

Photoinduced Charge Transfer Properties of ZnWO₄/CdS Composite and its Photocatalytic Activities under visible Light

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Abstract. ZnWO₄/CdS composite photocatalyst had been successfully synthesized by a facile hydrothermal process. The catalysts were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV-vis diffuse reflectance spectrum (DRS). The results showed that the as-obtained samples consist of ZnWO₄ growing on the primary CdS nanorods. The ZnWO₄/CdS composite had similar visible light photocatalytic activity compared to single CdS nanorods, meanwhile the stability of the sample were improved. Furthermore, the photoinduced charge transfer properties of ZnWO₄/CdS composite were investigated by means of transient photovoltage (TPV) techniques in detail. The enhanced photocatalytic stability of ZnWO₄/CdS composite was ascribed to the low recombination ratio of photo-induced electron-hole pairs owing to the interconnected interface of ZnWO₄/CdS composite.

Introduction

Photocatalytic degradation of organic pollutants by semiconductor photocatalysts has the potential to be a beneficial technology for environmental purification [1-3]. As an important photocatalyst, CdS has been reported for photocatalytic hydrogen production from water and mineralization of organic pollutants under visible light irradiation [4, 5]. However, the stability of CdS photocatalytic activity is still indispensable. Many efforts have been made on the improvement of stability, such as morphologies, crystallinity, nanocomposite and ion doping [4-6]. M. Luo and co-worker found that 1.2 mol % Ni-doped CdS hollow spheres showed the highly efficient for organic pollutants RhB. Moreover, this catalyst showed improved stability, and the activity did not decrease significantly after four recycles [4]. S. L. Xiong et al. had prepared CdS with various novel nanostructures on a large scale in a water/EA binary solution. The morphologies and crystal structure of the CdS photocatalyst did not change after the photocatalytic reaction. This result demonstrates that CdS nanocrystals are stable and do not photocorrode during the photocatalytic process [6]. Although many methods for enhanced stability of CdS have been tried, the composite photocatalyst based on ZnWO₄ has not been reported. Instead of using a single photocatalyst, coupling of photocatalyst with other semiconductors, metals, or molecules to form a junction structure has been found to be significantly beneficial for enhancing the stability [5]. H. Zhao et al. investigated the stability and durability of ZnO/CdS nanocomposite. They found that no noticeable degradation of photocatalytic H₂ evolution was detected in four repeated runs for the whole photocatalytic reaction, indicating the good stability and durability of the ZnO/CdS-T120 sample. In this work, we chose ZnWO₄ as a functional component for the preparation of ZnWO₄/CdS composite. As is well known, ZnWO₄ has been found as a photocatalyst with excellent stability [7]. Furthermore, both CdS and ZnWO₄ have matched crystalline structure. It can be expected to construct perfect ZnWO₄/CdS composite structure and enhance stability of CdS.

Charge transfer propertise plays an important role not only in electronic or photovoltaic devices but also in photocatalytic systems. The transient photovoltage (TPV) technique allow us to analyze the buildup of the photovoltage signal and dynamic properties of photo-induced charge

carriers [8]. These technique could give insight into the transfer behavior of photo-induced charge carriers in the system, including the generation, separation and recombination of the photogenerated charges. An outstanding example was C doping TiO_2 (C- TiO_2) photocatalysts reported by H. Y. Li and co-workers [9]. They demonstrated that the presence of interstitial carbons could improve the separation extent and restrain the recombination of the photoinduced electron and hole carriers in C- TiO_2 , which was beneficial to improve the photocatalytic ability of samples.

In this paper, we successfully prepared ZnWO_4/CdS composite photocatalyst. In the degradation of rhodamine B (RhB) under visible light irradiation, the ZnWO_4/CdS composite photocatalysts exhibited similar photocatalytic activity than that of single CdS nanorods, meanwhile the stability of composite was improved. The high stability was obtained when ZnWO_4/CdS mole ratio was 1.0. The TPV measurements suggest that the photo-induced charge transfer properties of ZnWO_4/CdS composite is related to the photocatalytic activity of samples.

