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Preparation and photocatalytic activity of cuprous oxide/carbon nanofibres composite films

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ABSTRACT

Cuprous oxide (Cu_2O) nanocrystals have been successfully synthesized using copper acetate as precursors via a polyol process. The as-synthesized products were easily deposited on the surface of carbon nanofibres (CNFs) and then were characterized through XRD, FESEM, TEM and FTIR, etc. The photocatalytic performance of these composite films was evaluated using methyl orange as a model organic compound under visible light irradiation. Results showed that the shape of Cu_2O nanparticles could be changed from irregular nanoparticle to cubic, flower-like particle assembled by Cu_2O nanocubes with the change of the reaction conditions. All of these Cu_2O/CNFs composite films showed the satisfied photocatalytic activity to methyl orange even after 3 cycles of degradation experiment due to the protectable function of carbon fibre films to the Cu_2O nanocrystals. The Cu_2O/CNFs composite films may offer a feasible method for the potential application of Cu_2O nanocrystals in the treatment of organic contamination.

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconductor (direct band gap of 2.0–2.2 eV) with unique optical and magnetic properties, low cost, abundant availability, easy accessibility and low toxicity [1,2], has important applications in the hydrogen production, superconductor, solar cell, negative electrode material for lithium ion batteries [3–6], and visible-light driven photocatalyst of organic pollutants [7–11]. However, limited actual photocatalysis efficiency has restricted its application. A proposed reason is that photocarrier generated under light illumination in micronsized Cu_2O grains cannot be efficiently transferred to the crystal surface but is easy to recombine with hole. Subsequently, only a small number of electrons and holes are trapped and participate in photocatalytic reactions, resulting in low efficiency. So nanosized Cu_2O particles have been selected to decrease recombination ratio of electron and hole. But Cu_2O nanocrystal is deactivated by photocorrosion easily, its dispersion and stability is not so good [12,13]. Therefore, Cu_2O is often combined with other oxide semiconductors and some high specific surface area materials to promote its performance and stability [14,15]. For example, Cu_2O was loaded on the carbon nanotubes (CNTs) to obtain a stable or enhanced catalytic activity [16–18]. But high cost and poor dispersion of CNTs may be a barrier for the wide application of the method.

Recently, carbon nanofibres (CNFs) have attracted considerable attentions due to their potential application as heat-management materials, composite reinforcement, high-temperature catalysis, membrane-based separation, and as components for nanoelectronics and photonics [19,20]. CNFs are typically produced either by chemical vapor deposition (CVD) or by pyrolyzing electrospun nanofibres from polyacrylonitrile (PAN) and from pitch [21–24]. CNFs produced by pyrolyzing electrospun nanofibres from PAN with typical diameters of few hundreds of nanometer and fibres interconnected to form three-dimensional web, has large surface areas as well as high chemical and mechanical stabilities. Fe/Co/Ni ternary alloy nanoparticles and Cu have been deposited on the PAN-based CNFs for potential fuel cell and lithium-ion batteries applications [25,26].

In this work, Cu_2O nanoparticles with different shapes have been homogeneously coated on CNFs using copper acetate as precursor via a polyol process. By the method, the aggregation of Cu_2O was inhibited and the photocatalytic activity of Cu_2O under visible light was improved in the presence of CNFs as an effective support [27,28].

2. Experimental

2.1. Materials and methods

All reagents used in this work were of analytical grade and were used without further purification. The CNFs were prepared by pyrolyzing electrospun nanofibres from PAN at 1073 K [21,23],

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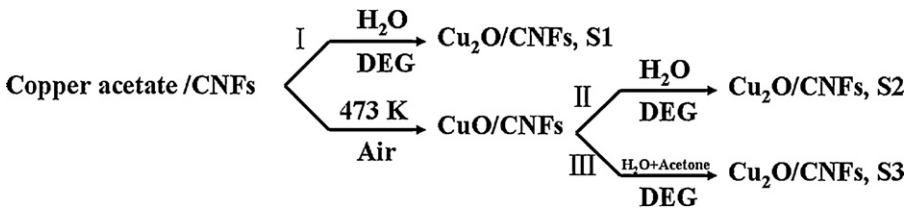

Scheme 1. Schematic presentation for the preparation of Cu_2O/CNFs composite films.

which were then dispersed in 5 mol/L nitric acid solution for 12 h at 333 K. Subsequently, the CNFs were filtered and washed with deionized water to remove residual acid and dried at 333 K. Scheme 1 showed the approach to prepare the Cu_2O/CNFs composite films. 100 mg of obtained CNFs and copper acetate (1.0 g) were mixed with 50 mL of diethylene glycol (DEG) in a 250 mL round-bottomed flask, which was then heated to 413 K under vigorous magnetical stirring. Subsequently, 2.5 mL of deionized water was added and reaction temperature was kept at 413 K firstly for 20 min and then 453 K for 2 h. A yellow-black suspension was obtained. After cooled to room temperature, the suspension was filtered, washed by absolute ethanol for 3 times and dried in a vacuum oven at 333 K for 6 h. The obtained yellow-black Cu_2O/CNFs composite film was labeled as S1. Red Cu_2O particle, prepared using the above-mentioned method in the absence of CNFs, had been used as control.

