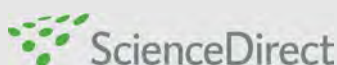


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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Degradation of methylene blue with H₂O₂ over a cupric oxide nanosheet catalyst

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ABSTRACT

Cupric oxide (CuO) nanosheets were prepared by the hydrothermal method with the use of cetyltrimethylammonium bromide (CTAB) and were used as the catalyst for the oxidation degradation of methylene blue with H₂O₂. The effects of temperature, oxidant concentration, and catalyst dosage were evaluated. The catalytic reaction obeyed first order kinetics, and the activation energy was 54 kJ/mol. Although the CuO nanosheets show high activity, their stability and reusability still need improvement.

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1. Introduction

Organic dyes are used in many industries, including the traditional textile industries and new areas of applications such as their use in food, pharmaceutical products, cosmetics, solar cells, and optical data discs and computers. Most of the applications are based on producing color changes by dyes in aqueous solution [1]. However, these solutions cause serious environmental problems when dyes containing industrial effluents are discharged into water bodies. Most organic dyes create acute problems in the ecosystem as they are toxic, mutagenic, and carcinogenic for aquatic life and humans [2,3].

The removal of organic dyes from natural and industrial wastewater has drawn attention because of the highly toxic effect of these contaminations on animals, plants, and human beings. Many methods, including biological methods, physical methods, and chemical methods, have been developed to remove organic dyes from wastewater [4,5]. The use of a biological

method is limited because many organic dyes are resistant to biodegradation and are toxic in microbial processes. Although physical methods such as filtration and adsorption seem easy and economical, their efficiencies are very low because of the high solubility of dye compounds in water. Besides, it is difficult to find a suitable adsorbent for many organic dyes [6,7]. As a result, the use of chemical methods to mineralize or transform refractory molecules into products that can be biodegraded is a matter of great interest. Among the chemical methods, chemical oxidation is the most promising and frequently used technique because of its simplicity, low cost, and potential for solving the environmental problems. Therefore, extensive research efforts have been directed towards the development of new catalysts for the removal of organic dyes from wastewater. One suitable method is the use of catalytic oxidation with hydrogen peroxide. The catalyst decomposes H₂O₂ to highly reactive hydroxyl radicals, which can decompose the synthetic dyes. Also, H₂O₂ is an environmental benign ox-

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dant compared to other oxidants (e.g., HClO/CIO⁻, ClO₂, KMnO₄, K₂Cr₂O₄). It is also well known that solid catalysts are advantageous over homogeneous ones because of their easy separation and recyclability. The most used solid catalysts are based on transition metal oxides.

Cupric oxide (CuO) is a nontoxic and cost-efficient material, which is a p-type semiconductor with a narrow band gap. It has been widely investigated because of its properties and applications in a wide range of fields, including energy storage [8–12], catalysis [13,14], ion exchange, biosensors [15–17], and particularly, for environmental treatment [18–20]. Recently, much effort has been devoted to developing routes for the facile synthesis of CuO nanostructures and investigating their catalytic properties. Meshram et al. [21] reported that platelet-like CuO nanostructures efficiently catalyzed the degradation of methylene blue (MB) in aqueous solution with H₂O₂ as oxidant. Hong et al. [22] demonstrated that urchin-like CuO microspheres prepared by a simple water-ethylene glycol solvothermal method are good catalysts for the degradation of pyronine B.

Here, we present a simple and efficient hydrothermal method to make crystalline CuO nanosheets. The chemical oxidation degradation of a cationic organic dye, methylene blue, was selected as the test reaction to evaluate the catalytic performance of the CuO nanosheets. The effects of temperature, catalyst dosage, and H₂O₂ amount on the catalytic activity were investigated.