Experimental

Synthesis of ZnWO_4 and CdS photocatalysts. Sodium tungstate dehydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 5 mmol) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 5mmol) were added into 30mL deionized water under stirring at room temperature, based on our previous paper [10]. The pH value of the mixed solution was adjusted to 9.0 using the dilute HCl and NaOH solution (0.5 M). After being vigorously stirred for about 30 min, the solution was loaded into a 50 mL Teflon-lined autoclave. The autoclave was heated at 180°C for 48 h under autogenous pressure and then cooled to room temperature naturally. The white precipitate was collected and washed with ethanol and distilled water several times. Finally the sample was dried in a vacuum oven at 50°C for 4 h. CdS nanorods were grown through a simple hydrothermal method [11]. The typical process is that 1.9 g of $\text{Cd}(\text{NO}_3)_2$ and 1.42 g of thiourea were added into a Teflon-line stainless steel autoclave that had been filled with ethylenediamine. The autoclave was maintained at 180°C for 48 h and allowed to cool down to room temperature. A yellow precipitate was filtered and washed several times with absolute ethanol and deionized water to remove the residue of organic solvent.

Synthesis of ZnWO_4/CdS composite photocatalyst. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in H_2O , respectively. Then the above solutions were mixed together to form a white suspension and 0.4 mmol of CdS nanorods (ZnWO_4/CdS molar ratio 1.0) were added into the suspension under vigorously stirring. After stirring for 30 min, the resulting suspension was added into a Teflon-lined auto-clave. The autoclave was sealed and heated to 180°C for 15 h. The precipitate was collected and washed with ethanol and distilled water several times. Then, the sample was dried in a vacuum at 50°C for 4 h. The composite photocatalyst was marked as 1.0 ZnWO_4/CdS . For comparison, the single ZnWO_4 and CdS sample were also prepared via the same solvothermal method.

Characterization. The obtained products were characterized by X-ray diffraction (XRD) patterns on a Rigaku D/Max-22550 diffractometer with $\text{Cu K}\alpha$ radiation over the range of $20 \leq 2\theta \leq 70$. The morphology and microstructure were obtained by a transmission electron microscopy (TEM, TECNAIG² FEI Company). UV-vis diffuse reflectance spectra (DRS) were recorded on a UV-3600 (Shimadzu) spectrophotometer. The TPV measurements consisted of a laser radiation pulse (wavelength of 355 nm and 532 nm, pulse width of 5 ns) from a third-harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.). The TPV signal was recorded by a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix).

Photocatalytic Experimental. The photocatalytic activities of the samples were evaluated by the degradation of the RhB under a 500W mercury lamp illumination. Powder photocatalyst (20 mg) was dispersed into 20 mL of RhB solution (10 mg/L). Before illumination, the suspensions were

vigorously stirred in dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst powder and RhB. After that, the solution was exposed to visible light irradiation ($\lambda > 420$ nm) under magnetic stirring, and 0.8 mL of the suspension was taken from the reaction cell at certain intervals and separated by a centrifugal machine during the process. Finally, the UV-vis spectra of the centrifuged solution were recorded using a Maya 2000-Pro spectrometer (Ocean Optics).

Results and discussion

Characterization of Composite Photocatalysts. The crystallographic phases and compositions of the single ZnWO_4 , CdS and ZnWO_4/CdS composites are investigated by XRD. As shown in Figure 1, the pure-phase CdS is a wurtzite structure. When the mole ratio of ZnWO_4/CdS is 1.0, the diffraction peaks of monoclinic structure ZnWO_4 (JCPDS 73-0554) appear, whereas the peak intensities of CdS become weaker. No other impurity peaks are found in ZnWO_4/CdS composite, suggesting that the composites have a two-phase composition: CdS and ZnWO_4 , there is no appreciable chemical reaction during the hydrothermal process.

