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HYDROTHERMAL SYNTHESIS OF NiS/CdS NANOCOMPOSITES WITH ENHANCED VISIBLE-LIGHT PHOTOCATALYTIC PERFORMANCE

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Novel NiS/CdS heterostructures with enhanced visible-light photocatalytic activity were successfully prepared via a facile two-step hydrothermal process. The synthesized materials were characterized using X-ray diffraction, high-resolution transmission electron microscopy and UV-Vis diffuse reflectance spectroscopy. The photocatalytic activity was investigated by the degradation of quinoline under visible light irradiation. The experimental results reveal that the CdS samples are hexagonal phases with high crystallinity and purity. As-prepared NiS/CdS heterostructures exhibit a higher photocatalytic activity than pure CdS or NiS. The improvement was ascribed to the formation of p-n NiS/CdS heterojunction, which can promote the light absorption capability of photocatalyst and separation of excited electron-hole pairs.

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1. Introduction

Semiconductor photocatalysis has attracted tremendous interest for its potential applications in environmental remediation [1]. For the sake of efficient utilization of sunlight energy, developing visible-light-driven photocatalyst is necessary for photocatalysis application. As an n-type semiconductor, cadmium sulfide (CdS), with a large direct band gap of 2.4 eV, has been recognized as one of the most promising semiconductors that can utilize visible light for photocatalytic reactions [2, 3]. However, two obstacles, the fast recombination of photoexcited charge carriers and the photocorrosion in aqueous solution via self-oxidation, have restricted the practical applications of CdS in the fields of environmental remediation. Therefore, it is necessary to develop effective strategies to reduce the recombination of photogenerated carriers and suppress the photocorrosion of CdS.

Coupling CdS with another semiconductor has been demonstrated as an effective way to accelerate the separation and transfer of photogenerated carriers. For example, $CoFe_2O_4$/CdS [4], ZnO/CdS [5] and Ag_3PO_4/CdS heterostructure [6] were reported to exhibit improved photocatalytic performance. Especially, combining p-type and n-type semiconductors is the most

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effective strategy, because a number of p-n junctions will form at the interface. The p-n heterojunction, with an internal electric field, can significantly promote the separation of photogenerated charge carriers and further improve the degradation efficiency [7]. As a p-type semiconductor, nickel sulfide (NiS), with a band gap of 0.5 eV, is also reported to be a good photocatalyst in the degradation of pollutants [8, 9]. NiS has been used to couple with n-type semiconductors to form p-n heterojunctions, such as NiS/TiO_2 [10] and NiS/ZnS semiconductors [11], and their results show that these p-n heterojunctions exhibit enhanced photocatalytic performance under visible light irradiation. NiS/CdS p-n heterojunctions have been reported as good catalysts for photocatalytic H_2-production [12, 13], but the NiS/CdS as photocatalysts for degradation of pollutants has not received prior investigation.

Herein, we reported the preparation of NiS/CdS p-n heterojunctions via a two-step hydrothermal method and its application for photocatalytic degradation of quinoline under visible light irradiation. The as-prepared NiS/CdS heterostructure exhibits enhanced photocatalytic efficiency compared with pure CdS or NiS, which could be attributed to the synergistic effect of NiS and CdS, including the enhancement of light-harvesting capacity and the effective separation of photogenerated carriers.

2. Experimental

2.1 Sample preparation

All the reagents were of analytical grade and were used without further purification. Distilled water was used in all experiments. Firstly, CdS nanoparticles were prepared by the solvothermal method. In a typical synthesis, 2.01 g of $CdCl_2 \cdot 4H_2O$ and 2.4g of $Na_2S \cdot 9H_2O$ were dissolved in 30 mL of distilled water, resepectively. After all the $CdCl_2 \cdot 4H_2O$ and $Na_2S \cdot 9H_2O$ have dissolved, the two solutions were mixed together. After stirring for 24 hours, the mixture were added into an autoclave with an inner Teflon lining and maintained at 180 ^{0}C for 24 h. After that, the yellow precipitate was collected, washed with distilled water and ethanol three times, and then dried in an oven at 80 ^{0}C for 5 h. NiS nanoparticles were deposited on the surface of obtained CdS nanoparticles based on hydrothermal reaction between nickelous acetate and sodium sulfide. The prepared CdS (1.086 g) were ultrasonically dispersed in water, and then a certain volume of an aqueous solution containing $C_4H_6NiO_4 \cdot 4H_2O$ (0.198 g) and $Na_2S \cdot 9H_2O$ (0.191 g) was quickly added. The mixed solution volume was adjusted to 60 mL with deionized water and stirred for 30 min at room temperature. After that, the suspension was transferred to a 100 mL Teflon-lined autoclave and maintained at 150 ^{0}C for 6 h. The final products were, respectively, rinsed three times with distilled water and ethanol, and dried at 80 ^{0}C for 5 h. Pure NiS powders were prepared through the same procedure without adding CdS particles