2. Experimental

2.1. Preparation of CuO nanosheets

CuO nanosheets were prepared in an autoclave by the hydrothermal method. CuCl₂·2H₂O (0.5 g) and CTAB (0.5 g) were dissolved in 15.7 mL H₂O under stirring to form a blue solution. Then 1 mL NaOH aqueous solution (0.3 g/mL) was added dropwise. After vigorous stirring for 1 h, the solution was transferred to a Teflon-lined stainless steel autoclave (20 mL capacity), sealed, and heated at 120 °C for 6 h. After cooling the autoclave to room temperature, CuO nanosheets were collected by centrifugation, repeatedly washed with ethanol and distilled water, and then dried under vacuum at 70 °C for 12 h.

2.2. Characterization

Transmission electron microscopy (TEM) images were taken with a Tecnai-12 instrument operated at 120 kV. Field emission scanning microscopy (FESEM) was performed on a Hitachi S4800 instrument. The crystallographic structure of the samples was established using powder X-ray diffraction (XRD, D8 Advance, Bruker).

2.3. Catalytic degradation of MB

For the MB degradation study, a stock solution of 6.0×10^{-5} mol/L was prepared. In each degradation study, 10 mL of the stock solution was mixed with 2.5 mL H₂O₂ (30%) and 10 mg CuO nanosheets and kept at the desired temperature. The deg-

radation progress was monitored by spectrometric measurements using a Shimadzu UV-2501 spectrophotometer. The effects of various experimental parameters such as the temperature, catalyst dosage, and H₂O₂ amount were investigated.

3. Results and discussion

3.1. Characterization of CuO nanosheets

The successful synthesis of CuO nanosheets and their crystallinity were evident from the XRD pattern displayed in Fig. 1. The diffraction peaks in Fig. 1 matched the standard XRD pattern of CuO (JCPDS card No. 10-0319) well. The peaks observed at $2\theta = 32.5^\circ, 35.4^\circ, 38.7^\circ, 48.7^\circ, 53.5^\circ, 58.3^\circ, 61.5^\circ, 66.2^\circ, 67.9^\circ, 72.4^\circ,$ and 75.0° were attributed to the Bragg reflections of the (110), (111), (11 $\bar{1}$), (20 $\bar{2}$), (020), (202), ($\bar{1}$ 13), (311), (220), (311), and (004) planes, respectively. The sharp and strong intensity of the XRD peaks demonstrated the good crystallinity of the product.

The morphology, shape, and size of the nanoparticles were obtained by FESEM and TEM analysis. The FESEM image of the CuO is illustrated in Fig. 2A, which shows a uniform sheet shape with a smooth surface. The CuO nanosheets have a width of ~400 nm and a length of several μm . A typical TEM image of the CuO nanosheets is displayed in Fig. 2B. The sheet shape and μm size were in agreement with the FESEM observations. More detailed structural information on the CuO nanosheets was obtained by high resolution TEM (HRTEM). Careful observation by HRTEM revealed lattice fringes, suggesting the single crystalline nature of the CuO nanosheets. The interplanar distance calculated from the line profile (Fig. 2D) was 0.285 nm, which was in good agreement with (11 $\bar{1}$) crystal planes of CuO.

3.2. Catalytic degradation of MB

3.2.1. Kinetics of the catalytic degradation of MB

The oxidation degradation of MB by H₂O₂ was chosen as the model reaction to investigate the catalytic performance of the CuO nanosheets. As shown in Fig. 3A, without the CuO nanosheets, the oxidation of MB in the presence of H₂O₂ was very slow even with a large excess of H₂O₂. The decolorization

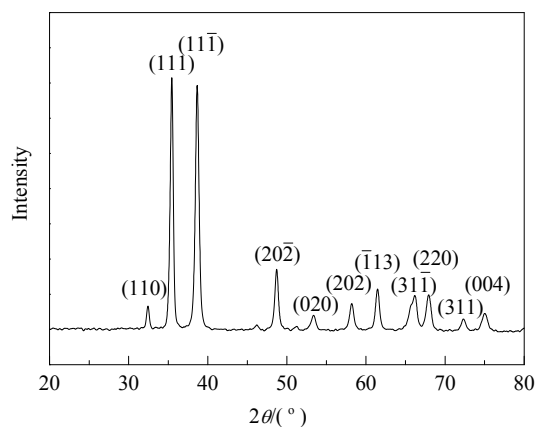


Fig. 1. XRD pattern of the CuO nanosheets.

