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Preparation of Fenton reagent with H_2O_2 generated by solar light-illuminated nano-Cu_2O/MWNTs composites

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Abstract

This paper introduces the preparation of needle-shaped cuprous oxide (Cu_2O) particles 3–10 nm in diameter and 40–150 nm in length on multiwall carbon nanotubes (MWNTs) by anodic oxidation of copper electrode in alkaline solution. Steady-state concentration of H_2O_2 as high as 0.42 mM is produced in aqueous suspension of nanosized Cu_2O/MWNTs composites illuminated by simulated solar light in the presence of formate and oxygen. Assisted by Fe^{2+}-EDTA, these photogenerated H_2O_2 can be used as Fenton reagent; hydroxyl radicals have been detected indirectly. The results for the degradation of brilliant red dye indicate that the effect of this new Fenton system (1 g/L nanosized Cu_2O/MWNTs composites + Fe^{2+}-EDTA + simulated sun light) can approach that of traditional Fenton system (4 mmol/L H_2O_2 + Fe^{2+}-EDTA). This system is superior to the classical Fenton system in that it can act effectively for a long time.

Keywords: Nano-Cu_2O/MWNTs composites; Anodic oxidation; Simulated solar light; H_2O_2; Fenton reagent

1. Introduction

Hydrogen peroxide (H_2O_2) plays a significant role as primary oxidant in environmental systems. H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H_2O_2 concentrations [1]. The most common environmental application of H_2O_2 is in the Fenton reagent (H_2O_2 + Fe^{2+}) [1]. Recent reports showed that among the advanced oxidation processes (O_3, O_3/H_2O_2, UV, UV/O_3, UV/H_2O_2, O_3/UV/H_2O_2 and Fe^{2+}/H_2O_2), Fenton reagent was the fastest one for phenol degradation [2]. For the destruction of dispersed dyes, better results of treatment were obtained with the Fenton process than those obtained with the methods of electrochemical oxidation or using ozone or hypochlorite [3]. However, the cost problem associated with H_2O_2 consumption hinders the wide scale application as Fenton reagent in industry. Although H_2O_2 can be produced on a cathode by Electro-Fenton, such treatment is limited to solutions containing <1000 ppm chemical oxygen demand (COD) [4].

Currently, many researchers focus their attention on utilizing solar energy and are investigating highly effective photocatalysts. Semiconductor photocatalysts such as TiO_2 and ZnO have been investigated widely [5]. But these semiconductor photocatalysts can only be excited by ultraviolet or near-ultraviolet radiation that occupies only about 4% of the solar light. Cu_2O is one of the few photocatalysts that can be excited by visible light which covers the main band of incoming solar light. However, Cu_2O has not been commonly used due to two reasons. Firstly, the light-generated charge carriers in micron-sized Cu_2O grains can not be efficiently transferred to the surface and are lost due to recombination, which results in low solar energy conversion efficiency (<1%) [6,7]. Secondly, nanosized Cu_2O is easy to aggregate or be oxidized. Therefore, the preparation of stable nanosized Cu_2O particles is a key to improve solar energy conversion efficiency. Jongh's group and our laboratories have discovered the oxygen cathode property of Cu_2O [8–10]. This property can lead to the H_2O_2 production on the surface of Cu_2O by illumination of visible light. In order

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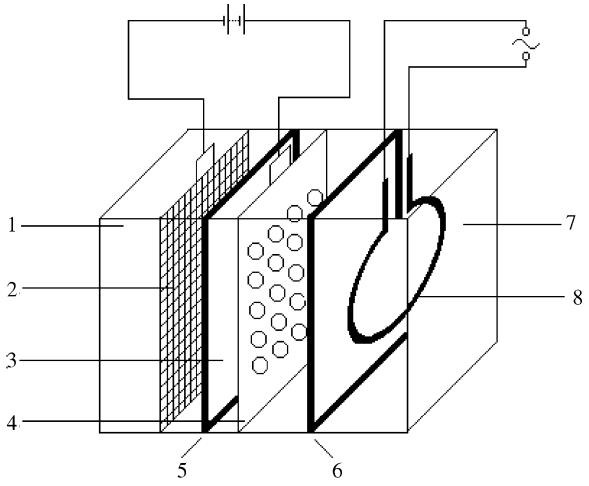
to effectively utilize solar energy to produce H_2O_2, we introduce a new method, for the first time to our knowledge, to generate H_2O_2 by using photoexcited nanosized Cu_2O. The Fenton process using such H_2O_2 can largely reduce the costs for equipment or the energy consumption in wastewater treatment.