2.2 Photocatalytic activity

Quinoline was selected as a model chemical to evaluate the activity of the catalysts. A 500 W Xe lamp was used as the light source of a homemade photoreactor. The short wavelength components (< 420 nm) of the light were cut off using a glass optical filter. For a typical photocatalytic experiment, 0.02 g NiS/CdS powders were added to 100 mL quinoline solution (50 mg/L) in the beaker with stirring. Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption/desorption equilibrium. For a given duration, the concentration of quinoline (after the removal of photocatalysts) was monitored at 313 nm using a UV-vis spectrophotometer (UV-2100).

3. Results and discussion

The crystal structure and phase composition of CdS and NiS/CdS samples were investigated by XRD measurements. As shown in Fig. 1, the diffraction peaks can be easily indexed to the hexagonal phase of CdS, which are in good agreement with the data in the standard card (JCPDS41-1049), and no byproduct peaks were found. The major peaks at 24.9^0, 26.4^0, 28.2^0, 36.6^0, 43.7^0, 47.9^0 and 51.9^0 can be indexed as (100), (002), (101), (102), (110), (103) and (112) planes, respectively, which is in agreement with the reported result [2, 14]. According to Scherrer's equation, $D_c=K\lambda/(\beta\cos\theta)$ (where λ is the X-ray wavelength, β is the FWHM of the diffraction line, θ is the diffraction angle, and K is a constant, which has been assumed to be 0.9), and based on the full width at half maximum (FWHM) of the (101) peak, an average particle diameter of 27.4 nm for CdS can be calculated. By comparing the XRD pattern of NiS/CdS to the diffraction profile of CdS, the NiS phase is not detected in the composite sample, which may be attributed to the weak crystallization and high dispersion of NiS particles deposited on the surface of CdS [12].

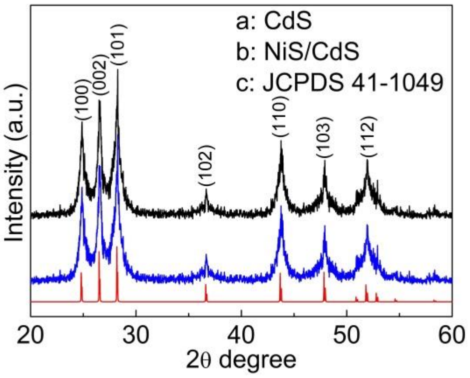

Fig.1 XRD patterns of CdS and NiS/CdS nanoparticles

The detailed structural information about the NiS/CdS sample was investigated by TEM and HRTEM. Observed form the TEM image (Fig. 2a), it is difficult to distinguish between NiS and CdS particles, and the size of the nanoparticles is uniform and in the range of 20-50 nm, which agrees well with the crystallite size (27.4 nm) calculated from the XRD line broadening. In fact, the HRTEM image (Fig 2b) confirmed the co-existence of NiS and CdS in the composite. The obvious interface between NiS and CdS particle can be observed from HRTEM image (Fig 2b), and clearly well-defined lattice fringes are measured to be 0.21 nm and 0.34 nm, which are assignable to the interplanar spacing of (102) plane of NiS [15] and (002) plane of CdS [12], respectively.