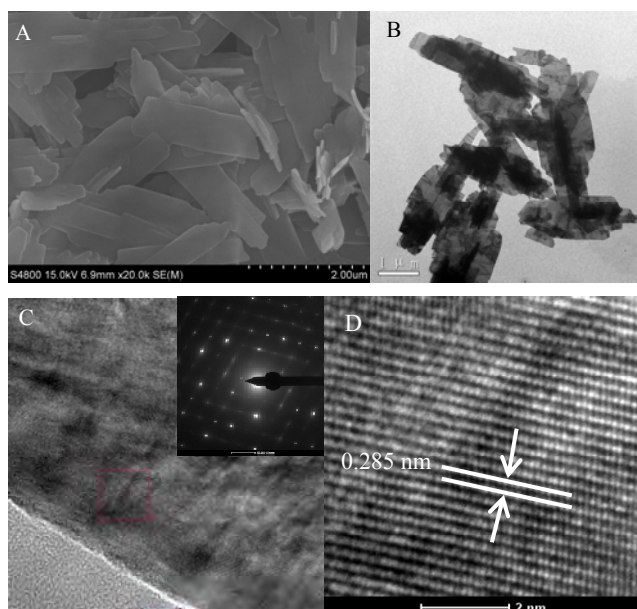


Fig. 2. SEM (A), TEM (B), and HRTEM (C and D) images of the CuO nanosheets. The inset in C is a selected area electronic diffraction pattern of the CuO nanosheets.

rate was only 16.6% in 3 h. This is due to the chemical stability of MB.

Figure 3B shows that the addition of CuO nanosheets to the dye solution caused fading and ultimate bleaching of the color of the solution, as indicated by the gradual decrease in the absorbance with time. In this experiment, the concentration of H_2O_2 used as an oxidant largely exceeded that of MB. As soon as H_2O_2 was added, the CuO nanosheets started the catalytic oxidation of MB. As the initial concentration of H_2O_2 was very high, it remained essentially constant throughout the reaction. Therefore, for the evaluation of the reaction rate, pseudo-first order kinetics with respect to MB is a reasonable assumption. Because the ratio of the absorbance A_t of MB at time t to its initial value A_0 measured at $t = 0$ equals the concentration ratio C_t/C_0 of MB, the reaction rate constant (k) for the first order reaction is $\ln(A_t/A_0) = kt$.

Figure 3C shows the semi-log plot of the concentration of MB as a function of reaction time. A straight line plot showed that the degradation of MB is a pseudo-first order reaction. The