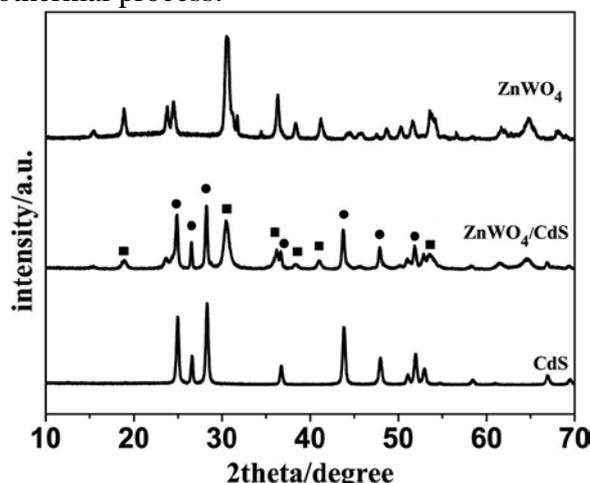


Fig. 1 XRD patterns of the ZnWO_4 , CdS, and the ZnWO_4/CdS composite.

Figure 2 shows the TEM images of ZnWO_4 , CdS, and ZnWO_4/CdS composite photocatalyst, respectively. The pure CdS synthesized at 180 °C for 48 h possesses the rod-like structure, as shown in Figure 2a. It shows that the length of CdS nanorods is ca. 1 μm and its diameter is ca. 50 nm of nanorods. Figure 2b and c show that the ZnWO_4 (the length of nanorods is ca. 300 nm and its diameter is ca. 30 nm) tend to attach on the backbone of the CdS, which is in accordance with the XRD results. The ZnWO_4 can grow into irregular nanorods structure due to the high intrinsic anisotropic nature¹⁰. Figure 3 shows the diffuse reflectance spectra of the photocatalysts. The absorption at ca. 390 nm is due to the band gap transition of ZnWO_4 [12]. The CdS photocatalyst shows an absorption edge at 525 nm. The spectra of ZnWO_4/CdS composite show similar spectra of CdS nanorod, the peak intensities of composite become weaker.

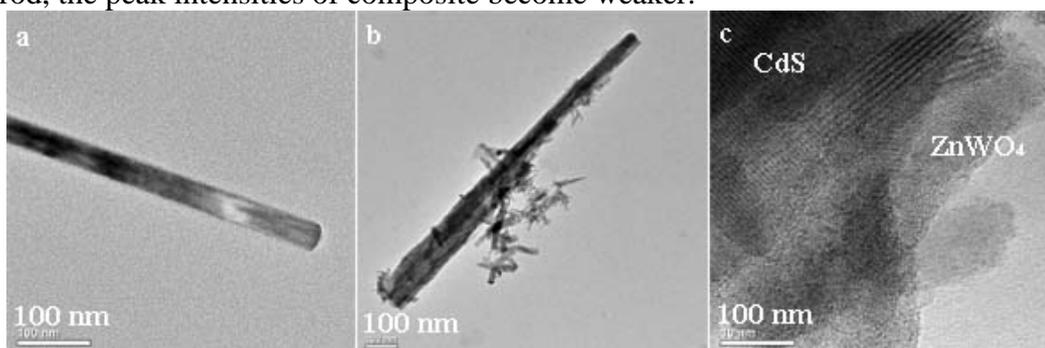


Fig. 2 Low-magnification images of the as-obtained samples: (a) CdS, (b) ZnWO_4/CdS composite; (c) High-magnification image of ZnWO_4/CdS composite.

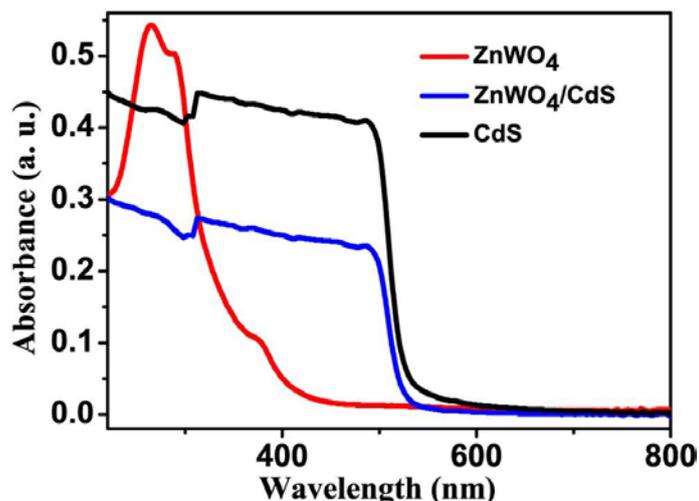


Fig. 3 The UV-vis diffuse reflectance spectra of CdS, ZnWO₄, ZnWO₄/CdS composite.

