

Preparation and photocatalytic activity of Cu₂O nanoparticles

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An electron beam irradiation route has been developed for the preparation of Cu₂O nanoparticles, with poly(ethylene glycol) (PEG, $M_w = 10\,000$) as a template, and without using a further reducing reagent. Under various synthetic conditions, the composition of Cu₂O was changed by adjusting the PEG concentration and pH values of the starting solutions. Transmission electron microscopy data revealed that the morphology evolves from an irregular shape into a sphere and cube with increasing the concentration of PEG, and cube to irregular shape with increasing pH of starting solutions. UV-vis diffuse reflectance spectroscopy data indicated that the Cu₂O particles absorbed visible light. The photocatalytic activity of Cu₂O was evaluated by studying the decomposition of phenol and methyl orange in aqueous solution under irradiation with visible light.

Keywords: Cu₂O; poly(ethylene glycol); electron beam irradiation; photodegradation

1. Introduction

Tailoring the structure, size, and shape of inorganic materials is an important goal in syntheses of various materials due to possibility of obtaining unique shape and size-dependent properties. Cuprous oxide (Cu₂O), an important p-type semiconductor, is a relatively non-toxic material [1]. It has the band gap of 2.17 eV, and it has been shown to be useful for lithium ion batteries [2, 3], magnetic storage media [4], sensors [5] and catalysts [6]. The size and shape of Cu₂O particles are fundamentally important factors determining their properties [3, 7, 8]. Therefore, one of the challenges in syntheses of Cu₂O nanocrystals is to control not only the size but also shape of the crystal. In the past few years, numerous Cu₂O nanostructures such as hollow spheres [9], nanowires [10, 11], nanocages [12–14], octahedra [7, 15, 16], nanocubes [17], have been synthesized. Among these morphologies, nanocubes and octahedra may be the most interesting,

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owing to their tailor-made properties, and on the other hand, as they possess the highest symmetries, other more complex particle structures can be derived from these simple structural forms [18]. The selection of organic additives can be very important for controlling the morphology and size of Cu_2O nanoparticles. The organic additives often adsorb selectively onto different crystal faces and retard their growth rates, affecting the final morphology of the crystals [19]. For example, Cu_2O nanocubes can be formed in the presence of cetyltrimethylammonium (CTAB) [17], nanowires have been synthesized with poly(vinyl pyrrolidone) (PVP) as soft templates [10]. Recent reports revealed that the non-ionic surfactants PEG200, PEG400, PEG600, PEG8 000 or PEG20000 can be applied to adjust both the size and shape of Cu_2O nanoparticles [20–26].

A variety of techniques, including electrodeposition [27], γ -irradiation [28], oxidation of copper [29], solution-phase synthesis [4] etc., have been employed to make Cu_2O form into various shapes. Here, in the present work, we utilize the electron beam irradiation method to fabricate Cu_2O nanoparticles. The effects of the PEG concentration and pH of the solution on the shape of the products are studied. X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and UV-vis diffuse reflectance spectrometry were applied to study the structure, morphology, size and optical properties of the Cu_2O samples. The photodegradation of phenol and MO were employed to evaluate the photocatalytic activities of Cu_2O nanocrystals under visible light illumination.

2. Experimental

Syntheses of Cu_2O samples. All reagents were analytical grade and were used as received. Milli-Q purified water was used for all of the experiments. Typically, the Cu_2O nanoparticles were prepared by the following procedure. Varied amounts of PEG and 1.25 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 96 cm^3 of water and ultrasonicated for 20 min. Next, 3.1 cm^3 isopropanol (as a scavenger of oxidative radicals such as $\cdot\text{OH}$ produced during water-radiolysis) was added to the mixed solution. Then the solution was adjusted to advisable sensible pH values by ammonia solution, irradiated by the GJ-2-II accelerator (Dynamitron, 2 MV, 10 mA, manufactured from Shanghai Xianfeng electrical factory) at an absorbed dose of 280 kGy. Yellow orange precipitates were obtained after irradiation and were then collected by centrifugation, following by washing with water and absolute alcohol three times, respectively. Finally, they were dried in a vacuum oven at 60°C for 4 h.

