PREPARATION OF CUPROUS-OXIDE NANOPARTICLES USING ASCORBIC ACID AS REDUCING AGENT AND ITS PHOTOCATALYTIC ACTIVITY

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Abstract. In this present paper, cuprous-oxide (Cu$_2$O) nanoparticles were successfully fabricated using ascorbic acid as a reducing agent. The purity and characteristics of Cu$_2$O nanoparticles were determined with XRD and FT-IR techniques. The morphology and particle size of the material were characterized using SEM and TEM, respectively. The results show that the concentration of sodium hydroxide affects the morphology and particle size of the material. Furthermore, the Cu$_2$O nanoparticles with a particle size of 70–80 nm exhibit good photocatalytic activity on photodegradation of Rhodamine B under visible light, and the photocatalytic degradation ratio of Rhodamine B is 70%.

Keywords: cuprous-oxide nanoparticles, ascorbic acid, photocatalytic degradation, photocatalytic activity, Rhodamine B

1 Introduction

Cu$_2$O with a small band gap of about 2 eV [1] is a p-type semiconductor. It is considered as a promising material in electronics, solar energy conversion, and catalysis [2, 3]. According to Hu et al., the conductive degree of the pastes-copper powder depends on the morphology and size of the Cu$_2$O precursor [4]. Varying efforts have also been devoted to the preparation of Cu$_2$O with various morphologies such as cube [5, 6], sphere [7, 8], tubular-like [5], and octahedron [9, 10]. Nevertheless, the majority of approaches utilize inconvenient techniques such as irradiation of microwave [6, 8] or organic additive as modifier [5, 7]. In this study, Cu$_2$O nanoparticle was prepared by reducing Cu (II) in alkaline media using ascorbic acid as a reducing agent without a template. The influence of the NaOH concentration on the shape of Cu$_2$O nanoparticles was investigated.

Furthermore, its photocatalytic activity in photodegradation of Rhodamine B under visible light was also studied.

2 Experimental

2.1 Materials

Copper sulfate (CuSO$_4$.5H$_2$O), ascorbic acid (C$_6$H$_8$O$_6$), sodium hydroxide (NaOH) purchased from Beijing Chemical Reagent Company, and ethanol as a solvent were of analytical grade and were used without further purification.

2.2 Preparation of Cu$_2$O nanoparticles

In different sequences of the experiment, the volumes of CuSO$_4$, NaOH, and C$_6$H$_8$O$_6$ solutions were kept constant at 20, 40, and 50 mL, respectively. The concentration of CuSO$_4$ and
ascorbic acid is 0.5 and 0.1 M, respectively. Whereas, the concentration of NaOH is 0.5, 1.0, and 1.5 M.

Firstly, the precursor was prepared by dropping 40 mL of NaOH solution into 20 mL of the CuSO₄ solution under stirring in a 200 mL flask at room temperature. Secondly, 50 mL of the ascorbic acid solution was added into the mixture by dropping on the surface of the precursor solution under vigorous stirring to form a brick-red mixture with stable colour. Finally, the products were collected by centrifugation, washed five times with distilled water and three times with ethanol, and then dried at 60 °C for 24 h [11].

The XRD study of the powder was carried out using an X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation (λ = 1.541 Å). The morphology and particle size of the Cu₂O nanoparticles were investigated using SEM (Hitachi S4800, Japan) and TEM (JEM 1400, JEOL, Japan). The FTIR spectra of the material were taken on an FT-IR 8400S spectrometer (Shimadzu, Japan) using KBr pellets.

2.3 Photocatalytic degradation of Rhodamine B

0.1 g of Cu₂O powder with a particle size of 76 nm was added to a 200 mL flask containing 100 mL of a RhB (Beijing, China) solution with a concentration of 2 mg/L. Cu₂O is dispersed in the solution with vigorous stirring. The whole system is placed under sunlight or the light of a mercury lamp (E27-125 W) for 4 hours. The sample was taken every 30 minutes to determine the transmittance of the solution. The sample is centrifuged at a rate of 1000 rpm for 15 minutes to remove the catalyst before UV-VIS measurement. The degree of degradation of RhB was calculated according to the following formula

$$\alpha(\%) = \frac{C_0 - C}{C_0} \times 100$$

where C₀ and C are the initial concentration of RhB and the concentration of RhB at the time of taking the sample, respectively [10].