Photoinduced Charge Transfer Properties. Figure 4 shows TPV spectra of as-obtained samples. There are several interesting features: (I) the TPV signals of ZnWO₄ and CdS are positive, which indicates that photo-induced electrons move toward the bulk and photo-induced holes move toward the surface [13, 14]. (II) Two peaks can be observed in the TPV response of samples, the peaks at the time shorter than 10⁻⁶ s (P1) and the time longer than 10⁻⁶ s (P2), respectively. (III) When the time is shorter than 10⁻⁶ s (P1), the TPV signals of ZnWO₄ and CdS arise immediately with the laser pulse. It is a typical behavior for the surface photovoltage in semiconductors where charges carriers are separated in the electric field of the surface space-charge region [15]. The TPV response of ZnWO₄/CdS composite (P1) is negative, indicating that the electrons aggregate on surface of ZnWO₄/CdS composite. This phenomenon demonstrates that the ZnWO₄ grown on the surface of CdS nanorods is collecting photoinduced electron, which is beneficial to improve the stability of ZnWO₄/CdS composite photocatalyst. (IV) At time longer than 10⁻⁶ s (P2), the time of TPV maximum of ZnWO₄/CdS composite in comparison to that of the bare CdS is strongly retarded, which is typical for diffusion photovoltage. These result indicates that ZnWO₄ grown on the surface of CdS can restrict a part of photoinduced hole and inhibit the photocorrosion of CdS [16]. The larger retardation time is, the lower recombination rate of electron-hole pairs will be. This means that photo-induced charges will have more time to participate in the photocatalytic reaction before recombination.

Photocatalytic Activity. The degradation of RhB under visible light irradiation ($\lambda > 420$ nm) is investigated in Figure 5. The ZnWO₄ experiment in visible light irradiation shows that the degradation of RhB is negligible. CdS exhibits much higher photocatalytic activity than that of other samples, as shown in Figure 5. Meanwhile, the result indicates that the ZnWO₄/CdS composite photocatalysts possess similar activity compared with that of single CdS, and RhB degradation is complete within 25 min. To evaluate the stability of the ZnWO₄/CdS composite, the circulating runs in the photo-degradation of RhB under visible light ($\lambda > 420$ nm) are recorded in Figure 6. As shown in Figure 6, the photocatalytic activity of ZnWO₄/CdS composite does not exhibit any significant loss after three recycles for the photodegradation of RhB, which implies that the ZnWO₄/CdS composite have high stability. This fact demonstrates ZnWO₄ grown on the surface of CdS plays an important role in inhibiting the photocorrosion of CdS, according with the results of TPV.

