Preparation of \( \text{Cu}_2\text{O} \) Particles and their Photocatalytic Properties

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Abstract. Photocatalytic technology is a potential way for the environmental problems caused by antibiotics contained in water. In this paper, \( \text{Cu}_2\text{O} \) particles were prepared by hydrothermal method. The microstructure and morphology of \( \text{Cu}_2\text{O} \) were characterized by XRD, SEM. The optical and electrochemical properties of the prepared samples were studied by UV-Vis and photocurrent. The results show that the prepared \( \text{Cu}_2\text{O} \) have an octahedral morphology and exposes more (111) crystal planes, with a particle size of 2-5 \( \mu \text{m} \), and has the better optical absorption performance at 500-600 nm. Finally, the photocatalytic performance of the samples was evaluated using Norfloxacin as the target degradation pollutant. The results show that the degradation rate of Norfloxacin over the prepared \( \text{Cu}_2\text{O} \) was 79.8%. The \( \cdot \text{OH} \) and \( \cdot \text{O}_2^- \) play a major role in degradation of Norfloxacin.

Keywords: Hydrothermal method; Cuprous oxide; Photocatalyst.

1. Introduction
With the development of industry and society, people's living standards have been greatly improved, but the environmental problems that come with them become increasingly obvious [1]. Among them, antibiotic pollution in the water environment has become more and more important [2]. These antibiotics (such as Norfloxacin(NOR), Ciprofloxacin, Moxifloxacin etc.) with stable chemical properties are difficult to decompose naturally. In addition, these antibiotics will seriously affect ecosystem balance and human health [3]. Therefore, how to remove antibiotic pollutants effectively has become a research hotspot at present.

Traditional water treatment methods include physical methods [4], biological methods [5], and advanced oxidation methods [6]. Although physical methods can separate antibiotics from the water environment, they cannot be decomposed completely. Biological methods are also difficult to handle with high concentrations of antibiotic contaminants, and antibiotic abuse can also create resistance. Therefore, the use of advanced oxidation technology has become the most widespread method at this stage. Among them, photocatalytic oxidation technology highlights its potential advantages in degrading organic matter due to its strong oxidation ability, preparation simple, no secondary pollution, and low energy consumption [7]. It is the key link for photocatalysis technology to the preparation of a photocatalyst with good photocatalytic stability. Currently, catalysts such as TiO\(_2\) [8], ZnO [9], Cu\(_2\)O [10-13] etc. are reported. Cu\(_2\)O, a p-type semiconductor photocatalyst, has a band gap of 1.9 eV-2.2 eV [14]. It has the advantages of non-toxicity, easy availability of raw materials, and large light absorption range (200-600 nm), making it a potential semiconductor photocatalyst.

There are many reports on the synthesis methods of Cu\(_2\)O, and the preparation methods and conditions...
of nanocrystalline morphology. At present, the main synthesis methods are liquid phase synthesis method [15], photochemical synthesis method [16], low temperature solid phase method [17], electrolytic method [18], and microwave intervention method [19]. Compared with the above method, the hydrothermal method is simple to operate, the temperature is easy to control, and the morphology and exposed surface of the sample can be easily adjusted. Therefore, it is widely used in the preparation of Cu2O. Ho et al. [20] synthesized Cu2O microcrystals with different morphologies by hydrothermal method, and evaluated the degradation performance of Cu2O with different morphologies using methyl orange as the target degradation pollutant. Ma et al. [21] synthesized a flower-like Cu2O crystallite with a polyhydric alcohol as a reducing agent, and the prepared sample has excellent photocatalytic effect. Obviously, the morphology and externally exposed crystal plane of photocatalyst have a great effect on their photocatalytic performance, so that the control of the morphology and externally exposed crystal plane is extremely important. In addition, the semiconductor composition [22], doping, sensitization [23] et al. are used to enhance the photocatalytic performance of Cu2O.

In this paper, copper acetate was used as the copper source and glucose was used as the reducing agent, Cu2O particles were prepared by hydrothermal method. The morphology and external crystal surface of the prepared samples were controlled by changing the preparation temperature and reaction time. The photocatalytic activity of the prepared sample was evaluated using target degradation. This study provides guidance for the practical application of Cu2O.

