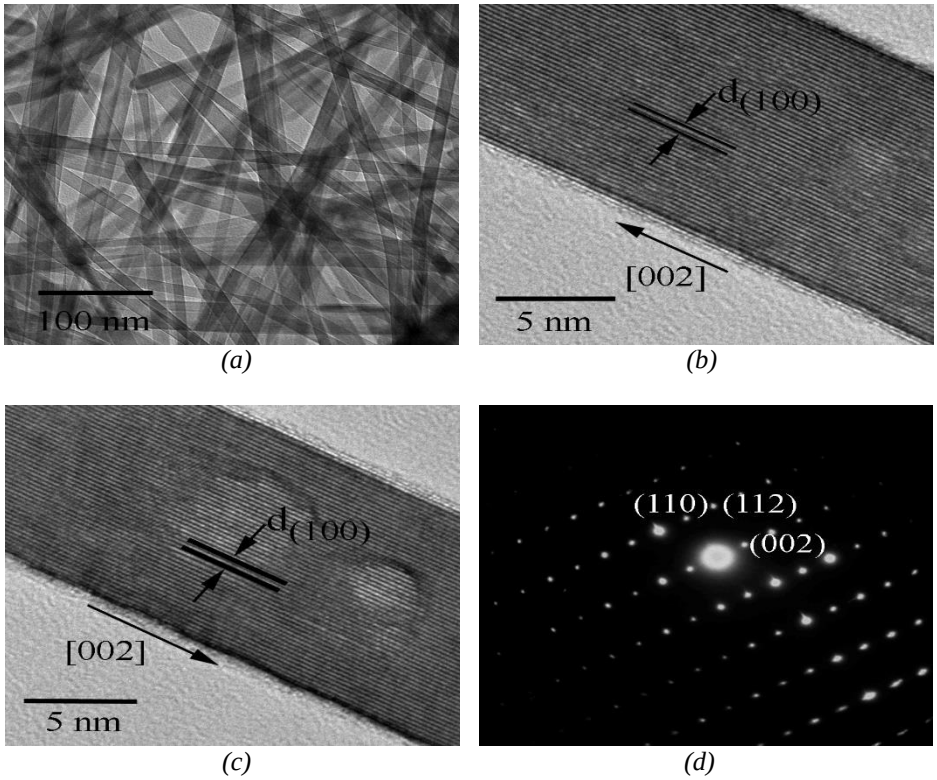
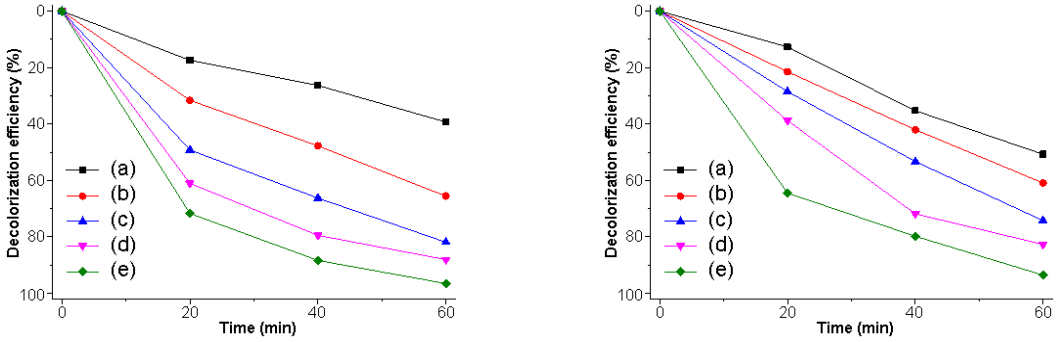


Fig. 4. TEM and HRTEM images, and SAED pattern of CdS nanowires synthesized by reflux-assisted solvothermal method at160 ^{o}C for 24 h.

The photocatalytic activities of CdS nanoparticles, nanorods and nanowires were evaluated by determining the degradation of MO and RhB solutions under visible light irradiation within 60 min as the results shown in Fig. 5. The pure MO and RhB solutions without CdS NWs as a photocatalyst were not degraded under visible light, certifying that both dyes were not photolysis under visible light irradiation. The photocatalytic activities of as-synthesized CdS samples were controlled by the product morphologies in sequence as follows: nanowires > nanorods > nanoparticles. Clearly, the CdS nanowires with aspect ratio of >300 show the highest photocatalytic activity for dye degradation under visible light irradiation within 60 min due to the best diffusion of photo-induced electrons to surface of CdS nanowires [2, 10, 12, 13]. In this research, the photocatalytic efficiencies of MO and RhB photodegraded by CdS nanowires were 99.66% and 93.63% within 60 min under visible light. The kinetic reaction rates of MO and RhB photodegradation by the photocatalyst can be expressed through the pseudo-first order model as follows.