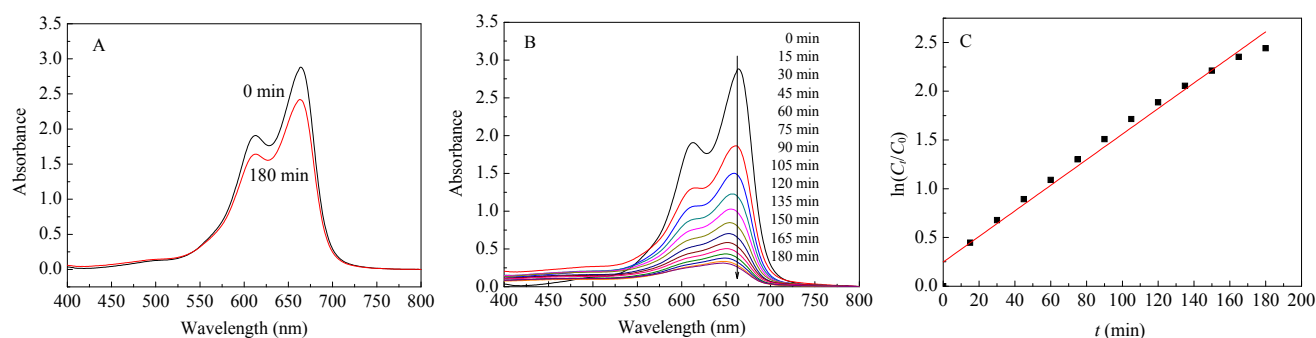


Fig. 3. (A) UV-Vis spectra of MB oxidized with H_2O_2 without CuO nanosheets (reaction conditions: 2.5 mL 30% H_2O_2 , 10 mL 6.0×10^{-5} mol/L MB, 25 °C); (B) UV-Vis spectra of MB oxidized with H_2O_2 and CuO nanosheets (reaction conditions: 10 mg CuO nanosheets, 2.5 mL 30% H_2O_2 , 10 mL 6.0×10^{-5} mol/L MB, 25 °C); (C) Plot of $\ln(C_t/C_0)$ versus time for the oxidation of MB by CuO nanosheets.

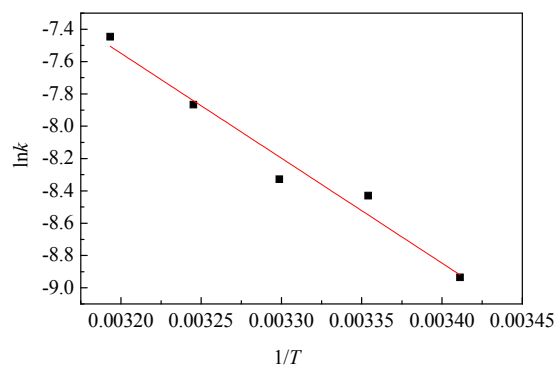


Fig. 4. Plot of $\ln k$ versus $1/T$ in the temperature range of 20–40 °C.

rate constant k was calculated from the slope of the line and a value of 0.013 min^{-1} was obtained.

The rate constant was measured at five different temperatures (20, 25, 30, 35, and 40 °C). Figure 4 shows the plot of rate constant versus temperature T , which shows a linear relationship between $\ln k$ and $1/T$. The activation energy was calculated to be 54.0 kJ/mol.

3.2.2. Effect of various experiment parameters

A number of reports have demonstrated that catalyst dosage has a large influence on the reaction rate. Figure 5A displays the decomposition rate of MB with different catalyst dosages. There was a critical dosage (20 mg) of the catalyst, at which the decolorization efficiency was the best. The effect of catalyst dosage on the decolorization rate can be explained as follows. When a very small amount of catalyst was used, the catalyst was well dispersed in the reaction medium, and thus all active surface sites were available. Accordingly, the rate increased with catalyst dosage. Once the catalyst dosage reached a certain amount (20 mg in this study), the adsorption of MB onto the catalyst surface reached an optimum state. The decrease of catalytic activity at higher catalyst dosages was because all dye molecules were adsorbed on the catalyst and the addition of a larger amount of CuO would have no effect on the degradation rate, while there was increased opacity of the reaction suspension due to the excess amount of CuO sheets.

The effect of the initial H_2O_2 dosage on the decomposition efficiency of MB is shown in Fig. 5B. The oxidation degradation

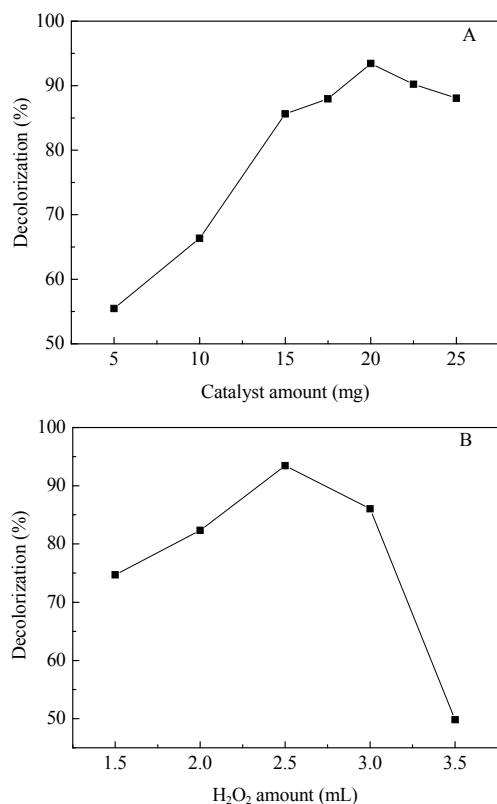


Fig. 5. Effects of catalyst dosage (A) and H₂O₂ amount (B) on the decolorization rate of MB aqueous solution. Reaction conditions: 2.5 mL 30% H₂O₂ (A), 10 mL 6.0 × 10⁻⁵ mol/L MB, 25 °C, 1 h, 20 mg CuO nanosheets.