2. Experimental Part

2.1. Preparation of Cu2O Particles

A total of 0.6 g of copper acetate (Cu(CH3COO)2, AR, Tianjin Fuchen Chemical Reagent Factory, China) was added to 15 mL deionized water, and 12 mL 1.2 mol/L of sodium hydroxide (NaOH, AR, Chengdu Kelon Chemical Reagent Factory, China) was added slowly with stirring for 10 min, served as A. Then, 4 mL 0.2 mol/L glucose (C6H12O6, AR, Chengdu Kelon Chemical Reagent Factory, China) and 1.0 g of polyethylene pyrrolidone (PVP, AR, Chengdu Kelon Chemical Reagent Factory, China) was added to the solution A with stirring for 30 min. Then the solution was transferred into polytetrafluoroethylene-lined stainless steel reactor and keep it for a certain time (6 h, 8 h and 10 h) at a suitable temperature (140°C, 150°C and 160°C). Next, the solution was cooled to the room temperature. The product were collected and washed for three time using ethanol (CH3CH2OH, AR, Anhui Ante Food Co., Ltd., China) and deionized water, and was dried at 60°C for 4 h.

2.2. Characterization of the Samples

The crystalline of the Cu2O particles were obtained using a type 6100 X-ray diffraction (XRD, Shimadzu, Japan). The surface morphology of the Cu2O particles was characterized using a VEGA3 scanning electron microscope (SEM, TESCAN, Czech Republic). The photoelectric performance of the Cu2O particles was tested using a UV-3600 ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu, Japan) and a CHI660E electrochemical workstation (Shanghai Chenhua Co., China).

2.3. Photocatalytic Degradation Experiment

The photocatalytic degradation experiment of NOR (C16H18FN3O3, AR, Shanghai Jiapeng Technology Co., Ltd., China) were carried out according to the literature [24] using Cu2O particles as the photocatalyst. In order to determine its photocatalytic performance, 50 mg of the prepared sample was placed in a quartz tube, and 50 mL of 20 mg/L NOR solution was added. After dark adsorption for 30 min, it was placed under a 500 W xenon lamp for photocatalysis. In the experiment, after the light source was turned on, samples were taken every 30 min and centrifuged to determine the absorbance A of the supernatant at 269 nm. Then the degradation rate e calculated using the following equation (1):

\[
\varepsilon = \frac{A_t}{A_0} \times 100\%
\]

Where \(A_0\) is the initial absorbance value of 20 mg/L NOR and the \(A_t\) is the absorbance value of sample
at time \( t \).

3. Results and Discussion

3.1. Structure and Morphology

In order to study the effect of different hydrothermal temperature and reaction time on the crystal of \( \text{Cu}_2\text{O} \) samples, XRD patterns of samples were performed. It can be seen from Fig.1(a) that the strong and sharp diffraction peaks located at 29.54°, 36.42°, 42.30°, 61.34°, 73.52° and 77.32° of \( \text{Cu}_2\text{O} \) particles prepared at the temperature of 140°C and 150°C are well coincide with the cubic \( \text{Cu}_2\text{O} \) (JCPDS NO.05-0667) [25]. In addition, no other peaks appear in the spectrum, indicating that the prepared \( \text{Cu}_2\text{O} \) has high crystallinity and no impurities. In addition, the (111) crystal plane diffraction peak becomes stronger with increasing temperature. However, the appearance of Cu peaks indicates that the temperature (160°C) is too high, which leads to the excessive reduction during the reaction. Fig.1(b) shows the XRD patterns of different reaction time. From the figure, it can be seen that the intensity of the (111) crystal plane diffraction peak first increases and then decreases with the increase of the reaction time. When the hydrothermal condition is 150°C and 8 h, the diffraction peak of the (111) crystal plane is the strongest, which may be due to the long-term high-temperature reaction, the reaction speed is accelerated, and the (111) crystal plane has crystallized. Previous studies have shown that exposure to more (111) crystal planes in \( \text{Cu}_2\text{O} \) can improve its catalytic activity and stability [26]. Therefore, it can be concluded that the preparation conditions of \( \text{Cu}_2\text{O} \) were 150°C and 8 h.

