Research Article

Synthesis of CuS/ZnO Nanocomposite and Its Visible-Light Photocatalytic Activity

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The CuS/ZnO nanocomposite was successfully synthesized by a simple mechanical method, without adding any surfactants. TEM images showed that CuS existed in the nanocomposite and the size of CuS/ZnO nanocomposite particle was around 35 nm. CuS worked as an electron absorber in the nanocomposite, which was beneficial for the improvement of photocatalysis of ZnO. It was also proved by the experiments performed under the visible light irradiation that CuS could help ZnO degrade methylene blue (MB). The catalytic efficiency of the nanocomposites reached the highest value when 0.5 wt% CuS was added. In addition, compared with pure ZnO, the CuS/ZnO nanocomposite exhibited a better photochemical stability up to 5 catalytic cycles. More importantly, CuS did not reduce the antibacterial property of ZnO. All these results indicated that as-prepared samples had some potential values in practical applications.

1. Introduction

Zinc oxide (ZnO) has attracted much attention due to its easy obtained and high exciton binding energy (60 meV) at room temperature [1]. Owing to these outstanding characteristics, ZnO can serve as a functional material in many fields, such as catalysts, antiseptics, antibacterial agents, sensors, solar cells, and light-emitting diodes (LED) [2]. However, in practical applications, the performance of ZnO is limited by several factors, for example, wide band gap, lower quantum efficiency, and slower reaction rate of photocatalysis. In order to enhance the photocatalytic activity of ZnO, plenty of work has been carried out in narrowing the band gap and inhibiting the recombination of photogenerated electron-hole pairs, such as doping or modifying ZnO with metallic ions or nonmetallic ions [3–11], controlling different crystal forms and different calcination temperatures. In the last several decades, many researches have been focused on ZnO modified with metallic elements to improve its photocatalytic performance, including SnO₂ [12], CdS [13], and GaN [14].

However, to the best of our knowledge, we only found one article about ZnO mixed with CuS [15]. In that article, the CuS nanoparticle/ZnO nanowire heterostructures on a mesh substrate were prepared through a simple two-step solution method, and their photocatalytic activity was studied.

Here, CuS/ZnO nanocomposite particles were synthesized by a simple mechanical lapping method. It was found that CuS could remarkably improve the visible light photocatalytic activity of ZnO. At the same time, the antibacterial property of nanocomposites was not changed by adding CuS.

2. Experimental

2.1. Reagents and Instruments. All chemicals are analytical grade reagents and were purchased from the Sinopharm Chemical Reagent Company without further purification. Reagent chemicals used in the experiment are as follows: Zn(NO₃)₂·6H₂O (99%), urea (99%), Cu(Ac)₂ (99%), and Na₂S (98%).

The crystal structure of the sample was characterized by an X-ray diffractometer (D/max-III C, Rigaku Electric Co., Ltd., Japan) with Cu K α radiation (40 kV, $\lambda = 0.15418$ nm). The morphology of the sample was observed by a H600A-II transmission electron microscope (TEM). The optical transmittance spectrum was carried out using a Shimadzu UV-3150 spectrometer at the range from 200 nm to 600 nm.

2.2. Preparation of CuS/ZnO Nanocomposite Particles. 0.02 mol Zn(NO $_3$) $_2$ ·6H $_2$ O and a certain amount of urea were dissolved in distilled water in a baker, and the baker was transferred into a water bath, stirring at a constant temperature of 75°C for 0.5 h. Then, the temperature of the water bath was elevated to 95°C and we kept stirring for 3.5 h. Afterwards, the white ZnO precursor was obtained, washed with distilled water, and dried at 60°C for 12 h. Finally, the precursor was calcined at 400°C for 1 h to obtain the desired ZnO nanomaterials.

A certain amount of Cu(Ac) $_2$ and Na $_2$ S were, respectively, dissolved in water/alcohol (the volume ratio is 3:1) solution. Then the two kinds of solutions were mixed together, with stirring for 30 min at room temperature, making sure the pH value reached 4~5. Finally, the desired black CuS particles were obtained after being washed with ethanol and drying in vacuo at 60°C for 8 h [16].

