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Nanocrystalline Cuprous Oxide in Chitosan Membrane: Preparation, Characterization, and Photocatalytic Properties[1]

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Abstract—Crystalline Cu_2O nanoparticles were synthesized via the templating method by taking advantage of the chelation of chitosan with copper ions. Experimental data indicated that Cu_2O-embedded film exhibited higher photocatalytic activity toward methhyl orange degradation under visible light irradiation.

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1. INTRODUCTION

Cuprous oxide (Cu_2O) is a p-type semiconductor with a direct band gap of 2.17 eV [1], which offers it important application in hydrogen production, superconductor and photocatalytic degradation of organic pollutants under visible light [2–6]. However, the anodic photocorrosion of Cu_2O in such application has been a significant issue [7].

Chitosan is a natural polymer with $-NH_2$ group which makes chitosan chelate well with metal ions such as Cu^{2+}, Zn^{2+} and so on [8–12]. There are several distinct advantages for the chitosan templating approach [13–15]. Firstly, the chitosan membrane provides a stable matrix to prevent the agglomeration and corrosion of the nanoparticles embedded. Secondly, the nanoparticles embedded in chitosan membrane are easy to handle and recycle for catalytic purpose. Thirdly, chitosan has good adsorption for organic pollutant, leading to the enrichment of pollutants on the surface of the membrane.

In this paper, we report the synthesis of crystalline Cu_2O nanoparticles in chitosan membrane. The Cu_2O-embedded chitosan film was characterized by UV-Vis, XRD and SEM. Its photocatalytic properties is also performed.

2. EXPERIMENTAL

2.1. Materials

Cupric acetate anhydrous, methhyl orange, glucose and sodium hydroxide were purchased from Shanghai Chemical Reagent Company. All chemicals were of analytical purity and used without further purification. Chitosan was purchased from Yuhuan county Zhejiang province, whose degree of deacetylate was 90% and whose molecular weight was 210 kDa.

2.2. Preparation of Chitosan Membrane

Chitosan powder (2 g) was dissolved in 100 ml 1% (vol/vol) acetic acid solution under mechanical stirring at room temperature. When the solution became clear, the viscious solution was poured onto a piece of glass using tape casting method to prepare chiotsan membrane. The membrane was immersed in aqueous solution of sodium hydroxide (0.5 mol l^{-1}) to neutralize acetic acid, then washed with distilled water.

2.3. Preparation of Cu_2O-Chitosan Membrane

The preparation process of Cu_2O-chitosan membrane include two steps. In the first step, chitosan membrane (2 × 2 cm × 0.0203 g) was soaked in an aqueous solution of cupric acetate solution (50 ml, 0.01 mol l^{-1}) overnight, then thoroughly rinsed and immersed in deionized water for 24 h.

In the second step, the copper ion chelated chitosan membrane was soaked in glucose-containing alkaline solution. The solution was heated to 80°. Finally a brown film was obtained. After drying to constant weight at 80°C its weight is 0.0373 g.

In order to compare the photocatalytic activities between Cu_2O-chitosan and Cu_2O–Cu_2O powder was also synthesized by reducing cupric acetate with glucose-containing alkaline solution.

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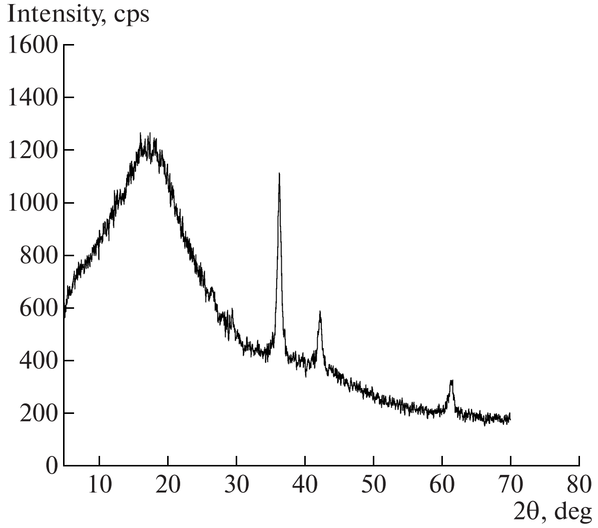

Fig. 1. XRD pattern of the Cu_2O-chitosan membrane.

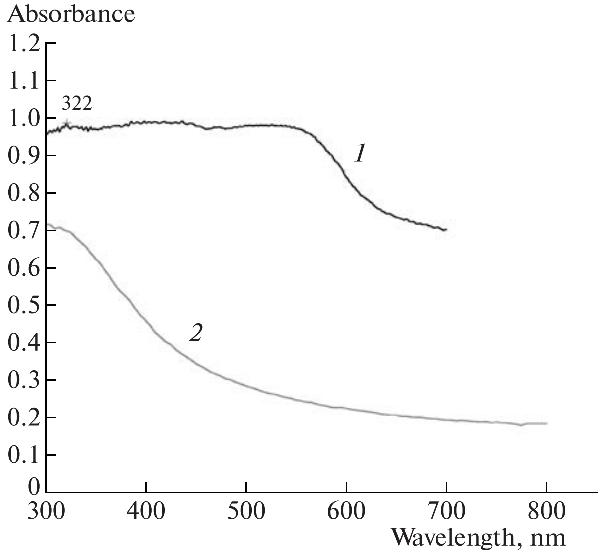

Fig. 2. UV-Vis absorption spectra of *1*, Cu_2O-chitosan and *2*, Blank-Chitosan.

