Enhanced photocatalytic degradation of methylene blue in aqueous solution by Cu/ZnO photocatalyst

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In order to improve the photocatalytic activity of ZnO nanorod, the Cu/ZnO nanorod was modified by copper sulfate ($CuSO_4$) and ZnO nanorod. Transmission electron microscope (TEM) was carried out to characterize the composites with different Cu contents, indicating that the modification does not alter the length and diameter of ZnO nanorod. The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activities of ZnO and Cu/ZnO nanorod. Cu/ZnO shows significantly higher photocatalytic activity (k_{app} = 0.0402 min^{-1}) than ZnO nanorod (k_{app} = 0.0172 min^{-1}) under sunlight irradiation. The degradation of MB accords with pseudo-first order kinetics, and the appear rate constants k_{app} of 7% Cu/ZnO nanorod was about 2.3 times higher than ZnO nanorod. The optimum synergetic effect was found at a weight ratio of 7.0 wt % (Cu/ZnO), and the optimum synergetic factor was 2.34.

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Photocatalytic degradation is an efficient and economic method to mineralize organic pollutants into carbon dioxide and water [1-2]. As a photocatalyst, ZnO has the advantages of high chemical stability, high photocatalytic activity, low price and nontoxicity [3-4]. However, the wide band gap of ZnO (3.37 eV) only allows it to absorb the ultraviolet light that occupies only a small fraction (3-5%) of the solar photons, which limits its wide use [5]. It is of paramount importance to improve the photocatalytic efficiency of ZnO by shifting its optical response from the UV to the visible range without the decrease of photocatalytic activity [6-7]. Hence, much effort has been devoted to developing a ZnO-based photocatalyst which is capable of efficient utilization of the visible light [7-9].

To extend the photoresponse of ZnO to the visible region, many modification methods, such as non-metal doping [10], noble metal deposition [11], and photosensitive material modification [12] have been reported. Recently, a little work has been done on using metal ion doping modified ZnO to degrade dyeing wastewater since metal ion and ZnO show interesting physical properties and application potential [13]. For example, Wang et al. used Au modified-ZnO for degradation of dyeing wastewater, and results showed that photocatalytic activity was enhanced [14]. However, in most cases, the photocatalytic degradation of organic pollutants is mainly for dyes, and little research has been performed on phenols, highly toxic and carcinogenic compounds, especially without the assistance of H_2O_2 under visible light, even in the longer wavelength of light [15-16].

In this paper, the ZnO nanorod was synthesized by the hydrothermal method, and Cu/ZnO nanorod was synthesized by modifying the prepared ZnO nanorod. The prepared photocatalysts were characterized by transmission electron microscope (TEM). The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activity of ZnO and Cu/ZnO nanorod. The sunlight photocatalytic performance of Cu/ZnO nanrod was enhanced to about 2.3 times compared with that of ZnO nanorod. The high photocatalytic activity came from the synergetic effect between Cu and ZnO, and the optimum synergetic effect was found at a weight ratio of 7.0 wt % (Cu/ZnO).

1. Experimental

1.1. Reagents and materials

Zinc acetate was purchased from Tianjin Hengxing Chemical Preparation Co., Ltd. Copper sulfate was purchased from Shanghai Tingxin Chemical Reagent Co., Ltd. All these reagents were of AR grades and used without further purification.

1.2. Synthesis of ZnO nanorod

The ZnO nanorod was synthesized by the hydrothermal method. Amounts of zinc acetate, ethanol, polyethylene glycol were placed within a high-pressure hydrothermal reactor as well as sodium hydroxide. A glass rod was then stirred continuously to enable sodium hydroxide to dissolve completely. Following this, the high-pressure hydrothermal reactor was put into a muffle furnace for heating. ZnO nanorods were obtained after centrifugal separation, scrubbing and drying.

1.3. Synthesis of Cu/ZnO nanorod

The Cu/ZnO nanorod was synthesized via modifying ZnO nanorod with $CuSO_4$. 0.5 g ZnO nanorod was placed into a round-bottom flask with 2 g ethanediol and 60 ml polyvinylpyrrolidone. The system was then put into ultrasonic cleaner lasting 10 min to allow all the reactants to mix. Magneton was added to the round-bottom flask after mixing and the solution labeled A.