Characterization. XRD was performed with a Rigaku D\Max-2550 powder X-ray diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). The TEM images were obtained on a JEOL JEM-200CX microscope operating at 160 kV. The DRS was measured with a Hitachi U-3010 spectrophotometer, in order to study the optical properties of the

products. Brunauer–Emmett–Teller (BET) surface areas of the samples were determined using a 3H-2000III nitrogen adsorption apparatus.

Photocatalytic properties of Cu_2O . A series of 0.05 g samples of Cu_2O were dispersed in 100 cm^3 phenol or MO solution (50 mg/dm^3) for 1 h in the dark, in order to obtain absorption equilibrium. Then the solution was irradiated with the radiation of a 500 W halogen-tungsten lamp, with air bubbles during the photocatalytic reaction. At certain intervals, 4 cm^3 of phenol or MO was centrifuged and analyzed.

3. Results and discussion

3.1. Effect of the PEG concentration on the morphology of Cu_2O

A common method used to adjust the size and shape of nanoparticles is to change the concentration of the capping surfactant or the capping group. Generally, upon increasing the concentration of the capping surfactant, the particle size decreases because the sites for further nucleation and growth are blocked by the addition of more capping agent.

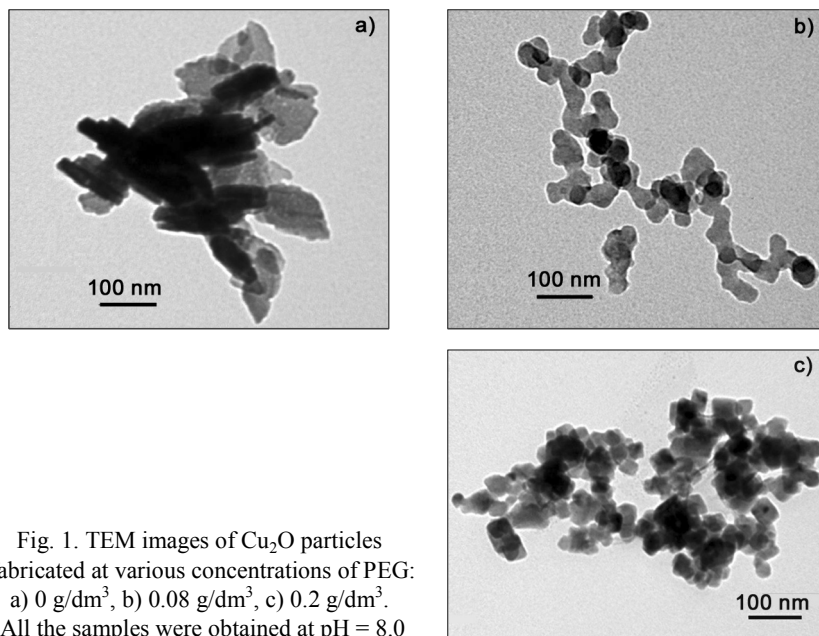


Fig. 1. TEM images of Cu_2O particles fabricated at various concentrations of PEG: a) 0 g/dm^3 , b) 0.08 g/dm^3 , c) 0.2 g/dm^3 . All the samples were obtained at pH = 8.0

Figure 1 shows the TEM images of the Cu_2O particles synthesized at various concentrations of PEG ranging from 0 to 0.20 g/dm^3 . As shown in Fig. 1a, Cu_2O particles with irregular morphology are obtained in the absence of PEG, and their sizes are

higher than 70 nm. With the addition of a small quantity of PEG (0.08 g/dm³), the as-prepared Cu₂O particles are spherical or square-like, having an average size of 22 nm (Fig. 1b). Cubic Cu₂O nanoparticles with edge lengths higher than 20 nm are obtained at higher concentrations of PEG (0.20 g/dm³, Fig. 1c). As one can see from Fig. 1, in this reaction system, it is obvious that Cu₂O nanoparticles fabricated at various amounts of PEG exhibit dramatically different morphologies.