3 Results and discussion

3.1 Formation of Cu₂O nanoparticles

As shown in Fig. 1, there is a change in colour during the reaction. It is obvious that the initial solution (CuSO₄) is blue and transparent (Fig. 1a). When NaOH was added, the colour of the reaction mixture became brick-red, the characteristic colour of Cu(OH)₂ (Fig. 1b). The brick-red characteristic colour of Cu₂O appeared after ascorbic acid was dumped into the reaction mixture (Fig. 1c). In this process, Cu²⁺ ions are reduced by ascorbic acid to form Cu₂O nanoparticles. The reactions are as follows [11]:

$$\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2$$  (1)

$$2\text{Cu(OH)}_2 + \text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{Cu}_2\text{O} + \text{C}_6\text{H}_6\text{O}_6 + 3\text{H}_2\text{O}$$  (2)

The total reaction is

$$2\text{Cu}^{2+} + \text{C}_6\text{H}_8\text{O}_6 + 4\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{C}_4\text{H}_6\text{O}_6 + 3\text{H}_2\text{O}$$  (3)

Fig. 1. CuSO₄ solution (a), CuSO₄ solution with NaOH (b), and reaction mixture with ascorbic acid (c)
3.2 Characterization of Cu₂O nanoparticles

As shown in Fig. 2, the colour of the Cu₂O nanoparticles in the reaction mixture and the powder state (inset in the figure) became darker with the NaOH concentration. This result may be due to the enhancement of the particle size (Table 1). The XRD patterns of the Cu₂O products are shown in Fig. 3. On the diffraction patterns, the Cu₂O products prepared with different concentrations of NaOH have characteristic peaks at 29.61°, 36.48°, 42.38°, 61.46°, 73.56°, and 77.52° corresponding to (110), (111), (200), (210), (311), and (222) plane of Cu₂O. These patterns indicate that the products are pure Cu₂O because no peaks of Cu and CuO are observed [9, 12].

Fig. 2. Colour of Cu₂O in reaction mixture and in powder state with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)

Fig. 3. XRD patterns of Cu₂O nanoparticles prepared with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)
As shown in Fig. 4, the FI-IR spectra of all Cu$_2$O products prepared with different concentrations of NaOH show a peak at 623 cm$^{-1}$ corresponding to the Cu–O bond of the Cu$_2$O crystal [13, 14]. The FI-IR spectra also reveal that there is a slight shift to lower wavenumber as NaOH concentration increases. This may be due to the decrease in particle size (Table 1).

![Fig. 4. FT-IR spectra of Cu$_2$O nanoparticles prepared with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)](image)

**Table 1.** Size of Cu$_2$O particles prepared with different concentrations of NaOH

<table>
<thead>
<tr>
<th>Note</th>
<th>NaOH concentration (mol/L)</th>
<th>Size of Cu$_2$O (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.5</td>
<td>71</td>
</tr>
<tr>
<td>b</td>
<td>1.0</td>
<td>76</td>
</tr>
<tr>
<td>c</td>
<td>1.5</td>
<td>80</td>
</tr>
</tbody>
</table>
As shown in Fig. 5, the TEM image and distribution histogram of Cu$_2$O nanoparticles prepared with NaOH concentration of 0.5 M (A, a) reveal that the Cu$_2$O particles have a spherical shape in the cluster state with a particle diameter of about 71 nm, and the particle size ranges from 30 to 89 nm with a nearly normal distribution. When the NaOH concentration is 1.0 M, the
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3.3 Photocatalytic performance

Fig. 6 depicts the degradation of RhB on Cu$_2$O nanoparticles with a size of 76 nm under sunlight and mercury light. It can be seen that the degree of degradation of RhB under sunlight is smaller than that under mercury light at 60 and 70%, respectively. It could be concluded that the degradation of RhB has a lower efficiency under sunlight compared with mercury light. However, for a large-scale application, sunlight should be chosen because of the low cost and convenient equipment.

4 Conclusions

A facile chemical approach with ascorbic acid as a reducing agent without a template was developed to prepare Cu$_2$O nanoparticles. The experiments show that pure Cu$_2$O nanocrystals were efficiently synthesized in the alkali media, and the concentration of NaOH has an impact on the particle size of the material. Cu$_2$O nanoparticles with a particle size of 76 nm have a good photocatalytic activity on photodegradation of RhB with degradation ratio of RhB reaching to 70% under visible light.

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![Degradation of RhB under visible light: sunlight and mercury light](image-url)
Conflict of interests
The authors declare that there is no conflict of interest regarding the publication of this article.

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References


