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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_2O) nanoparticles were successfully fabricated using ascorbic acid as a reducing agent. The purity and characteristics of Cu_2O 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_2O 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_2O 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_2O precursor [4]. Varying efforts have also been devoted to the preparation of Cu_2O 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_2O 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_2O 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 ($CuSO_4.5H_2O$), ascorbic acid ($C_6H_8O_6$), 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_2O nanoparticles

In different sequences of the experiment, the volumes of $CuSO_4$, NaOH, and $C_6H_8O_6$ 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 $CuSO_4$ 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 K_α radiation (λ = 1.541 Å). The morphology and particle size of the Cu_2O 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 Cu_2O 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. Cu_2O 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 C_0 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 Cu_2O nanoparticles

As shown in Fig. 1, there is a change in colour during the reaction. It is obvious that the initial solution ($CuSO_4$) 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 Cu_2O appeared after ascorbic acid was dumped into the reaction mixture (Fig. 1c). In this process, Cu^{2+} ions are reduced by ascorbic acid to form Cu_2O nanoparticles. The reactions are as follows [11]:

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

$$2Cu(OH)_2 + C_6H_8O_6 \rightarrow Cu_2O + C_6H_6O_6 + 3H_2O \quad (2)$$

The total reaction is

$$2Cu^{2+} + C_6H_8O_6 + 4OH^- \rightarrow Cu_2O + C_6H_6O_6 + 3H_2O \quad (3)$$

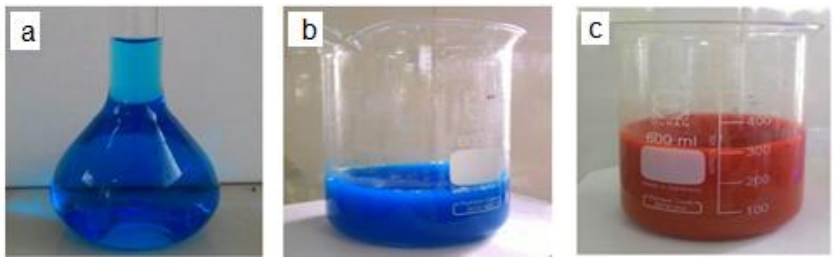

Fig. 1. CuSO4 solution (a), $CuSO_4$ solution with NaOH (b), and reaction mixture with ascorbic acid (c)

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3.2 Characterization of Cu_2O nanoparticles

As shown in Fig. 2, the colour of the Cu_2O 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 Cu_2O products are shown in Fig. 3. On the diffraction patterns, the Cu_2O 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 Cu_2O. These patterns indicate that the products are pure Cu_2O because no peaks of Cu and CuO are observed [9, 12].

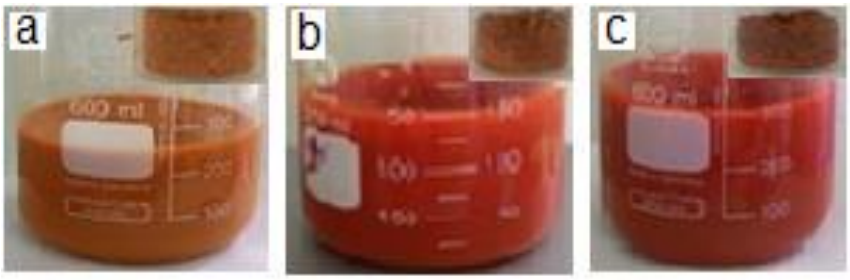

Fig. 2. Colour of Cu_2O in reaction mixture and in powder state with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)