Next, differing mass of $CuSO_4$ were added to beakers with 60 ml distilled water to prepare a series of ratios between Cu and ZnO. The glass rod was then stirred continuously until the materials dissolved and the solution labeled B.

Solution A was placed in an oil bath pot with a temperature setting of 150 ^{0}C. Using a dropping funnel, solution B was gradually poured into the solution A, while a condenser pipe was connected to the dropping to make the water vapor reflux condenser. The reaction was not discontinued until the round-bottom flask was no longer blue and the color remained unchanged. Following centrifugal separation, the obtained products were washed three times by distilled water and once with ethanol. Lastly, the Cu/ZnO nanorod was obtained after drying at 80 ^{0}C.

1.4. Characterization

Transmission electron microscopy (TEM) patterns were performed on a JEM-1011 transmission electron microscopy (Japan).

1.5. Photocatalytic activity test

The photocatalytic activities of samples were evaluated by the photocatalytic degradation of MB under sunlight. Aqueous suspensions of MB (10 mg/L) were placed in a quartz tube, and 10 mg of photocatalyst were added. Prior to irradiation, the suspensions were magnetically stirred in darkness for about 1 h [17-18]. The suspensions were kept under constant air-equilibrated conditions before and during illumination. At certain time intervals, 1 mL liquor was sampled and centrifuged to remove the particles. The filtrates were analyzed by recording variations of the maximum absorption band (664 nm for MB) using a UV-2550PC ultraviolet and visible spectrophotometer.

2. Results and discussion

2.1. TEM images

The TEM image of ZnO nanorod is clearly displayed in Fig. 1. From the TEM images, we find that the length of ZnO nanorod was at about 700-800 nm, and the diameter was at about 40-50 nm.

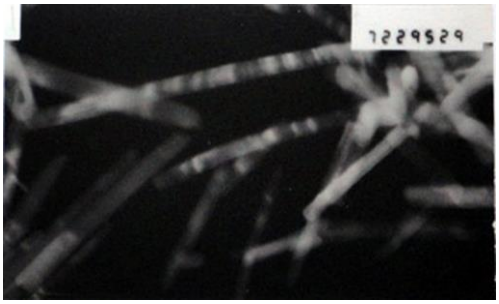


Fig. 1. TEM image of ZnO and Cu/ZnO nanorod × 72000

The TEM images of Cu/ZnO nanorod with different Cu contents are clearly displayed in Fig. 2 (a-d). As can be seen from Fig. 2(a) to Fig. 2(d), the length of Cu/ZnO nanorod was at about 700-800 nm, and the diameter was at about 40-50 nm. The results indicate that there was no change of ZnO in length and diameter when doped with Cu, meaning that the presence of Cu do not impact on the morphology of photocatalyst.

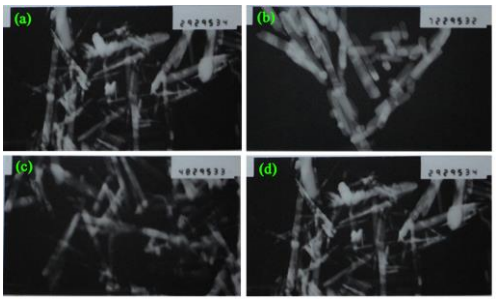


Fig. 2. TEM image of Cu/ZnO nanorod (a: Cu 1 wt % × 100000; b: 5 wt % × 72000; c: 7 wt % × 48000; d: 10 wt % × 29000)

2.2. Photocatalytic activity

Photocatalytic activity tests of samples were investigated by the degradation of MB in aqueous solution under sunlight irradiation. Fig. 3 shows the degradation of MB in aqueous solution in the presence of ZnO nanorod and Cu/ZnO nanorod with different Cu contents.