Figure 1. XRD patterns of \( \text{Cu}_2\text{O} \) at different temperatures (a) and reaction time (b).

In order to characterize the morphology of the prepared samples, SEM tests were performed, and the results are shown in Fig. 2. Fig. 2 (a) is the SEM image of \( \text{Cu}_2\text{O} \) reacted 6 h. It can be seen that the surface of the prepared sample with a smooth surface is not uniform. Most of the particles are octahedral, which may be due to the short reaction time and crystal incomplete growth. Fig.2 (b) is an SEM image of \( \text{Cu}_2\text{O} \) reacted 8 h. It can be seen from the figure 2(b) that the surface of the prepared sample is smooth, the size is uniform, the edges and corners are clearly octahedral, and the particle size is about 5 μm. Fig. 2 (c) is the SEM image of \( \text{Cu}_2\text{O} \) after 10 h of reaction. It can be seen that the sample is partially broken and the surface becomes rough at this time. This may be due to the reaction time being too long and the sample shows dissolution agree with XRD.

Figure 2. SEM of \( \text{Cu}_2\text{O} \) under reaction time conditions (a.6h; b.8h; c.10h).
3.2. Optical Performance

Fig. 3 (a) is a UV-Vis diffuse reflection diagram of Cu$_2$O. It can be seen from the figure that Cu$_2$O samples have relatively obvious absorption in the ultraviolet and visible light regions. The absorption value of Cu$_2$O particles increases rapidly at 600 nm, and the absorption reaches a maximum at 550 nm. There is no significant difference in the absorption boundary. However, the light absorption of sample prepared under 8 h reaction time significantly enhanced at 550 nm. Fig. 3 (b) is the curve of $h\nu$-$(\alpha h\nu)^2$.

The band gap of Cu$_2$O at 6 h, 8 h and 10 h are calculated as 1.97 eV, 1.96 eV and 1.93 eV, respectively. The results are accordance with the literature reported.

![Figure 3. UV-Vis (a) and $h\nu$- $(\alpha h\nu)^2$(b) of Cu$_2$O under different reaction time.](image)

3.3. Photocurrent Test

The photocurrent can be used to characterize the separation efficiency of the photogenerated carriers, i.e. the larger the photocurrent, the higher the separation efficiency of the photogenerated carriers. Fig. 4 shows the photocurrent response curve. From the figure, it can be seen that the sample prepared with a reaction time of 8 h has the largest photocurrent, indicating that the separation efficiency of photogenerated electrons and holes is higher [27].

![Figure 4. Photocurrent response curves of Cu$_2$O at different reaction time.](image)

3.4. Photocatalytic Degradation Test and Analysis

In order to evaluate the photocatalytic performance of the prepared samples, a photocatalytic test was performed using NOR as the target degradation product. As can be seen from the degradation rate curve in Fig. 5 (a), the degradation rate of NOR by Cu$_2$O at different reaction times could reach 71.23%, 79.87% and 70.12%, and the degradation rate of NOR solution without catalyst was 16.35% under the same conditions. From Fig.5 (b), (c) and (d), it can be seen that the main peak position shifted with the progress of photocatalysis, indicating that the catalyst decomposes NOR. In addition, the reducing of the absorption peaks at 272 nm and 324 nm may indicate that NOR is completely decomposed with the extension of light irradiation. The degradation kinetics curves of NOR over as-prepared samples were obtained and shown in Fig. 6. It can be seen that all curves fit the first order
kinetic curve. The kinetic constants of samples prepared under 6 h, 8 h, and 10 h are 0.0046 min⁻¹, 0.0081 min⁻¹, and 0.0056 min⁻¹, respectively. It is concluded that Cu₂O prepared with a reaction time of 8 h has the best degradation effect on NOR, which is consistent with the conclusions obtained from the previous characterization and testing. In order to determine the role of active species in the process of photocatalysis on the prepared samples, an active species capture experiment was performed. Potassium iodide (KI), isopropyl alcohol (IPA), and nitrogen (N₂) were used as scavengers to holes (h⁺), hydroxyl (•OH), and superoxide radical (•O₂⁻) for photocatalytic degradation, respectively [28]. The experimental results are shown in Figure 7. The figure shows that when IPA and N₂ are added during the degradation process, the degradation rate decreases from 79.87% to 23.52% and 30.33%, showing that •OH and •O₂⁻ play a vital role in photocatalysis. When KI was added, the degradation rate of NOR decreased from 79.87% to 55.65%, showing that h⁺ is related to degradation, but are not the key reactive species. Therefore, it may conclude that the photocatalytic degradation of NOR by the prepared catalyst mainly occurs through the synergistic effect of •OH and •O₂⁻.