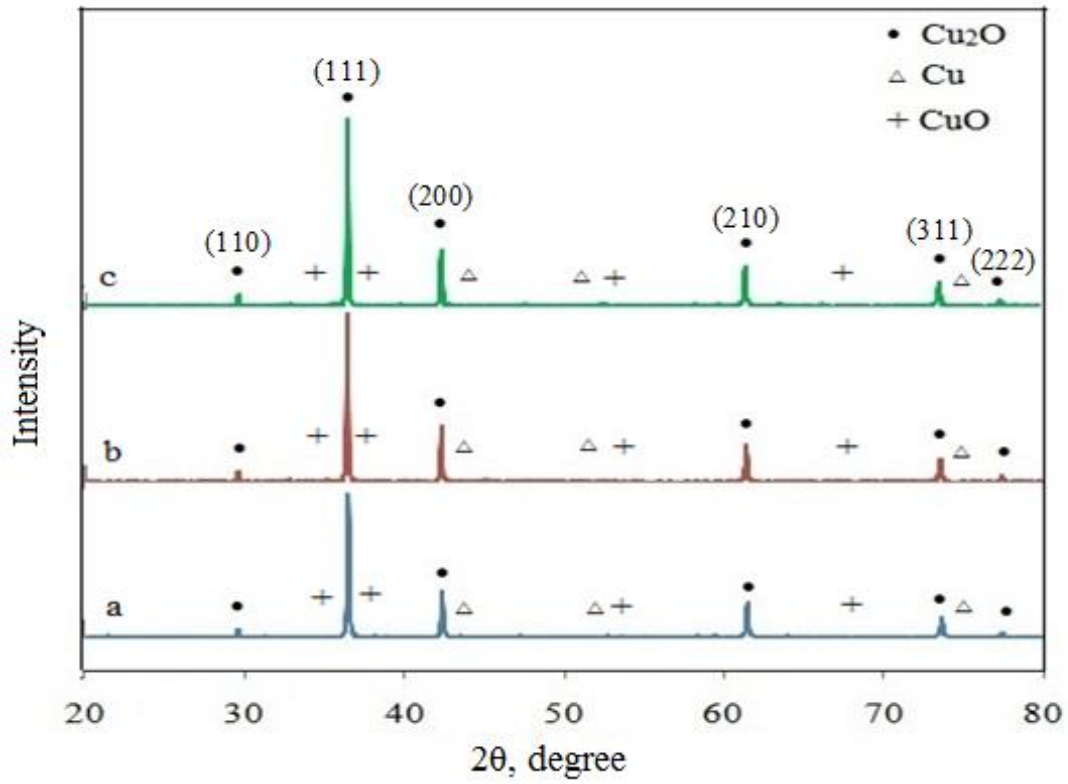

Fig. 3. XRD patterns of Cu_2O nanoparticles prepared with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)

As shown in Fig. 4, the FI-IR spectra of all Cu_2O products prepared with different concentrations of NaOH show a peak at 623 cm^{-1} corresponding to the Cu–O bond of the Cu_2O 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).