conversion of MB increased with the amount of H₂O₂ and reached a maximum when the amount of H₂O₂ added was 2.5 mL. After that, the decolorization efficiency drastically decreased as the amount of H₂O₂ was further increased. When the amount of H₂O₂ was first increased, more reactive radicals were generated on the surface of CuO. At a low concentration, H₂O₂ inhibits the recombination of photogenerated electrons and holes. However, at a high concentration, H₂O₂ is a powerful OH· scavenger, which would decrease the oxidation activity. Therefore, it is necessary to choose a proper amount of H₂O₂ according to the kinds and concentrations of pollutants in order to optimize the oxidation efficiency of H₂O₂.

3.2.3. Reusability of catalyst

To confirm the stability of the CuO nanosheets in the catalytic oxidation of MB, the nanosheets were recovered and reused. The recovered nanosheets were recycled three times for use in the degradation of the MB solution. At the end of each cycle, the catalyst was washed with distilled water three times followed by drying in an oven. The results are shown in Table 1. The decomposition efficiency of MB decreased rapidly with recycle number. The percentage of decolorization decreased to only 33.5% after three cycles. The decrease in catalytic activity was probably related to the gradual change in the morphology of the CuO nanosheets after each cycle. The morphology of the CuO nanosheets was examined after each cycle. As shown in Fig. 6, the CuO nanosheets became aggregated, leading to the

Table 1

Effect of recycle number on the oxidation of MB with H₂O₂ and CuO nanosheets.

Cycle number	1	2	3
Degradation efficiency (%)	96.5	62.3	33.5

Reaction conditions: 20 mg CuO nanosheets, 2.5 mL 30% H₂O₂, 10 mL 6.0 × 10⁻⁵ mol/L MB, 25 °C, 15 min.

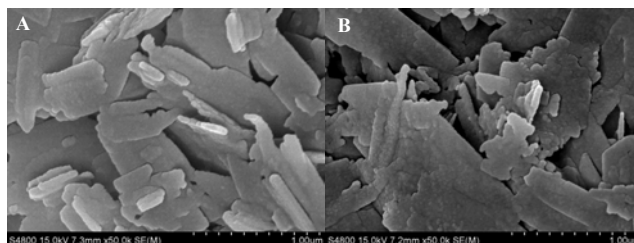


Fig. 6. SEM images of CuO nanosheets after one (A) and two (B) cycles.

decrease of catalytic activity. The aggregation of the CuO nanosheets is not conducive for the maintenance of the catalytic activity of the CuO nanosheets.

4. Conclusions

Crystalline CuO nanosheets were prepared by the hydrothermal method. As the catalyst for the photodegradation of methylene blue with H₂O₂, the CuO nanosheets showed high catalytic activity, but their stability and recycling performance still need improvement.