The target of the present study is to prepare stable nanosized Cu_2O by anodic oxidation of copper electrode in alkaline solution using multiwall carbon nanotubes (MWNTs) as carriers. Then, the nanosized Cu_2O is activated by simulated solar light to generate H_2O_2, with which a new kind of Fenton system is obtained. The effect of this Fenton system on degradation of brilliant red dye has also been discussed.

2. Experimental

The catalyst for MWNTs growth is Fe_2O_3/Al_2O_3 powder prepared by sol–gel method. The molar ratio of Fe/Al satisfied 1:3.2. MWNTs were fabricated by catalytic pyrolysis of the propylene (C_3H_6) at about 750 °C in a ceramic tube. Then, the as-prepared MWNTs were refluxed in concentrated nitric acid for 2 h at 140 °C to remove catalytic particles.

The electrodeposition of Cu_2O on MWNTs was performed in an electrolytic cell shown in Fig. 1. The cell was divided into anodic and cathodic baths by an anion exchange membrane. The cathodic electrolyte was a 150 mL aqueous solution of sodium hydroxide (0.05 mol/L); a piece of stainless steel net (area: 10 cm × 10 cm) was used as the cathode. The anodic electrolyte was a 250 mL solution containing 250 g/L sodium chloride and 20% (v/v) ethylene glycol with pH 10 adjusted by addition of sodium hydroxide. A piece of copper plate (99.99% purity; area: 10 cm × 10 cm) was used as the anode. At first, 0.5 g MWNTs as carriers were dispersed in the anodic electrolyte by ultrasonic means and the temperature of the reaction was controlled at about 80 °C. During the electrolysis, continual agitating was necessary and the electrolytic current was adjusted to 0.6 A. After 30 min, the anodic suspension was taken out and centrifuged. The obtained precipitates, which were Cu_2O/MWNTs composites, were washed immediately by distilled water till no chloride was present. At last, the composites were soaked in the alcohol solution containing 1‰ (g/g) benzotriazole (BTA) for 2 h and dried in vacuum at 120 °C.



1 cathodal bath 2 stainless steel net 3 anodic bath
4 copper plate 5 anion-exchange membrane
6 PTFE cloth 7 heating bath 8 electric heater

Fig. 1. The diagrammatic sketch of the electrolytic cell.

The morphologies of as-prepared Cu_2O/MWNTs composites were investigated by transmission electron microscopy (TEM, JEM-100CXII) and their phase compositions were investigated by X-ray diffraction (XRD) studies using a JEOL-JDX8030 X-ray diffractometer with Cu Kα radiation.

Brilliant red dye X3-B was selected as the model pollutant. The decolorization reactions of brilliant red dye were carried out in a quartz reactor. A 500 ml suspension of a mixture of brilliant red dye (200 mg/L), Fe^{2+}-EDTA (10 mmol/L) and Cu_2O/MWNTs composites (1 g/L) with pH adjusted to 6 by salt of phosphate (Na) buffer was bubbled with air during the whole reaction period. The irradiation light source was a 300 W Xe lamp. Before illumination, the whole suspension was placed in the dark overnight to ensure adsorption equilibrium of brilliant red dye on the Cu_2O/MWNTs surface. H_2O_2 generated by simulated solar light-illuminated on Cu_2O/MWNTs composites was detected by iodometrictitration method [11]. The analysis of hydroxyl radicals of our Fenton system was done through the colorimetric determination of 2,3-dihydroxybenzoate [12] using a Shimadzu UV-2550 spectrophotometer.

3. Results and discussion

3.1. Preparations and characterization of Cu_2O/MWNTs composites

The process for the production of Cu_2O is via the anodic dissolution of copper in an alkaline solution of sodium chloride [13–15]. The principal reactions are as follows:

Anodic reaction (anodic dissolution of copper):

$$Cu + nCl^- - e^- \rightarrow CuCl_n^{1-n} \ (n = 2, 3) \quad (1)$$

Cathodic reaction (hydrogen evolution):

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad (2)$$

Chemical reactions (hydrolysis precipitation):

$$CuCl_n^{1-n} + 2OH^- \rightarrow Cu(OH)_2^- + nCl^- \ (n = 2, 3) \quad (3)$$

$$2Cu(OH)_2^- \rightarrow Cu_2O \downarrow + H_2O + 2OH^- \quad (4)$$

Thus the net cell reaction is the summation of Equations (1)–(4), that is:

$$2Cu + H_2O = H_2 \uparrow + Cu_2O \quad (5)$$

Recent reports indicated that MWNTs have unique template or support functions in tailoring the size of particles, with particular success in synthesis of nanoparticles such as Pd, Ni