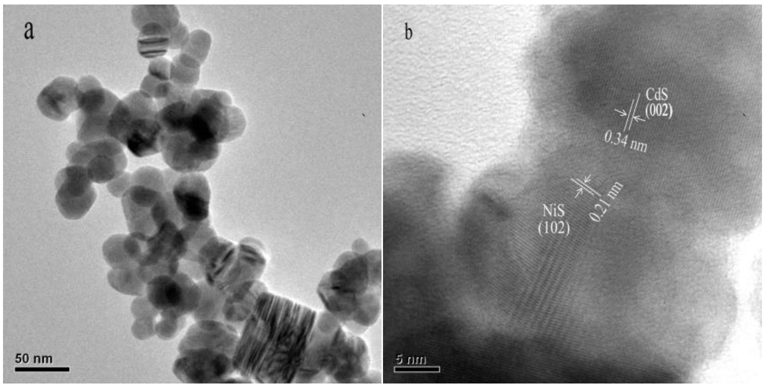

Fig.2 TEM and HRTEM images of NiS/CdS composites

The optical absorption properties of CdS and NiS/CdS samples were investigated by using a UV-vis diffuse reflectance spectrometer. As can be seen, the pure CdS sample (Fig. 3a) can absorb visible light with wavelengths shorter than 530 nm. And the band gap of CdS has been calculated by the following equation: $\alpha h\nu = A\,(h\nu - E_g)^{n/2}$, where α, ν, E_g and A are absorption coefficient, light frequency, band gap, and a constant, respectively. And n is determined by the type of optical transition of a semiconductor (n=1 for direct transition or n=4 for indirect transition). CdS is direct transition, thus, n is equal to 1. From the plot of $(\alpha h\nu)^2$ vs. $h\nu$, the value of Eg for CdS was estimated to be 2.38 eV (Inset of Fig.3), which is in accordance with the literature values [2, 12]. Compared with pure CdS, the NiS/CdS heterostructures (Fig. 3b) clearly show stronger absorption in the UV-visible-light range, indicating NiS/CdS heterostructure will generate more electron-hole pairs under irradiation.

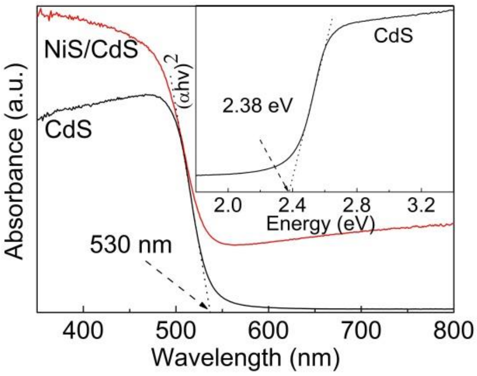

Fig.3 Diffuse reflectance spectra of CdS and NiS/CdS. Inset was the estimated band gap for CdS by Kubelka-Munk function

The photocatalytic activities of the prepared samples were measured on the degradation of quinoline under visible-light irradiation. Fig.4 shows the photodegradation of quinoline as a function of irradiation time over different catalysts. The NiS/CdS heterostructures show higher photocatalytic activities than individual NiS and CdS. After 10 h, the photodegradation efficiency for NiS and CdS were 23.8% and 29.1%, respectively, and the photodegradation efficiency for

NiS/CdS reached 50.1%. The high photocatalytic activity of the NiS/CdS heterostructure can be attributed to the increased light absorptivity and charge separation of CdS caused by the NiS particles. Compared with pure CdS, NiS/CdS can generate more electron-hole pairs under visible light irradiation, because NiS has a band gap of 0.5 eV. More importantly, p-n heterojunction will be constructed when the p-type NiS particles are deposited on the surface of n-type CdS particles. Consequently, an inner electric field will be formed at the equilibrium [16]. Driven by the internal field, the photo-generated holes will be gathered at the VB of NiS, and electrons will be gathered at the CB of CdS [12]. In this case, the photogenerated electron-hole pairs are effectively separated by the p-n heterojunction. Then the separated electrons and holes are free to form reactive oxygen species, and these highly active species($\bullet$OH, $O_2\bullet^-$ or h^+) will degrade quinoline. In this manner, the photocatalytic performance of CdS particles was significantly enhanced by the surface modification with tiny NiS particles.

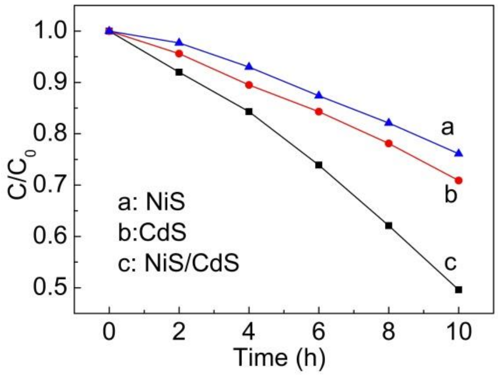

Fig.4 Photocatalytic activities of NiS, CdS and NiS/CdS samples

4. Conclusion

NiS/CdS nanocomposites are synthesized by a facile two-step hydrothermal process. Compared to CdS, NiS/CdS heterostructures exhibit a higher photocatalytic activity for degradation of quinoline under visible light irradiation with a rate of 50.1% in 10 h, which is attributed to the enhancement of visible light absorption promoted by NiS nanoparticles and the separation of excited electron-hole pairs due to the formation of p-n heterojunction between NiS and CdS.

Acknowledgments

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