References

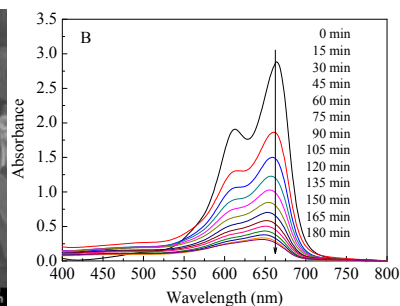
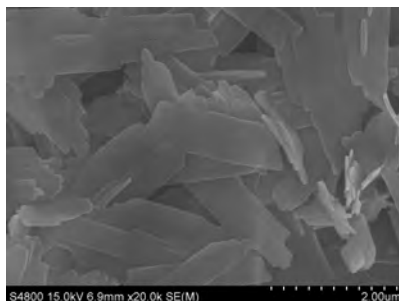
- [1] Zollinger H. *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*. VCH Publishers, New York, 1991. 379
- [2] Morais L C, Freitas O M, Goncalves E P, Vasconcelos L T, Beca G C. *Water Res*, 1999, 33: 979
- [3] Santhy K, Selvapathy P. *Bioresour Technol*, 2006, 97: 1329
- [4] Zhu M Y, Diao G W. *J Phys Chem C*, 2011, 115: 18923
- [5] Zhou L, Gao C, Xu W J. *ACS Appl Mater Interfaces*, 2010, 2: 1483
- [6] Uddin M T, Islam M A, Mahmud S, Rukanuzzaman M. *J Hazard Mater*, 2009, 164: 53
- [7] Francesca P, Sara M, Luigi T. *Water Res*, 2008, 42: 2953
- [8] Zhang Z L, Chen H, Che H W, Wang Y H, Su F B. *Mater Chem Phys*, 2013, 138: 593
- [9] Zhang Z L, Chen H, She X L, Sun J, Teo J, Su F B. *J Power Sources*, 2012, 217: 336
- [10] Choi C S, Park Y U, Kim H, Kim N R, Kang K, Lee H M. *Electrochim Acta*, 2012, 70: 98
- [11] Dubal D P, Gund G S, Holze R, Lokhande C D. *J Power Sources*, 2013, 242: 687
- [12] Sukhorukov Y P, Gizhevskii B A, Mostovshchikova E V, Yermakov A Y, Tugushev S N, Kozlov E A. *Tech Phys Lett*, 2006, 32: 132
- [13] Zhu M Y, Diao G W. *Catal Sci Technol*, 2012, 2: 82
- [14] Zhang Z L, Che H W, Wang Y L, Gao J J, She X L, Sun J, Zhong Z Y, Su B. *RSC Adv*, 2012, 2: 2254
- [15] Sun S D, Zhang X Z, Sun Y X, Yang S C, Song X P, Yang Z M. *ACS Appl Mater Interfaces*, 2013, 5: 4429
- [16] Sun S D, Zhang X Z, Sun Y X, Yang S C, Song X P, Yang Z M. *Phys*

Graphical Abstract

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Degradation of methylene blue with H₂O₂ over a cupric oxide nanosheet catalyst

Maiyong Zhu, Dehai Meng, Chengjiao Wang, Jian Di, Guowang Diao*
Yangzhou University; Jiangsu University



Cupric oxide (CuO) nanosheets were prepared by a hydrothermal method. The degradation of methylene blue using H₂O₂ as the oxidant over the CuO nanosheets was investigated.

Chem Chem Phys, 2013, 15: 10904

- [17] Hong L, Liu A L, Li G W, Chen W, Lin X H. *Biosens Bioelectron*, 2013, 43: 1
[18] Zhu J, Qian X F. *J Solid State Chem*, 2010, 183: 1632
[19] Reddy K J, McDonald K J, King H. *J Colloid Interface Sci*, 2013, 397:

96

- [20] Martinson C A, Reddy K J. *J Colloid Interface Sci*, 2009, 336: 406
[21] Meshram S P, Adhyapak P V, Mulik U P, Amalnerka, D P. *Chem Eng J*, 2012, 204-206: 158
[22] Hong J M, Li J, Ni Y H. *J. Alloys Compounds*, 2009, 481: 610

CuO纳米片催化H₂O₂氧化降解亚甲基蓝

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摘要: 以十六烷基三甲基溴化铵(CTAB)为保护剂, 采用水热法成功制备了CuO纳米片. 将制备的CuO纳米片在H₂O₂存在下用于催化氧化降解亚甲基蓝, 探讨了其在不同反应条件(如温度、氧化剂浓度及催化剂用量)下对亚甲基蓝降解反应的影响. 该催化反应符合一级动力学模型, 活化能为54.0 kJ/mol. CuO纳米片表现出非常高的催化活性, 但其稳定性与重复利用性有待于进一步提高.

关键词: 氧化铜; 纳米片; 亚甲基蓝; 氧化降解

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