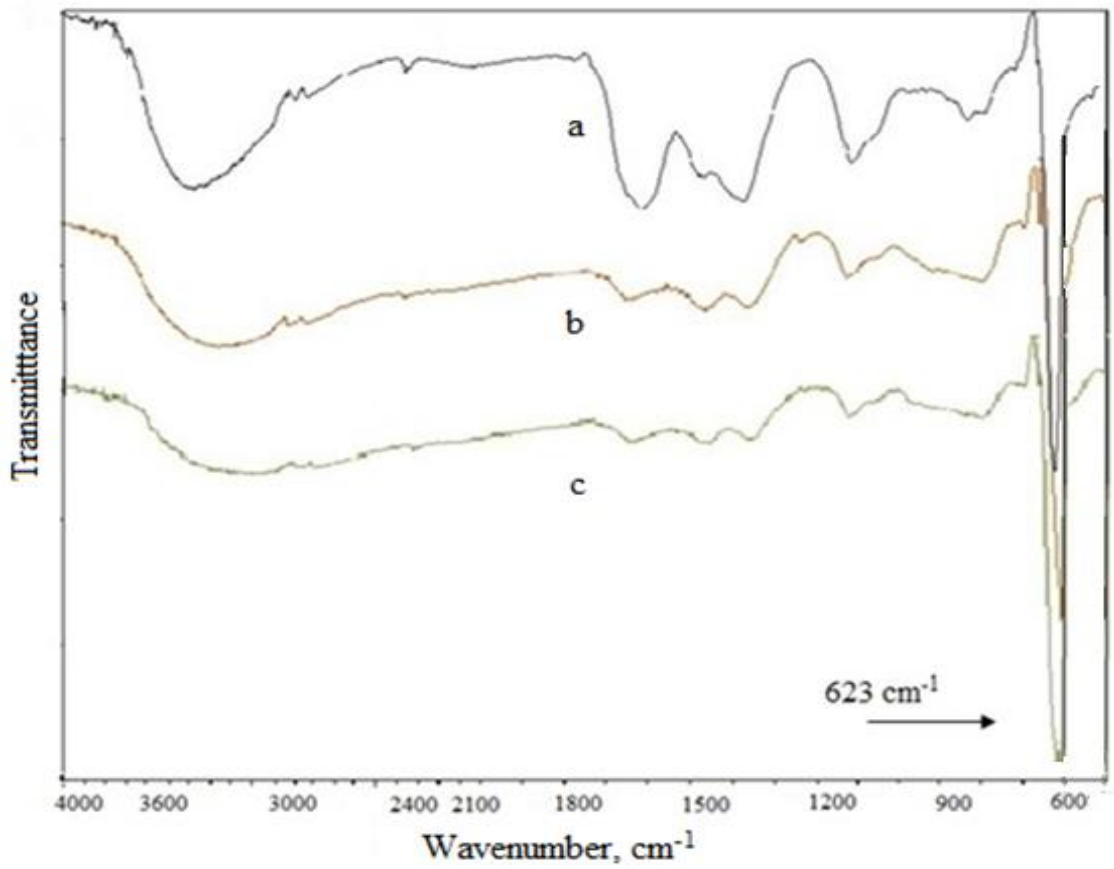

Fig. 4. FT-IR spectra of Cu_2O nanoparticles prepared with different NaOH concentrations: 0.5 M (a), 1.0 M (b), and 1.5 M (c)

Table 1. Size of Cu_2O particles prepared with different concentrations of NaOH

Note	NaOH concentration (mol/L)	Size of Cu_2O (nm)
a	0.5	71
b	1.0	76
c	1.5	80

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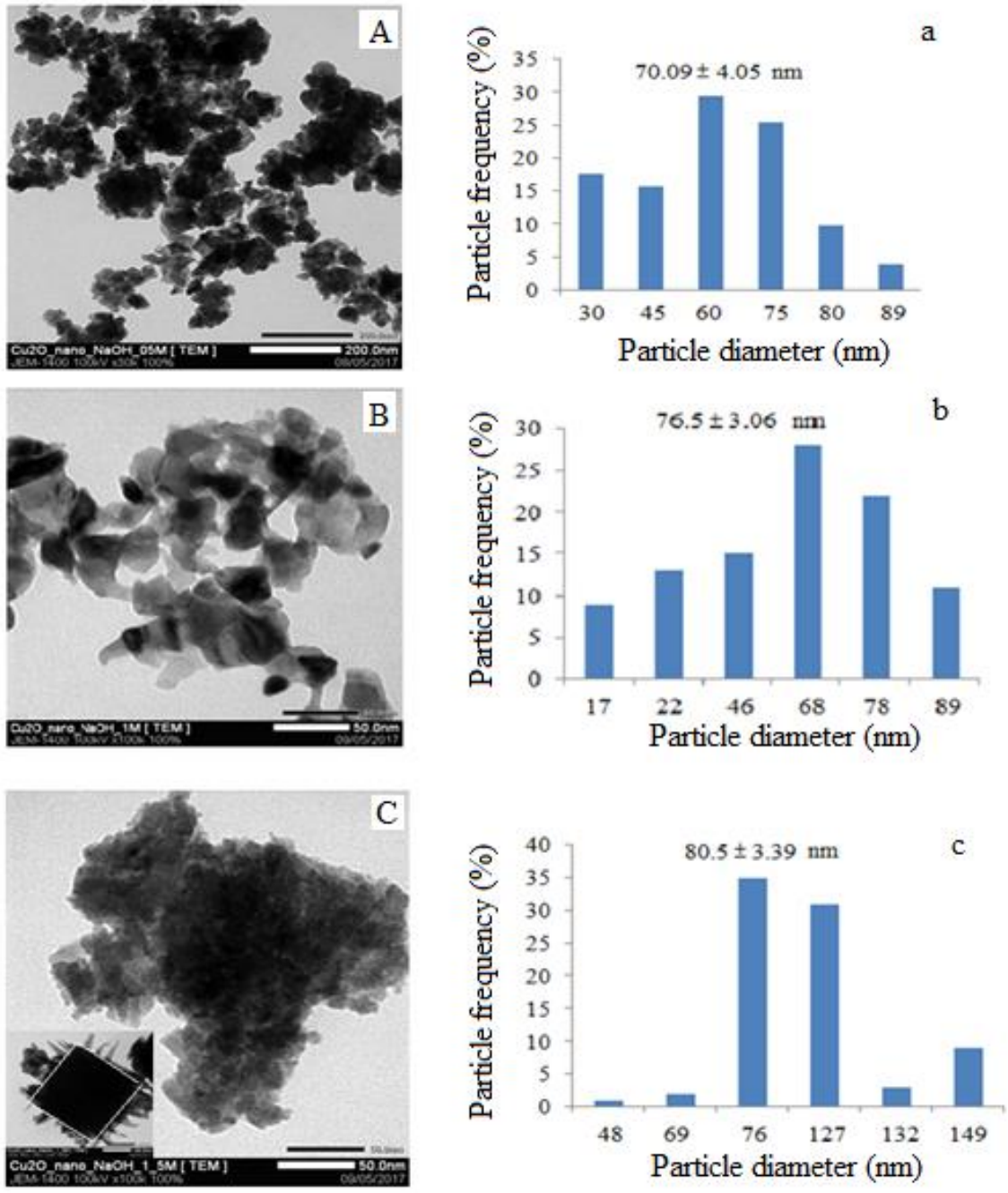

