Green Microwave Synthesis of Cuprous Oxide Microparticles And the Photocatalytic Degradation Properties

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Abstract: Cu_2O microparticles with three different morphology were prepared by a green, facile and additive free microwave synthesis method with household common microwave oven. The morphology of cuprous oxide can be easily controlled by adjusting the amount of glucose added, via which the sphere, cube and octahedron cuprous oxide were synthesized. The phase, morphologies and optical properties of cuprous oxide were characterized by XRD, SEM and UV-vis. The photocatalytic efficiency are evaluated by monitoring the photocatalytic degradation of Methylene blue (MB) solution under visible light irradiation. The results show that the spherical, cubic and octahedral cuprous oxide exhibited the high degradation efficiency.

1 INTRODUCTION

Cuprous oxide (Cu_2O) is a typical P-type semiconductor material with a band gap of approximately 2.17 eV, with unique optical and electrical properties and photoelectrochemically properties[S. Kakuta et al.,2009;J.Y. Kim et al., 2009 and D.J. Norris et al. 2001]. With the development of nanotechnology, Cu_2O nanoparticles have widespread applications in solar energy conversion, photo catalytic degradation of organic pollutants and catalysis in organic synthesis[D.J. Norris et al. 2001].

Cu_2O nanoparticles can be prepared by the solid-phase synthesis, liquid-phase method and gas-phase method[H. Pang et al,2010; P. Liu et al.,2011 and K.D. Bhatte et al.,2010]. Comparatively speaking in the liquid-phase method, the chemical deposition method require relatively simple experimental conditions and are easy to operate, which is often used. However, in order to obtain nanoparticles with uniform morphology and particle size, most of the chemical deposition methods need to use drastic synthesis conditions like high temperature and pressure, use of toxic reagents, long reaction time, and requirement of external additives during the reaction[F.K. Liu et al.,2004; K.D. Bhatte et al.,2012; F.K. Liu et al.,2008; G.C. Xi et al.,2008].

Currently microwave assisted synthesis attracts more attention owing to its advantages like volumetric heating, fast kinetics, selectivity, less energy requirements and time economy[QingweiZhu et al.,2011; Manohar A. et al.,2013]. There are also some studies about preparation of cuprous oxide powders by microwave methods. However, microwave method prepared Cu_2O nanocomposites reported in the literature need either the addition of surfactants[QingweiZhu et al.,2011] or use of toxic reducer [Manohar A. et al.,2013], or microwave irradiation time is as long as 0.5-1 hours, or require special microwave reaction equipment[E. Lu Hipolito et al.,2017; Jun Liu et al.,2009]. Therefore, it is still a challenge to develop simple and controllable routes for the visible-light responsive Cu_2O with excellent photocatalytic performance via microwave assisted synthesis.

Based on the above considerations, this work described a facile and additive free microwave method for creating high photocatalytic activity Cu2O, which synthesize three types of cuprous oxide microcrystals with household common microwave oven. The phase, morphologies and optical properties of three types of cuprous oxide were characterized by XRD, SEM, and UV-vis.

Their photocatalytic activities are determined by monitoring the photocatalytic degradation of MB.

2 EXPERIMENT

2.1 Synthesis of Cu_2O Nanoparticles

Nanocrystalline formation was carried out in domestic Galanz microwave oven operating at 180 W and frequency of 2.45 GHz. In a typical Cu_2O synthesis process, 15ml aqueous solution of sodium hydroxide (4M) was added slowly into 200ml aqueous solution of $CuSO_4 \cdot 5H_2O$ (0.1 M) in a beaker at room temperature (the whole process lasts for 2min) while stirring for 30min. The calculated volume of glucose solution (1.0 M) was slowly added into the above solution and then placed in a microwave oven. Reaction was performed at 180 W for 10 minutes. The products were collected by centrifugation, washed with deionized water and absolute ethanol, and dried in a vacuum at 50 °C for 24 h.

2.2 Method of Characterization

The morphologies were examined using SEM on a Hitachi S-4800. The formed Cu2O powder was then characterised by X-ray diffraction (XRD) (Brukar D8 advance X-ray diffractometer using CuKα=1.54060 Å) with scanning 2 theta (θ) angle ranging from 15° to 100°. UV–vis diffuse reflectance spectra were obtained by UV–vis spectrophotometer equipped with an integrated sphere (TU-1901, China). BaSO4 was used as a reference for the measurements.