The TEM observations lead us to believe that the concentration of PEG plays an important role in controlling the morphology of the Cu₂O. As a non-ionic surfactant, PEG has twisted polymeric segments, and the polymeric chain is alternately hydrophilic and hydrophobic [26]. The hydrophilic groups have oxygen atoms which can coordinate with Cu²⁺ to form Cu(II)–PEG complex. The non-combined PEG molecules may adsorb on the surface of the particles. They may adsorb onto a certain crystallographic plane, thereby influencing the surface energies and external growth environments of the crystal faces, thus, affecting the growth kinetics. Based on previous reports, Murphy [30] pointed out that preferential adsorption of molecules and ions in solution to different crystal faces causes the nanoparticles to grow into various shapes, by controlling the growth rates along different crystal axes. When PEG is absent or the quantity is small, the PEG molecules cannot effectively wrap the neonatal Cu₂O, thus the crystals exhibit irregular shapes. In the presence of excessive PEG, more and more PEG molecules adsorb on the <100> crystal faces, thus lowering the surface energies, and cubic shapes of Cu₂O are obtained. Consequently, a dramatic change in the morphology occurs.

3.2. Influence of pH of the starting solution on the products

Control experiments were carried out to investigate the influence of pH of starting solutions on the products. The morphology of the Cu₂O particles obtained at various

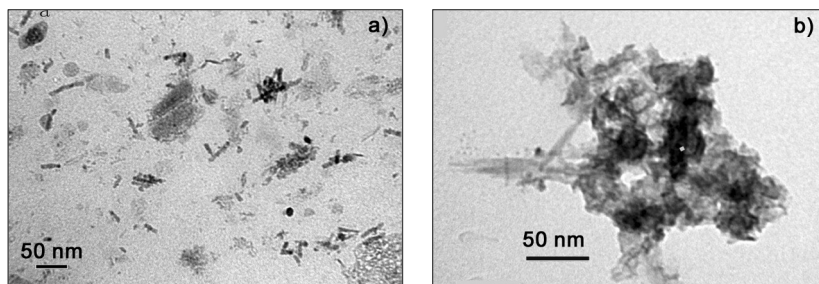


Fig. 2. TEM images of Cu₂O particles fabricated under various pH: a) 8.86, b) 9.40. Both samples were fabricated at 0.20 g/dm³ PEG

pH values was characterized by TEM, as shown in Fig. 2. The TEM image of the Cu₂O synthesized at pH = 8.86 shows irregular shapes, some of them aggregated (Fig. 2a). When pH of the solution is adjusted to 9.40, the products also have irregular

morphologies, and they agglomerate strongly (Fig. 2b). With the increase in pH values of the solution from 8.00 to 9.40, the particles become smaller: at pH = 9.40, small particles aggregate very rapidly. The fact that the smaller particles are obtained at higher pH of the starting solution is also confirmed by the XRD pattern, which is presented in Fig. 3. It is obvious that the diffraction peaks of the Cu₂O sample prepared at 8.00 pH are narrower and have higher intensities than those of the samples prepared at pH between 8.86 and 9.40. This suggests that Cu₂O crystals formed at pH in the range 8.86–9.40 have smaller dimensions. The average particle sizes calculated from Scherrer's equation, based on the Cu₂O <111> diffraction peaks, are 18.8, 14.5, 12.0 nm, which are prepared at pH of 8.00, 8.86, 9.40, respectively. The results of the XRD analysis also confirmed that all diffraction peaks corresponded to Cu₂O phases. No obvious peaks of impurity were found.

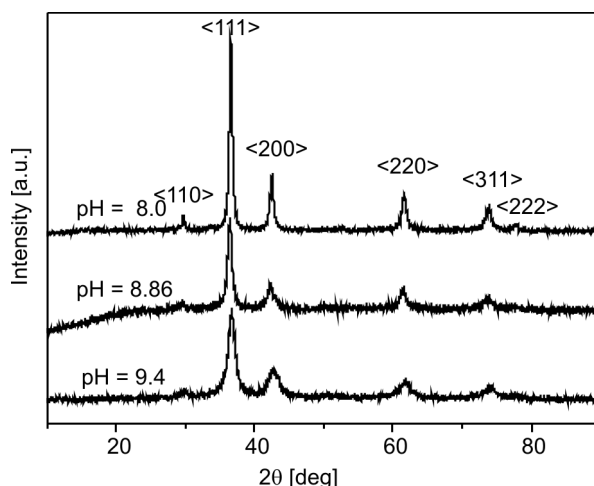
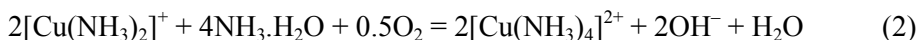
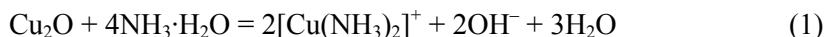