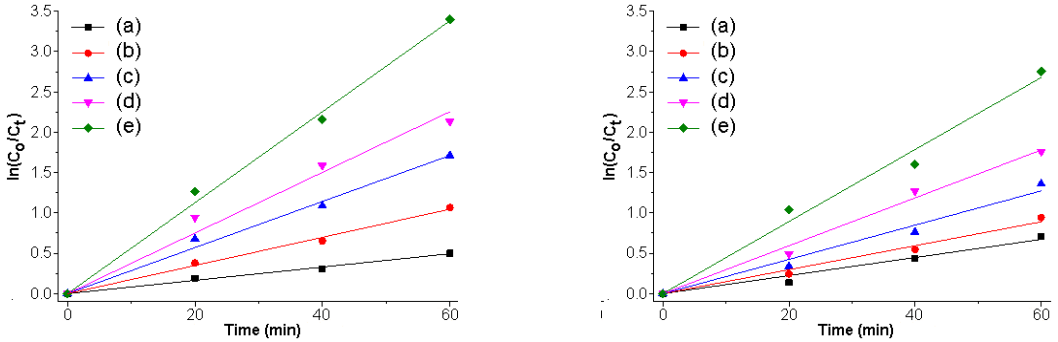
$$\ln(C_o/C_t) = K_{app}t \quad (2)$$

, C_o and C_t are the absorbance of dye solutions at time 0 and t, respectively. K_{app} is the apparent rate constant and t is the visible irradiation time [3, 11, 19]. Fig. 6 shows the plots of $\ln(C_o/C_t)$ versus irradiation time for the photodegradation of MO and RhB by photocatalysts. They show linear lines for decomposition of both MO and RhB dyes, certifying the pseudo-first order kinetics of dye photodegradation [3, 11, 19]. The photodegradation rates of MO and RhB are 0.0566 and 0.0445 min^{-1} by CdS nanowires under visible light irradiation.



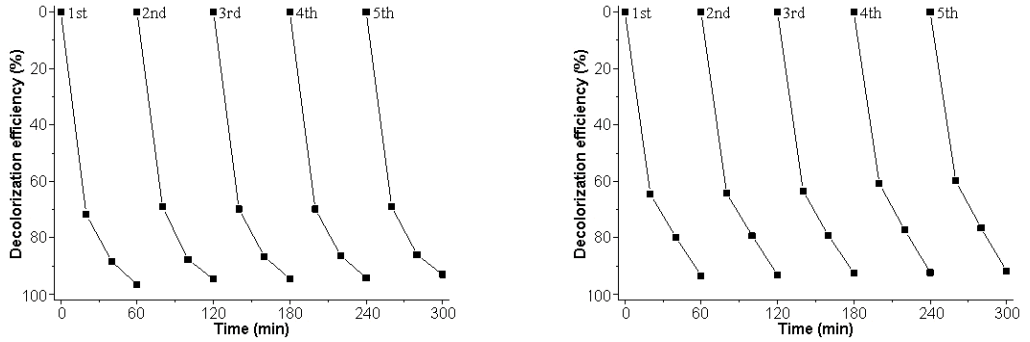
(a) *(b)*

Fig. 5. Decolorization efficiency of (A) MO and (B) RhB in the solutions containing as-synthesized CdS products synthesized by reflux at (a) 60 °C and (b) 80 °C for 2 h, and reflux-assisted solvothermal method at (c) 120 °C for 12 h, (d) 160 °C for 12 h and (e) 160 °C for 24 h.



(a) *(b)*

Fig. 6. Pseudo-first order plots for (A) MO and (B) RhB photodegradation in the solutions containing as-synthesized CdS products synthesized by reflux method at (a) 60 °C and (b) 80 °C for 2 h, and reflux-assisted solvothermal method at (c) 120 °C for 12 h, (d) 160 °C for 12 h and (e) 160 °C for 24 h.



(a) (b)

Fig. 7. Recyclability of CdS nanowires for photodegradation of (a) MO and (b) RhB under visible light irradiation.

The photostability and reusability of as-prepared CdS nanowires were investigated for five-cycle run as the results shown in Fig. 7. At the end of each photocatalytic run, the CdS nanowires were collected, washed with water and ethanol, dried and reused for the next photocatalytic run. They can be seen that the photocatalytic activities of CdS nanowires showed a

slight decrease in MO and RhB photodegradation after five-cycle run under visible light irradiation, indicating that the CdS nanowires have high photocatalytic stability for dye degradation under visible light irradiation. The CdS nanowires showed a potential of being convenient recyclable photocatalysis for wastewater treatment.

4. Conclusions

CdS nanowires with aspect ratio of > 300 were synthesized by a reflux-assisted solvothermal method at 160 ^{o}C for 24 h. Under the visible light irradiation, CdS nanowires showed photocatalytic degradation of 99.66% for MO and 93.63% for RhB under visible light within 60 min. CdS nanowires showed high photocatalytic stability for dye degradation under visible light irradiation after five-cycle run.

Acknowledgments

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