2.2 Photocatalytic Reaction

0.2 g sample of Cu_2O was dispersed in 10 mg/L MB solution at 25 ◦C in a 250ml quartz reactor and was illuminated with a 250 W tungsten lamp. Before irradiation, the suspensions were sonicated in the dark for 30 min to make the powder disperse well in the solution. After that, 1ml of H_2O_2 was added into above suspension and then the lamp was turned on to conduct the photocatalytic reaction at room temperature while magnetic stirring was kept all along with the reaction. At regular intervals, 10 ml of the suspension was sampled and separated by centrifugation at 8000 rpm for 10 min. The concentration of remaining pollutant was measured by its absorbency (A) at 484 nm with a Hitachi UV-3010 spectrophotometer[P. Chen et al.,2004].

3 EXPERIMENT

3.1 Characterization of Prepared Cu2O

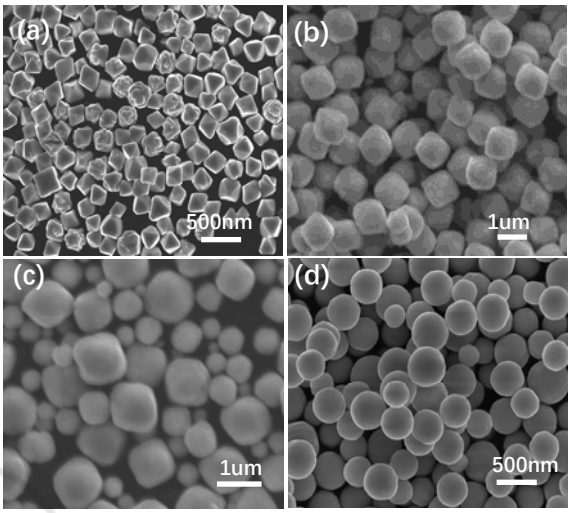

Figure 1: SEM images of the Cu2O samples with different morphologies.

(a)octahedron, (b) cube, (c) sphere and cube,(d) sphere

Fig. 1 shows the morphology of Cu_2O sample prepared at the molar ratio of glucose solution to copper sulfate of 0.6, 1.0, 1.25 and 2.0 respectively. Fig.1(a) shows most of the crystals are octahedral shape with the size about 200-400 nm. Fig.1(b) discloses cubic shape crystal with the size about 0.8-1um. The spherical crystals are shown in Fig.1(d) with the particle size about 200-350nm. The crystals shown in Fig.(c) have a spherical and square mixed crystals. As can be seen from Fig.1, the three types of cuprous oxide particles are well dispersed without any particles aggregate. The amount of reducing agent glucose determines the saturation of the Cu^+ in the system, which determines the mode growth and the final morphology of the cuprous oxide nuclei[Xiaoyan Zhou et al.,2014]. The SEM results the morphology of cuprous oxide should can be controlled by adjusting the amount of glucose added.

The XRD patterns of four kinds Cu_2O in Fig. 2 shows that all diffraction peaks, they are (110), (111), (200), (220), (311) and (222) planes, which can match well with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card No. 78-2076. No impurity peaks were observed in this pattern, which fully demonstrates that the

crystallinity of Cu_2O is very good and the purity is high.

The ultraviolet absorption spectra of Cu_2O powders was shown in Fig.3, which indicates that three prepared samples exhibit broad and strong absorption peaks in the visible region. The sphere, cube and octahedron Cu_2O has the maximum absorption peak at 511nm, 512 nm, and 495 nm respectively. The forbidden band width of cuprous oxide is calculated according to a classical semiconductor formula $\alpha EP=K(EP-Eg)^{1/2}$. The band gaps calculated for spheres, cubes, and octahedron Cu_2O were 2.42 eV, 2.42 eV, and 2.50 eV, respectively, which corresponds to a typical nanosize Cu_2O[W. Wang et al.,2011].