Fig. 3. XRD patterns of the products fabricated at various pH

It is well known that Cu₂O can be dissolved in ammonia solution to produce a complex [Cu(NH₃)₂]⁺, which is unstable and easily oxidized to a blue complex [Cu(NH₃)₄]²⁺. This dissolution resembles chemical etching [31]. The dissolution reactions of Cu₂O are as follows:



Since pH of the starting CuSO₄ solution is adjusted drop by drop with ammonia solution, a homogeneous [Cu(NH₃)_{*n*}]²⁺ solution forms, when more and more ammonia solution is added to the solution, there is still some NH₃ remaining, so the freshly formed Cu₂O is etched by the excess ammonia solution. Upon increasing pH, there are more NH₃·H₂O to dissolve Cu₂O in order to accelerate the etching reactions, the cubic Cu₂O will be dissolved into irregular and smaller particles. For this reason, the parti-

cles are easier to conglomerate (Fig. 2). If $\text{pH} = 10.00$, the yield of the precipitates decreases significantly after EB irradiation, the precipitates disappear within 10 min and the solution becomes blue.

Based on the above results, it is clear that the concentration of PEG and pH of the starting solution play a key role in determining the morphology of the final products.

3.3. Diffuse reflectance spectra (DRS)

The DRS of Cu_2O fabricated at $\text{pH} = 8.00$ and in the presence of 0.2 g/dm^3 PEG is shown in Fig. 4. The sample has an intense absorption in the visible range, which implies the possibility of high photocatalytic activity of Cu_2O under visible light irradiation. The steep gradient of the spectra indicates that the visible light absorption does not originate from a transition from the impurity level but is due to the band-gap transition.

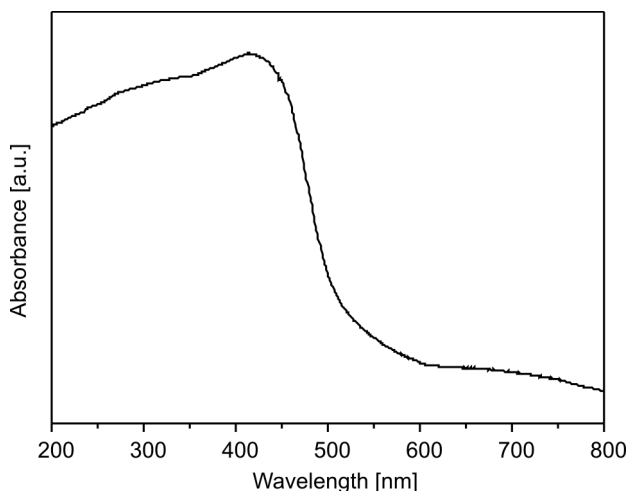


Fig. 4. Diffuse reflectance spectra of the as-prepared Cu_2O

3.4. Photocatalytic performance of Cu_2O samples

Successful synthesis of Cu_2O is a potential way of investigating the photocatalytic properties of Cu_2O nanoparticles. The degradation of phenol and MO by visible light was investigated. The photocatalytic reactivity of Cu_2O was quantified by the ratio, denoted C/C_0 , between the residual concentration and the initial concentration of phenol and MO. The ratio C/C_0 , depends on the irradiation time. Blank tests (phenol and MO without any catalyst) under visible light exhibited little photolysis. The phenol and MO concentration only decreased by 1.9% and 4.3% after 150 and 70 min of irradiation, respectively, which demonstrated that the photodegradation of phenol and MO was extremely slow without a catalyst under visible light illumination. The degrada-

tion of phenol and MO with Cu₂O in the dark was similar to that of the blank test. Therefore, the degradation of phenol and MO after treatment with Cu₂O was most likely due to the photocatalysis of Cu₂O.