Another process had been used to prepare Cu_2O/CNFs composite film with different shapes. 50 mL absolute ethanol solution of 1.0 g copper acetate and 100 mg CNFs were mixed and dried at 473 K for 10 h to obtain the CuO/CNFs composite film precursor. Then, 2.5 mL deionized water was also added and the temperature was kept at 413 K for 20 min. Finally, the mixture was heated at 453 K for 2 h, and the yellow-black suspension obtained was labeled as S2. Furthermore, another Cu_2O/CNFs composite film was prepared using the same process as mentioned above except replacing 2.5 mL deionized water with a mixture of 1.0 mL deionized water and 1.5 mL acetone. The obtained suspension was labeled as S3.

2.2. Characterization

X-ray diffraction (XRD) analysis (ARL X'TRA, Thermo Electron) was performed using a monochromatic Cu Kα radiation with a wavelength of $\lambda/2 = 154.06$ pm in the range of 20°–80° at a scanning rate of 5°/min. The morphology of Cu_2O/CNFs composite films was characterized by field emission scanning electron microscopy (FESEM, Cold-Field Emission SEM S-4700-II, Hitachi) equipped with a field emission gun (FEG). Transmission electron microscopy (TEM, JEM-1230, JEOL) was carried out at 80 kV and HRTEM observation was carried out on a JEM-2010 instrument (JEOL) at 200 kV. The Fourier transform infrared (FTIR) data were collected on a Nicolet 5700 (Thermo Electron Corp.), in which the samples were mixed with KBr in the mass ratio of 1:20.

2.3. Photocatalytic reaction

50 mg of the as-prepared products were dispersed in a 50 mL mixture of methyl orange (MO, 10 mg/L) at pH 3.0. The mixture was kept in a dark environment for 5 h to evaluate the adsorption property, and the photocatalytic activity was evaluated by the degradation of MO under illumination of a 40 W fluorescent lamp with constant stirring for 5 h at room temperature. A UV–vis spectrophotometer (U-2900, HITACHI) was used to monitor the absorbency of methyl orange solution at 463 nm for every hour. Photocatalytic reaction of the same sample was repeated for three times to evaluate the stability of Cu_2O/CNFs composite films. The samples were filtered and washed by distilled water for three times, and dried in a vacuum oven at 333 K before they were used for next evaluation.

3. Results and discussion

Fig. 1 showed the XRD patterns of CNFs, CuO/CNFs composite film and different Cu_2O/CNFs composite films prepared by poylol methods, respectively. A broad peak at $2\theta = 26°$ in Fig. 1a appeared, which could be ascribed to the (0 0 2) plane of graphite in CNFs [21]. In the pattern of CuO/CNFs composite film (Fig. 1b), seven peaks at 32.7°, 35.9°, 39.1°, 49.3°, 62.0°, 66.5° and 68.0° were ascribed to (1 1 0), (1 1 1), (1 1 1), (2 0 2), (1 1 3), (0 2 2) and (2 2 0) crystal planes of CuO crystals respectively, when compared with the standard JCPDS file of CuO (No. 45-0937). The XRD result indicated that CuO was synthesized firstly without any detectable impurity after copper acetate was treated at 473 K. The CuO may result from the formation of Cu_2O on the surface of CNFs. Fig. 1c–e showed the typical XRD patterns of Cu_2O/CNFs composite films, where five peaks with 2θ values of 29.9°, 36.8°, 42.6°, 61.6° and 73.8° were corresponded to (1 1 0), (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of Cu_2O crystals with a cubic phase (standard JCPDS file No. 05-0667). It can also be observed that there was a broad peak at 26° of 2θ in Fig. 1b–e, which corresponded to the CNFs, respectively. There was no obviously difference among the XRD patterns of Fig. 2c–e. From the XRD patterns, it can be concluded that the obtained composite films were composed of cubic Cu_2O and CNFs.

Fig. 2 showed the FESEM images of CNFs and CuO/CNFs composite film. Three-dimensional CNFs were formed through pyrolyzing electrospun method, in which diameter of nanofibres is about 290–370 nm (Fig. 2a). Even after heat treatment at 473 K, the mats were connected well and stable, which indicated it was a suitable support. Spherical CuO particles with a diameter of ca. 2 μm were

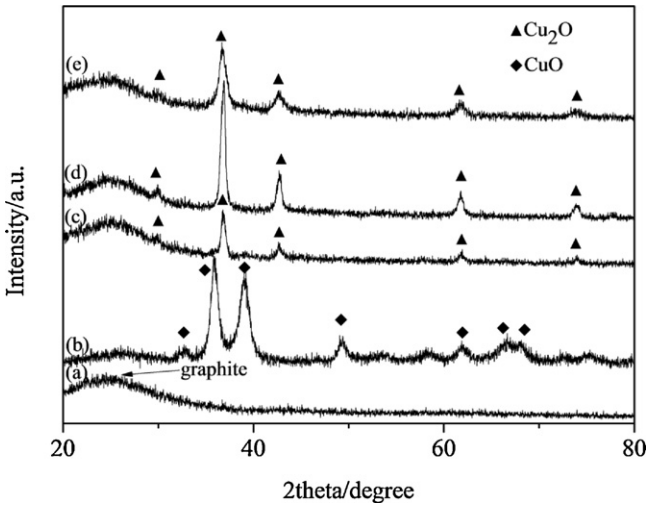

Fig. 1. XRD patterns of (a): CNFs film, (b): CuO/CNFs composite film, (c): S1, (d): S2, and (e): S3.