Figure 5. The degradation rate of NOR (a), the evolution of the absorption spectra of NOR overtime in the presence of Cu₂O with different reaction time (b:6h; c:8h and d:10h)

4. Conclusion
In this paper, Cu₂O particles were prepared by hydrothermal method, and their structure and photoelectric properties were characterized and analyzed. The photocatalytic performance of Cu₂O particles under different reaction times was studied using NOR as a degradation model. The results show that the prepared Cu₂O particles have a better orientation on the (111) crystal plane. With the increase of reaction time, the morphology and particle size of the samples changed significantly. When the reaction time was 8 h, the degradation rate of NOR within 210 min was 79.8%. The degradation of NOR conforms to the first order kinetic curve, •OH and •O₂⁻ play a major role.
Figure 6. Kinetics of degradation of NOR. Figure 7. Photocatalytic activity of sample with different scavenges.

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References
[1] L. Aljerf. Reduction of gas emission resulting from thermal ceramic manufacturing processes through development of industrial conditions. Scientific Journal of King Faisal University, 2016, 17(1): 1-10.
[2] V. Sharma. Oxidative transformations of environmental pharmaceuticals by Cl₂, ClO₂, O₃, and Fe (VI): kinetics assessment. Chemosphere, 2008, 73: 1379-1386.
[3] Lei Tong, Ping Li, Yanxin Wang, et al. Analysis of veterinary antibiotic residues in swine wastewater and environmental water samples using optimized SPE-LC/MS/MS. Chemosphere, 2009, 74: 1090-1097.
[4] A. Silvia, J. Peres, A. Gil-Alvarez, et al. Effective adsorption of non-biodegradable pharmaceuticals from hospital wastewater with different carbon materials. Chemical Engineering Journal, 2017, 320: 319-329.
[5] D. Noemi, Z. Alberto, A. Navalon, et al. Removal of quinolone antibiotics from wastewaters by sorption and biological degradation in laboratory-scale membrane bioreactors. Science of the total Environment, 2013, 442: 317-328.
[6] Jinze Lyu, Junwei Shao, Yanhong Wang, et al. Construction of a porous core-shell homojunction for the photocatalytic degradation of antibiotics. Chemical Engineering Journal, 2019, 358: 614-620.
[7] A. Kumar, A. Kumar, G. Sharma, et al. Sustainable nano-hybrids of magnetic biochar supported g-C₃N₄/FeVO₄ for solar powered degradation of noxious pollutants-synergism of adsorption, photocatalysis & photo-ozonation. Journal of Cleaner Production, 2017, 165: 431-451.
[8] Jianwen Shi, Jingtang Zheng, Yan Hu, et al. Photocatalytic degradation of methyl orange in water by samarium-doped TiO₂. Journal Citation Reports, 2008, 25 (4): 489-496.
[9] D. Bahnmann. Ultrasound metal oxide particles: preparation, photophysical characterization, and photocatalytic properties. Israel Journal of Chemistry, 1993, 33(1): 115-136.
[10] Chunhua Yuan. Study on preparation and photocatalytic properties of La-Cu₂O/MgO composites. Materials Science and Engineering, 2018, 381: 012059.
[11] H. Sudrajat. Unraveling structural properties of Cu₂O loaded on g-C₃N₄ for enhanced photocatalytic hydrogen generation. Materials Research Express, 2018, 5(6): 065519.
[12] Hongbin Yu, Zijia Rong, Ying Lu, et al. Preparation of CeO$_2$-quantum dots/Cu$_2$O nanocomposites with enhanced photocatalytic properties [J]. Journal of Nanoscience and Nanotechnology, 2018, 18: 5794-5798.