2.4. Photocatalytic Activity Measurement

The reactor was illuminated by four halogen lamps (10 W) which predominantly emit light at 470 nm. In a typical reaction, a piece of Cu_2O-chitosan membrane (2 × 2 cm, 0.0373 g) or Cu_2O power (0.0170 g) was first immersed in an aqueous methhyl orange (MO) solution (20 mg/l, 100 ml) in the dark for 24 h to establish the adsorption equilibrium, then immersed in another MO solution (20 mg/l, 50 ml), the photocatalytic activities of the samples were assessed by monitoring the adsorbance of MO at 460 nm at given irradiation time intervals. In order to evaluate the effect of pH on photocatalysis, the MO solution was adjusted to pH 3 (using hydrochloride acid), 7 (no need to adjust) and 11 respectively before illumination.

2.5. Characterization of Cu_2O-Chitosan Membrane

X-Ray diffraction (XRD) patterns of the Cu_2O-chitosan membrane was carried out on a Bruker D8 Advance X-ray diffractometer with Cu K radiation operated at 40 kV and 40 mA. The data were recorded in the 2θ range of 4°–70° with a step width of 0.02°. The morphology of Cu_2O-chitosan film was characterized by SEM (QUANTA 200). UV-Vis absorption spectra were recorded on aU-3310 spectrophotometer.

3. RESULT AND DISCUSSION

3.1. XRD

The XRD patterns of the Cu_2O-chitosan film (Fig. 1) showed multiple diffraction peaks over a broad chitosan background. The peaks were found at 2θ = 29.84°, 36.37°, 42.60°, and 61.72° which could be readily assigned to (110), (111), (200), (220) lattice planes of Cu_2O crystal respectively [16]. These peaks are rather broad, indicating that Cu_2O crystals existed with nanosize. According to Scherrer's formula, the average crystal size for the cuprous oxide particles in the film was calculated to be 12.8 nm, and the average crystal size for the Cu_2O powder was calculated to be 14 nm. No other diffraction peaks arising from metal Cu or CuO appear in the XRD patterns.

3.2. UV-Vis

The UV-Vis absorption spectra of samples are presented in Fig. 2. In the optical absorption spectrum of the Cu_2O-chitosan membrane, the absorption threshold is red-shifted to 555 nm in comparison to 300 nm for blank Chitosan film. In addition, the absorption threshold for the Cu_2O embedded in the chitosan film is somewhat blue shifted in comparison to those of larged-sized Cu_2O particles $\left(\lambda = \frac{1240}{E_g} = \frac{1240}{2.17} = 571\text{ nm}\right)$, indicating that there might be quantum confinement effect likely due to the presence of nanosized Cu_2O particles.

3.3. SEM

The SEM images of Cu_2O-chitosan are shown in Fig. 3. It is easy to find that Cu_2O particles were dispersed homogeneously in the Chitosan film from the surface SEM (Fig. 3a) and inserted into the film from the cross SEM (Fig. 3b).

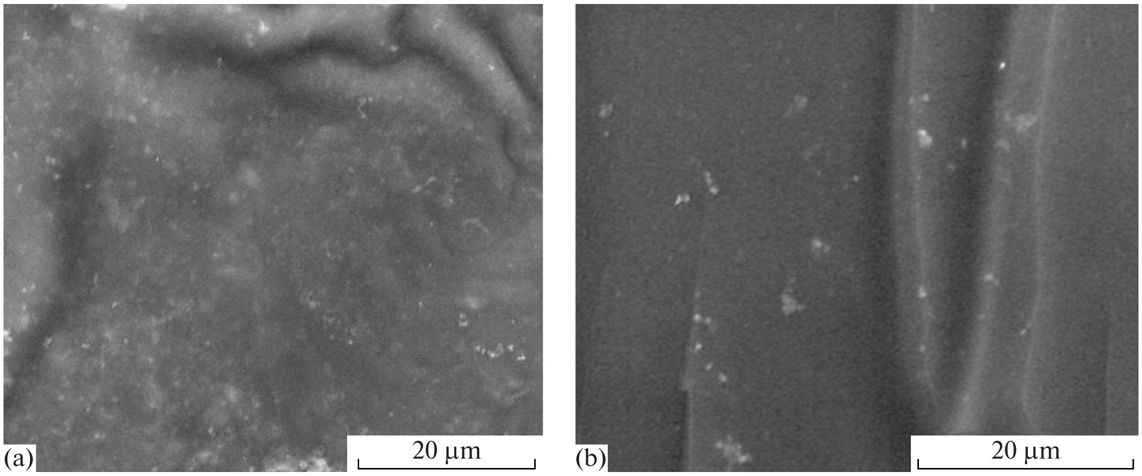

Fig. 3. The SEM images of Cu_2O- chitosan membrane. (a) surface SEM of Cu_2O-chitosan; (b) cross-section SEM of Cu_2O-chitosan.