CuS/ZnO nanocomposite particles were prepared by mixing CuS and ZnO powders together and mechanically grinding for 20 minutes. Samples with different concentrations (0.1 wt%, 0.5 wt%, 1 wt%, and 1.5 wt%) were obtained by adding different amount of CuS.

2.3. Photocatalytic Degradation of MB Solution. We tested the photocatalytic degradation of our samples in MB solution under visible light irradiation with our samples as the photocatalysts. For detailed steps one could refer to previous paper [17].

The stability of the photocatalyst was evaluated by the degradation of MB solution with reused photocatalyst for 5 times, and the same volume of new MB solution was added into the reactor each time.

2.4. Antibacterial Property. We used *Escherichia coli* to test the antibacterial properties of all the samples. First, the *Escherichia coli* should be cultured for 24 h in 37°C incubator. Then 0.5 g nanocomposite particles and 0.1 mL cultured bacterial suspension were added into 95 mL water. Third, the mixed liquor was shaken for 4 h in a water bath at 37°C, and 0.1 mL mixed liquor (the mixed liquor would be diluted 100 times at first) was taken into a culture dish. Fourth, the culture dish was put into the incubator for 18–24 h. At last, we took photos of the culture dish and calculated the antibacterial ratios as in the following formula:

$$\text{Antibacterial ratios} = \frac{A_0 - A}{A_0} \times 100\%, \quad (1)$$

where A_0 is the bacterial colony of blank sample and A is the bacterial colonies of samples dish.

FIGURE 1: XRD patterns of all samples.

3. Results and Discussion

3.1. XRD Analysis. The XRD patterns of the products were shown in Figure 1. All the diffraction peaks were in agreement with the standard data of wurtzite-type ZnO (JCPDS NO. 36-1451), indicating that no other impurities could be found in the nanocomposites. The crystalline size calculated by the Scherrer's formula showed that all these samples had a similar particle size around 35 nm. In addition, they had the same preferential orientation, as the intensities of their main peaks were close. There were no characterized peaks belonging to CuS in these XRD patterns, mainly due to the low modification amount.

3.2. TEM Analysis. Figures 2(a) and 2(b) showed the TEM images of pure ZnO and pure CuS, respectively. It was obvious that most of the pure ZnO nanoparticles were spherical, while CuS looked more like nanorods with a much smaller particle size than ZnO. Figure 2(c) exhibits the TEM image of CuS/ZnO nanocomposite particles. We could observe some small CuS nanorods in/on ZnO nanoparticles, suggesting that CuS existed in the nanocomposite particles, but it did not have an impact on the morphology of ZnO. The average size of nanocomposite particles was about 35 nm, which is in agreement with the values obtained from Scherrer's formula. Figure 2(d) exhibits the high-resolution TEM image of nanocomposite particles. From the image we were firmly sure that there were two different lattice planes in the nanoparticles. One interplanar crystal spacing was about 0.19 nm and that belonged to {102} of ZnO [18]; the other is 0.31 nm and belonged to {102} of CuS [19]. The XRD and TEM results indicated that the modification of CuS had few influences on the crystalline size, preferential orientation, and morphology of ZnO nanoparticles.

FIGURE 2: TEM images of different samples: (a) pure ZnO, (b) pure CuS, (c) CuS/ZnO, and (d) high-resolution TEM (HRTEM) image of CuS/ZnO.

FIGURE 3: UV-Vis reflectance spectra of as-prepared samples.

FIGURE 4: (a) The degradation curves of MB under visible light irradiation; (b) photochemical stability of (0.5 wt% CuS)/ZnO.

3.3. UV-Vis Reflectance Spectra of Different Samples. The UV-Vis analysis was shown in Figure 3. All the spectra have the characteristic spectrum of ZnO with its fundamental absorption sharp edge rising at 400 nm, indicating that the band gap energy was not changed with adding CuS into ZnO. Compared with pure ZnO, the CuS/ZnO nanocomposites absorbed more in the whole visible region due to the presence of CuS. In addition, with increasing the contents of CuS the enhancements of absorption increased, which meant that the photocatalytic activity may get better and better. This is mainly because CuS modification brought an increase of surface electric charge of ZnO in the nanocomposite, which would lead to changes of the fundamental process of electronic transference during the irradiation [20].