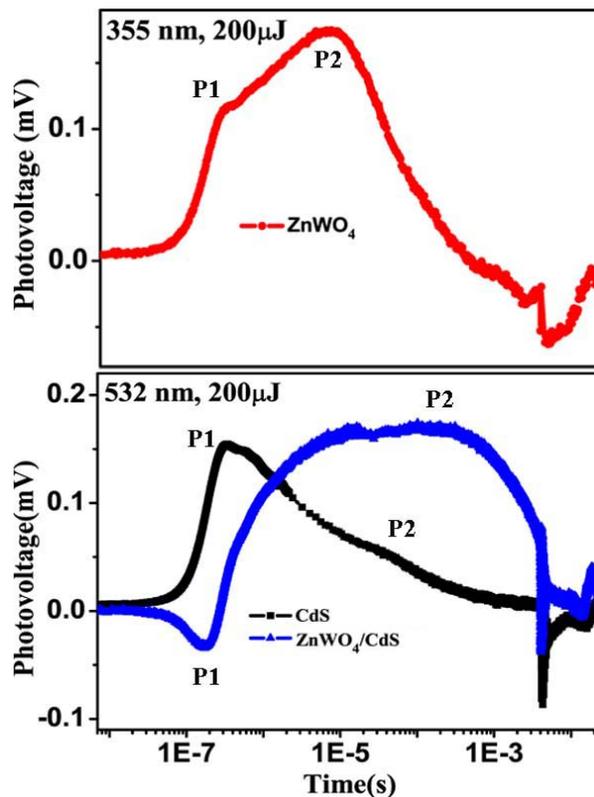


Fig. 4 TPV of the samples: ZnWO₄, CdS, ZnWO₄/CdS composite. ZnWO₄: the wavelength and intensity of the laser pulse is 355 nm and 200 μJ, respectively; CdS and ZnWO₄/CdS composite: the wavelength and intensity of the laser pulse is 532 nm and 200 μJ, respectively.

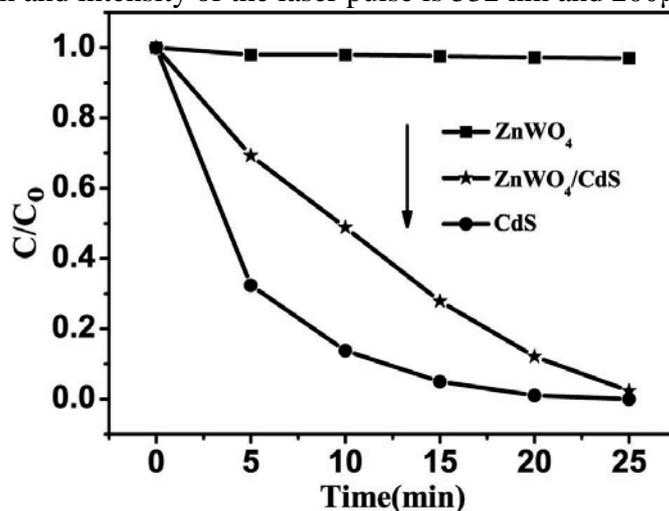


Fig. 5 The photocatalytic degradation of RhB (10 mg/L, 20 mL) by different photocatalysts with same weight (20 mg) under visible light irradiation ($\lambda > 420$ nm), where C is the absorption intensity of RhB at the maximum wavelength of 554 nm irradiated by different time and C_0 is the absorption intensity of RhB after the adsorption-desorption equilibrium on photocatalyst before irradiation.

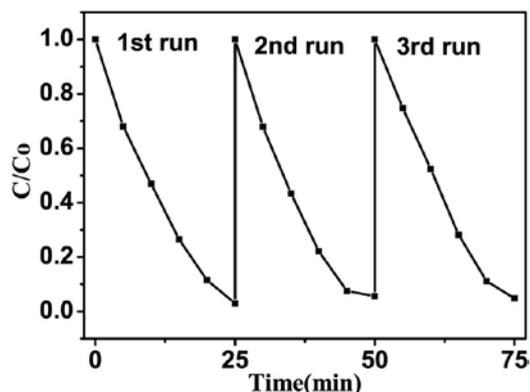


Fig. 6 Cycling runs of ZnWO₄/CdS composite under visible light irradiation ($\lambda > 420$ nm).

Conclusion

The ZnWO₄/CdS composite were successfully synthesized by a simple hydrothermal method. The as-prepared ZnWO₄/CdS composite was composed of ZnWO₄ grown on the primary CdS nanorods. The ZnWO₄/CdS composite exhibited enhanced photocatalytic stability in the degradation of RhB under visible light irradiation. The enhanced stability of ZnWO₄/CdS was attributed to the effective restriction of photo-induced hole on the surface of ZnWO₄ and the low recombination ratio of photo-induced electron-hole pairs. The information provided here is expected to be useful for the further improvement of CdS photocatalytic performances.

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