Fig. 5. TEM images and size distribution histogram of Cu_2O nanoparticles prepared with different concentrations of NaOH: 0.5 M (A, a); 1.0 M (B, b), and 1.5 M (C, c)

As shown in Fig. 5, the TEM image and distribution histogram of Cu_2O nanoparticles prepared with NaOH concentration of 0.5 M (A, a) reveal that the Cu_2O 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

particle diameter is 76 nm, and the particle size ranges from 17 to 89 nm with a nearly normal distribution. A different distribution is observed when the NaOH concentration is 1.5 M, and the particle size ranges from 70 to 130 nm with the mean of particle size of about 80 nm. When the concentration of NaOH increases, the Cu_2O nanoparticles tend to cluster, forming large particles with an octahedron shape (Fig. 5C). The mechanism for the formation of nanoparticle shapes via changing the concentration of NaOH was mentioned by Wang et al. [11]. According to this study, the shapes of the nanoparticles depend on the adsorbed quantity of the OH^- ions on the surface of the Cu_2O particles. When the concentration of NaOH is low, the adsorbed quantity of OH^- ions on the surface of Cu_2O particles is relatively small. Therefore, when the repulsion between single nuclei, primary particles, and molecule clusters is weak, aggregation is the overwhelming growth mode, and the crystal nuclei grow into spherical particles as a result of aggregation. When the concentration of NaOH increases, the adsorbed quantity of OH^- ions on the surface of Cu_2O particles is greater. This leads to the repulsion among primary particles, restraining the aggregation growth mode. Moreover, the high density of OH^- on the (111) facet restrains the growth of this (111) facet [11]. As a result, the morphology of Cu_2O is mostly octahedral.

3.3 Photocatalytic performance

Fig. 6 depicts the degradation of RhB on Cu_2O 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_2O nanoparticles. The experiments show that pure Cu_2O nanocrystals were efficiently synthesized in the alkali media, and the concentration of NaOH has an impact on the particle size of the material. Cu_2O 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.

Funding statement

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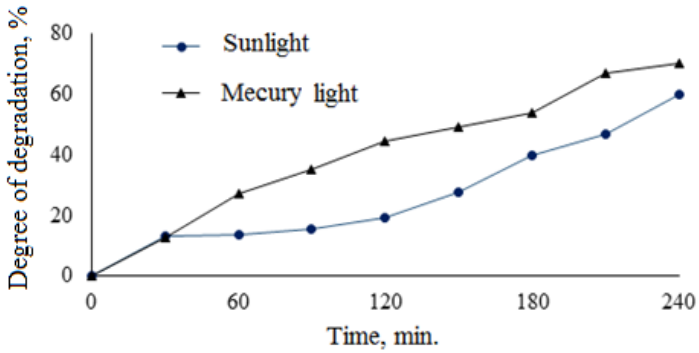

Fig. 6. Degradation of RhB under visible light: sunlight and mercury light

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Conflict of interests

The authors declare that there is no conflict of interest regarding the publication of this article.

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