3.4. Photocatalytic Degradation

The weight of Cu_2O (0.0373–0.0203 g) embedded in Chitosan is the same as Cu_2O powder (0.0170 g), so the mass content of Cu_2O in the composite film is 45.5 wt %. As shown in Fig. 4, it is easily found that pure Cu_2O powder has good photocatalytic activity only in acidic solution (pH 3). But unfortunately the Cu_2O power slowly disappear afer half an hour. It means that pure Cu_2O power cant be used as photocatalyst repeatedly. The cause for disappearance of Cu_2O may be the dismutation reaction. The equation of dismutation is as follows: $Cu_2O + 2H^+ = Cu + Cu^{2+} + H_2O$.

The photocatalytic activity of Cu_2O-chitosan membrane (Fig. 5) differs from pure Cu_2O: it exhibited higher photocatalytic activity toward MO degradation in neutral solution (pH 7) rather than in acidic solution (pH 3). There is no need to adjust the pH of the MO solution. Most importantly, the Cu_2O- chitosan membrane exhibited excellent photocatalytic activity even after 10 repeated cycles. It means that Cu_2O nanoparticles embedded in chitosan film are quite stable against photocorrosion. Such stability was further supported by the atomic absorption analysis results. For example, the concentration of Cu^{2+} ions in the solution mixture after photoreaction (3 h) was measured to be ~0.0094 mg l^{-1} for the Cu_2O-chitosan film.

These two photocatalysts all have poor photocatalytic activity in alkaline solution (pH 11).

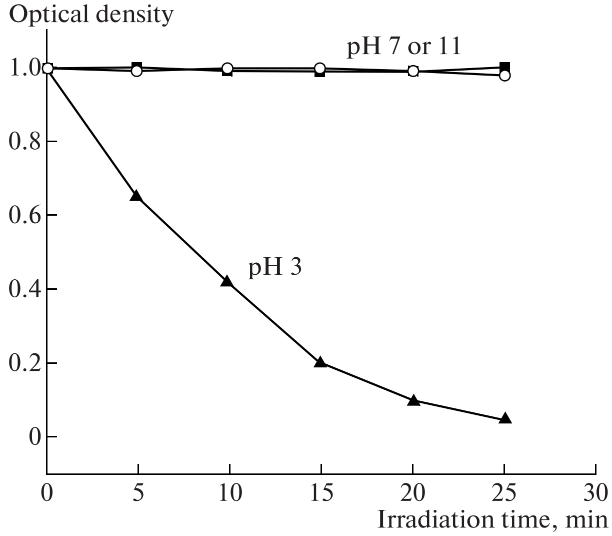

Fig. 4. Degradation of methhyl orange by Cu_2O powder under visible light irradiation.

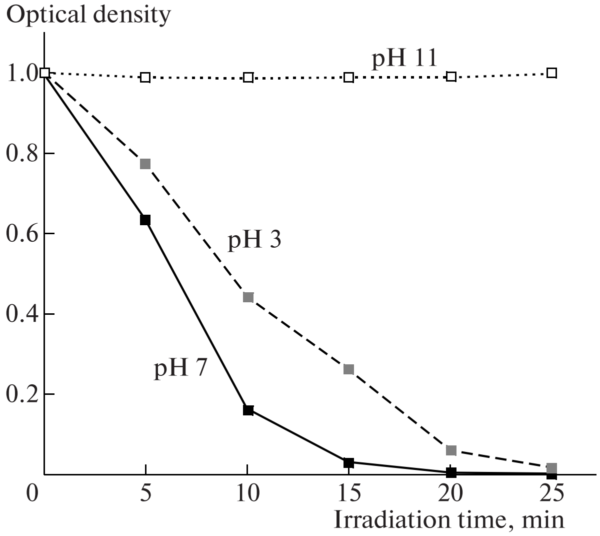

Fig. 5. Degradation of methhyl orange by Cu_2O-chitosan film under visible light irradiation.

4. CONCLUSIONS

Crystalline Cu_2O nanoparticles were synthesized via the templating method by chelating metal ions with $-NH_2$ group of chitosan. The Cu_2O-chitosan film was characterized by various methods, including UV-Vis, XRD, and SEM. The film exhibited excellent photocatalytic activity toward MO degradation under visible light. Unlike bulk Cu_2O nanoparticles, The Cu_2O nanocrystals embedded in chitosan membrane was found to be highly stable, with hardly any reduction in its activity even after 10 repeated reaction cycles.

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