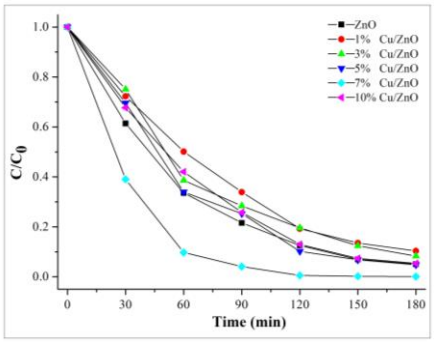


Fig. 3. The photocatalytic degradation of MB in the presence of ZnO and Cu/ZnO nanorod with different Cu contents under sunlight irradiation

The kinetics plots are shown by apparent first-order linear transform $-\ln(C/C_0) = k_{app}t$ in Fig. 4. The activity of ZnO nanorod and Cu/ZnO nanorod with different Cu contents can be evaluated by comparing the apparent first order rate constants (kapp) listed in Table 1. ZnO nanorod and 7% Cu/ZnO nanorod give apparent rate constants of 0.0172 min^{-1} and 0.0402 min^{-1}, respectively. The introduction of about 7% Cu to ZnO obviously enhanced the photocatalytic activity. It also suggests that the increasing degradation rate of MB can be seen with the increase of Cu content from 1% to 7%. When the Cu content higher than 7%, the degradation rate of MB beings to decrease.

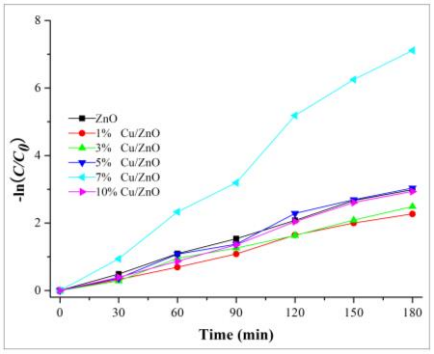


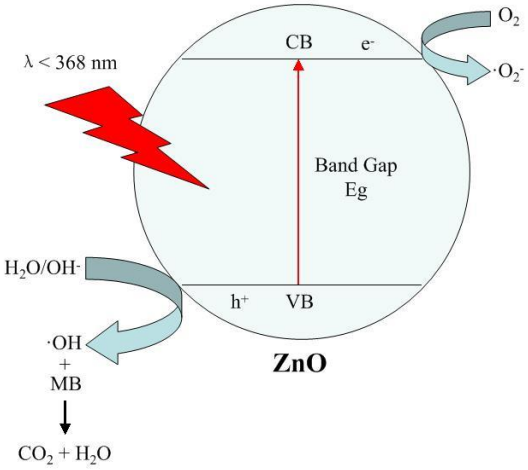
Fig. 4. Apparent first-order linear transform $-\ln(C/C_0) = k_{app}t$ of MB degradation kinetic plots for ZnO and Cu/ZnO nanorod with different Cu contents under sunlight irradiation

Table 1. Appear rate constants (k_{app}) of MB photodecomposition and linear regression coefficients from a plot of $-\ln(C/C_0)=k_{app}t$

photocatalysts	k_{app} (min^{-1})	R^2
ZnO	0.0172	0.9968
1% Cu/ZnO	0.0129	0.9924
3% Cu/ZnO	0.0139	0.9935
5% Cu/ZnO	0.0174	0.9855
7% Cu/ZnO	0.0402	0.9897
10% Cu/ZnO	0.0165	0.9912

2.3. Photocatalytic mechanism

The band-gap energy of ZnO was 3.37 eV, indicating that it only had response to small amount light (λ<368 nm). Under sunlight irradiation of the ZnO nanorod, the electrons can be excited and the electron-hole pairs generated. Excited-state electrons from the VB can be injected into the CB of ZnO nanorod and finally react with oxygen at the surface. This results in the formation of highly reactive particles, for example the superoxide radical ion $\bullet O_2^-$ and consequently the hydroxyl radical •OH. It is the $\bullet O_2^-$ and •OH that are responsible for the degradation of MB. The whole process can be clearly described in Scheme 1 [19-21].