[13] Haolan Xu, Wenzhong Wang, Wei Zhu. Shape evolution and size-controllable synthesis of Cu$_2$O octahedra and their morphology-dependent photocatalytic properties. Journal of Physical Chemistry B, 2006, 110(28): 13829-13834.

[14] B. Kumar, S. Saha, A. Ganguly, et al. A facile low temperature (350 °C) synthesis of Cu$_2$O nanoparticles and their electrocatalytic and photocatalytic properties. The Royal Society of Chemistry Advances, 2014, 4: 12043-12049.

[15] Yingchao Liu, Jinbo Xue, Chengzhong Chi, et al. Study on Structure and photocatalytic properties of Cu$_2$O nanocrystal synthesized by low temperature liquid-phase method [J]. Energy and Environment Materials, 2019, 623: 743-744.

[16] Jinlin Long, Jinguo Dong, Xuxu Wang, et al. Photochemical synthesis of submicron- and nano-scale Cu$_2$O particles [J]. Journal of Colloid and Interface Science, 2019, 333: 791-799.

[17] Byron Gates, Yadong Yin, Younan Xia. A solution-phase approach to the synthesis of uniform nanowires of crystalline selenium with lateral dimensions in the Range of 10-30 nm. Journal of the American Chemical Society, 2000, 122: 12582-12583.

[18] F. Sari, C. Lin, J. Ting. Synthesis and characterizations of Cu$_2$O/ Ni(OH)$_2$ nanocomposite having a double co-catalyst for photoelectrochemical hydrogen production. Chemical Engineering Journal, 2019, 368: 784-794.

[19] M. Bhosale, K. Bhatte, B. Bhanage. A rapid, one pot microwave assisted synthesis of nanosize cuprous oxide. Powder Science, 2013, 235: 516-519.

[20] J. Ho, M. Huang. Synthesis of submicrometer-sized Cu$_2$O crystals with morphological evolution from cubic to hexapod structures and their comparative photocatalytic activity. Journal of Physical Chemistry, 2009, 113: 14159-14164.

[21] Lili Ma, Jialin Li, Haizhen Sun, et al. Self-assembled Cu$_2$O flower-like architecture: polyol synthesis, photocatalytic activity and stability under simulated solar light. Materials Research Bulletin, 2010, 45: 961-968.

[22] Tiehu Han, Dongmei Zhou, Huigang Wang. The study on preparation and the effect of adsorption over photocatalytic activities of Cu$_2$O/titanate nanotubes (Cu$_2$O/TNTs). Powder Technology, 2016, 301: 959-965.

[23] Zhenghua Wang, Suping Zhao, Shiyu Zhu, et al. Photocatalytic synthesis of M/Cu$_2$O (M=Ag, Au) heterogeneous nanocrystals and their photocatalytic properties. CrystEngComm, 2011, 13: 2262-2267.

[24] Xiaojiao Yu, Jie Zhang, Jian Zhang, et al. Photocatalytic degradation of ciprofloxacin using Zn-doped Cu$_2$O particles: Analysis of degradation pathways and intermediates. Chemical Engineering Journal, 2019, 374: 316-327.

[25] Xiaojiao Yu, Song Kou, Jie Zhang, et al. Preparation and characterization of Cu$_2$O nanoparticles and its photocatalytic degradation of fluoroxypr. Environmental Technology, 2018, 39(22): 2967-2976.

[26] Lingling Wu, Lok-kun Tsui, Nathan Swami, et al. Photoelectrochemical stability of electrodeposited Cu$_2$O films. Journal of Physical Chemistry C, 2010, 114: 11551-11556.

[27] Y. Won, L. Stanciu. Cu$_2$O and Au/Cu$_2$O particles: surface properties and applications in glucose sensing. Sensors, 2012, 12: 13019-13033.

[28] Junhui Sun, Hua Yang, Tao Xian, et al. Polyacrylamide gel preparation, photocatalytic properties, and mechanism of BiVO$_4$ particles. Chinese Journal of Catalysis, 2012, 33(12): 1982-1987.