3.4. Photocatalytic Activity and Photochemical Stability of As-Prepared Samples. MB solution was chosen as model dye to evaluate the photocatalytic activity of the nanocomposite particles under visible irradiation, and the results were shown in Figure 4.

It could be observed from Figure 4(a) that the CuS/ZnO nanocomposites had a higher catalytic efficiency than pure ZnO and pure CuS. When the modifying concentration was low (less than 0.5 wt%), with the contents of CuS improving, the effect of cocatalyst was becoming better and better. However, when the modifying concentration was more than 0.5 wt%, the catalytic efficiency decreased on the contrary. This result did not match the UV-Vis reflectance spectra in Figure 3. The main reason why excess CuS would

FIGURE 5: The mechanism of photocatalysis process.

FIGURE 6: The pictures of the antibacterial property: (a) blank, (b) pure ZnO, and (c)–(f) nanocomposites.

make the photocatalytic efficiency of ZnO decrease was that CuS particles also acted as recombination centers at high CuS adding, caused by the electrostatic attraction of negatively charged CuS and positively charged holes [21]. As a result, when the modifying concentration was 0.5 wt%, the nanocomposite reached the best cocatalyst function and the photodegradation rate was about 96.5% at 30 min.

The stability of (0.5 wt% Cu)/ZnO nanocomposite and pure ZnO under visible light were shown in Figure 4(b). The activity of pure ZnO decreased dramatically from 79.3% to 55.7% after 5 catalytic cycles. In contrast, the (0.5 wt% CuS)/ZnO nanocomposite maintained a high catalytic activity after the same catalytic cycles and reached 77.9%.

3.5. Mechanism. The whole photocatalysis process of CuS/ZnO nanocomposite particles can be described in Figure 5. As we all know, the band gap of ZnO was very wide with a valence band of 2.415 eV and conduction band of -0.855 eV [15], while CuS had a narrow band gap of 0 eV [22]. Since

the band gap of CuS was narrower than that of ZnO, the photogenerated electrons may transfer to CuS nanoparticles loading on the surface of ZnO. Then, the transferred electrons were trapped by CuS due to its strong electron accepting ability, resulting in the effective separation of the electrons and holes [23]. Electrons accumulated at CuS particles can be transferred to oxygen molecules adsorbed on the surface to form free oxygen radicals, such as $\cdot\text{O}_2^-$, $\cdot\text{HO}_2$, $\cdot\text{OH}$, which would be helpful to the degradation of dye solution [24].

3.6. Antibacterial Property. Results of the antibacterial tests were shown in Figure 6. Compared with the blank sample, the CuS/ZnO nanocomposites had a perfect antibacterial property as good as the pure ZnO. It powerfully proved that CuS modification did not have influence on the antibacterial property of ZnO. The antibacterial ratios were listed in Table 1.

TABLE 1: The antibacterial ratios of all samples.

Materials	Antibacterial ratios (%)
(a) Blank	0
(b) Pure ZnO	98.9
(c) 0.1% CuS/ZnO	99.47
(d) 0.5% CuS/ZnO	99.47
(e) 1% CuS/ZnO	99.47
(f) 1.5% CuS/ZnO	97.36

4. Conclusions

CuS/ZnO was prepared successfully by grinding the obtained ZnO and CuS, both of which were synthesized by precipitation method. TEM images and XRD analysis revealed that CuS exactly existed in the nanocomposite particles and the average size of the nanoparticle was about 35 nm. Compared with the pure ZnO, the CuS-modifying ZnO can serve as an excellent enhanced photocatalyst under visible light irradiation. And when the modification ratio was 0.5 wt%, the assistant catalytic property was the best. The electronic interaction between CuS and ZnO was supposed to be responsible for the enhanced photocatalytic activity. The antibacterial property of ZnO was not changed after CuS modification. CuS/ZnO nanoparticles are promising for practical applications due to their remarkable photocatalytic stability and perfect antibacterial characteristics.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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