Scheme 1. Photocatalytic mechanism of ZnO nanorod

The photocatalytic mechanism of ZnO nanorod can be expressed as follows:

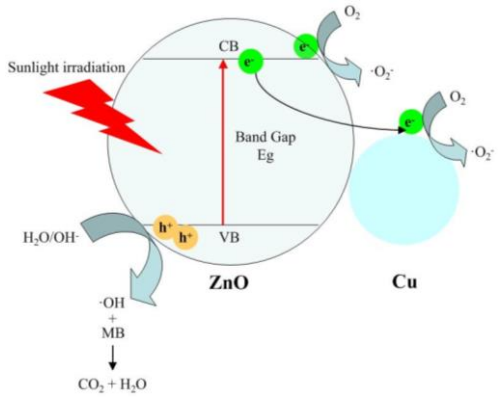
$$ZnO + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O/OH^- \rightarrow \cdot OH + H^+ \quad (2)$$

$$O_2 + e^- \rightarrow \cdot O_2^- \quad (3)$$

$$MB + \cdot OH/\cdot O_2^- \rightarrow CO_2 + H_2O \quad (4)$$

The synergetic effect between Cu and ZnO nanorod on the photocatalytic degradation of MB exists in Cu/ZnO nanorod owing to the well matched energy levels, and the optimum synergetic effect was observed at a weight ratio of 7.0 wt % (Cu/ZnO). The photocatalytic mechanism of Cu/ZnO nanorod can be explained as Scheme 2 [22-23].



Scheme 2. Photocatalytic mechanism of Cu/ZnO nanorod

The presence of Cu on the surface of ZnO nanorod can enhance the photocatalytic activity. The synergetic effect between Cu and ZnO nanorod on the photocatalytic degradation of MB exists clearly not for all the Cu/ZnO. An optimum of the synergetic effect is found for 7% Cu/ZnO nanorod. The synergetic factor (*f*) can be calculated by the apparent first-order kinetic expression [24]:

$$-\frac{dR}{dt} = k_{C/Z}[C_t] = k_C[C_t] + k_Z[C_t] + k_{C-Z}[C_t] \quad (5)$$

where $k_{C/Z}$ is the first-order rate of Cu/ZnO nanorod, k_C is the first-order rate of Cu, k_T is the first-order rate of ZnO nanorod, and $[C_t]$ is the concentration of MB at the same moment. Therefore, the photocatalytic degradation of MB involves the degradation of Cu and ZnO nanorod as well as synergy between Cu and ZnO nanorod$_2$. The synergetic factor can be calculated using the following equation:

$$f = \frac{k_{C/Z}}{k_C + k_Z} \quad (6)$$

Based on the Cu being used as a modifier with no obvious photocatalytic activity, *f* is calculated as follows:

$$f = \frac{k_{C/Z}}{k_Z} \quad (7)$$

Based on the apparent first-order kinetic constants for the degradation of MB in Table 1, the synergetic factors of the Cu/ZnO nanorod were 0.75 for 1% Cu/ZnO nanorod, 0.81 for 3% Cu/ZnO nanorod, 1.01 for 5% Cu/ZnO nanorod, 2.34 for 7% Cu/ZnO nanorod, and 0.96 for 10% Cu/ZnO nanorod, respectively.

3. Conclusions

The ZnO nanorod was synthesized via the hydrothermal method, and Cu/ZnO nanorod was synthesized via modifying the prepared ZnO nanorod. The length of ZnO and Cu/ZnO nanorod was at about 700-800 nm, and the diameter was at about 40-50 nm based on TEM images, indicating that the presence of Cu do not impact on the morphology of ZnO nanorod. The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activities of ZnO and Cu/ZnO nanorod. Cu/ZnO shows significantly higher photocatalytic activity (k_{app} = 0.0402 min^{-1}) than ZnO nanorod (k_{app} = 0.0172 min^{-1}) under sunlight irradiation. The degradation of MB accords with pseudo-first order kinetics, and the appear rate constants k_{app} of 7% Cu/ZnO nanorod was about 2.3 times higher than ZnO nanorod. The optimum synergetic effect was found at a weight ratio of 7.0 wt % (Cu/ZnO), and the optimum synergetic factor was 2.34.

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