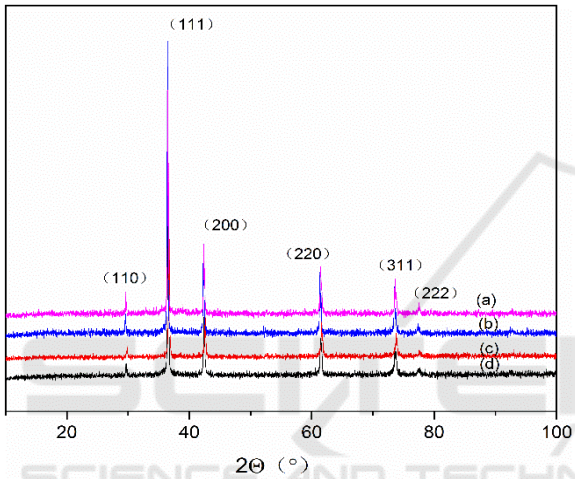

Figure 2: XRD pattern of different morphology of Cu_2O.

(a) sphere (b)octahedron；(c) cube；(d) mixed shape

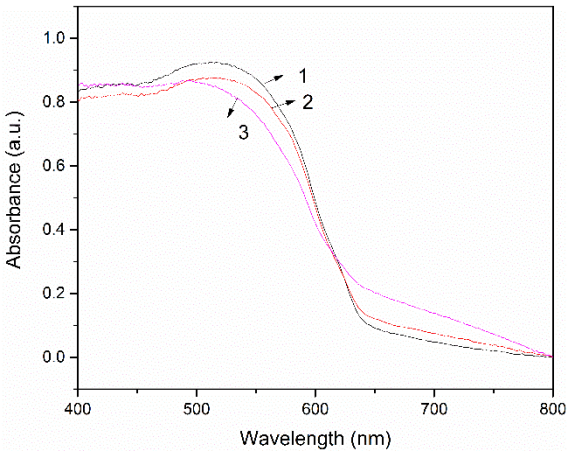

Figure3:UV–vis absorption spectra of Cu2O .

(1) sphere (2)octahedron；(3) cube；

3.2 Photocatalytic degradation of MB

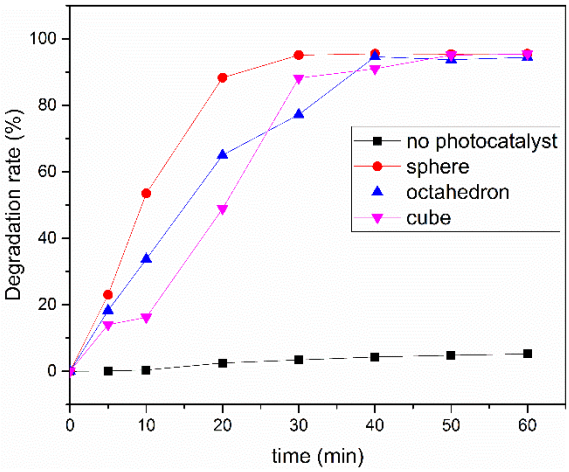

Figure 4:Catalytic degradation of MB curves byCu2O.

The photocatalytic abilities of cuprous oxide are evaluated by the photocatalytic discoloration of $10mgL^{-1}$ MB as shown in Fig.4. It can be seen that direct decomposition of MB without cuprous oxide is pretty low. As for the individual cuprous oxide, it can be found that sphere Cu_2O shows the highest photocatalytic activity with the almost complete discoloration at the beginning 30min. This is due to the fact that spherical Cu_2O has a relatively large specific surface area and can adsorb more substances at the beginning. However, when the degradation time exceeded 30 minutes, the cubic and octahedral cuprous oxide exhibited the same high efficiency of degradation as the spherical cuprous oxide.

4 CONCLUSIONS

Sphere, cube and octahedron cuprous oxide were synthesized by a facile and additive free microwave synthesis with household common microwave oven via adjusting the amount of glucose. The phase, morphologies and optical properties of three types of cuprous oxide were characterized by XRD, SEM, and UV-vis. SEM images indicate the three types of cuprous oxide particles are well dispersed without any particles aggregate. XRD and UV-vis spectrum show s all diffraction peaks of the three different morphology Cu_2O can match well with the standardCu_2O peak and all of the Cu_2O exhibit broad and strong absorption peaks in the visible region. The results of photocatalytic efficiency show that the spherical, cubic and octahedral cuprous oxide exhibited the high degradation efficiency.

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