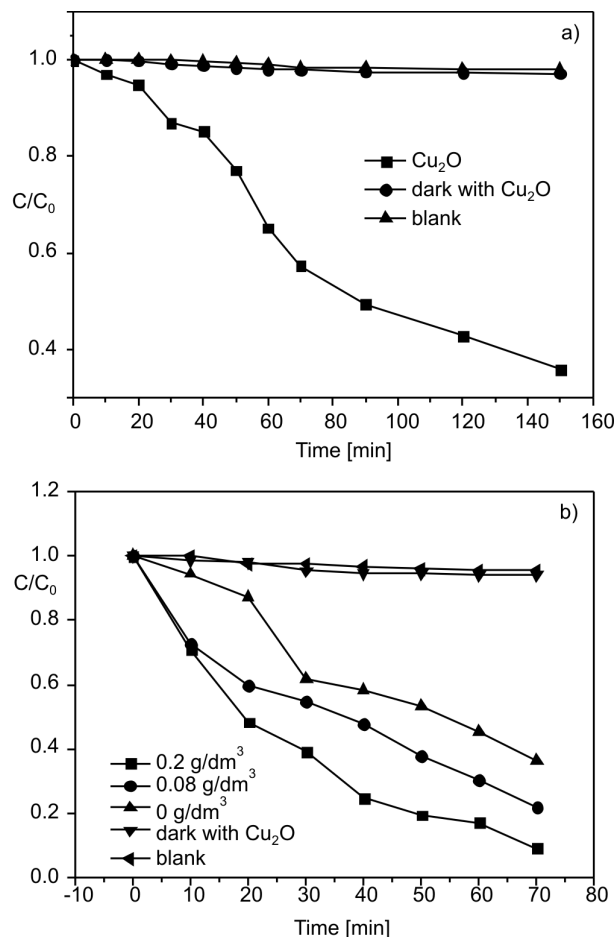


Fig. 5. Photodegradation of phenol (a) and MO (b) by Cu₂O samples

As is clearly shown in Fig. 5, Cu₂O nanoparticles were to a large extent responsible for the photodegradation reaction, both on phenol and MO after 150 and 70 min of irradiation, respectively. However, amongst all types of investigated Cu₂O crystals, cubic Cu₂O prepared with the starting solution at pH = 8.00 exhibited the highest photoefficiency for MO degradation. The photocatalytic activity is strongly dependent on the size, morphology, crystal structure, specific surface area or the efficiency of electron-hole (e^-/h^+) separation, etc., of a photocatalyst. The average diffusion time of randomly generated charge carriers from the bulk to the surface obeys the formula $\tau = r^2\pi^2D$, where r and D are the grain radius and the diffusion coefficient of the carrier, respectively [32]. From this formula we know that if the grain radius decreases,

the migration rate of e^-/h^+ to the surface accelerates, thus the photogenerated electron–hole pairs could effectively move to the surface, where they may degrade the adsorbed phenol and MO molecules. In general, particles that are of smaller size and have higher surface area are better for the degradation of pollutants. A higher surface area of the adsorbent possibly leads to higher adsorption capacity, while adsorption is a prerequisite for the degradation reaction. The BET surface areas of the samples prepared at PEG concentrations of 0.20, 0.08, 0 g/dm³ were ca. 22.6, 18.1, 11.4 m²/g, respectively, and the adsorption of MO on Cu₂O is consistent with the fact that the adsorption efficiency increases when the BET surface area increases. However, an exact reason for a high photocatalytic activity of the cubic Cu₂O still needs to be explored further.

4. Conclusion

Cu₂O nanostructures were successfully prepared with PEG as a template by electron beam irradiation in aqueous copper(II) sulfate solution. Factors affecting the morphology and size of Cu₂O products were the concentration of PEG and pH of the starting solution. The photodegradation experiments demonstrated that cubic Cu₂O nanoparticles exhibited higher photocatalytic activity than those of their spherical and irregular counterparts under visible light irradiation.

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