Preparation and characterization of micron copper oxide thin film based on copper through a simple method of electrodeposition

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In this paper, we reported the preparation of micron copper oxide thin film by heating reduction of copper via a simple chemical method. The precursors of micron copper oxide were synthesized by electrodeposition. The structural, morphological and element compositional analysis of the micron copper oxide were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results indicated that the product were cuprite structure Cu_2O and tenorite structure CuO mixture with the size of about 20 μm. Photoluminescence measurement was carried out and the PL spectra of micron copper oxide thin film revealed that two strong emission at around 544 nm and 489.2 nm. In addition, the degradation experiments of methyl blue reaches to 90 %.

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Keywords: CuO, Electrodeposition, Photoluminescence

1. Introduction

As a p-type semiconductor with a narrow band gap (1.2 eV) and the basic building block of several high-temperature superconductors, cupric oxide (CuO) has generated renewed interest. It has numerous interesting properties that can be exploited in fields such as gas sensing [1,2], solar-energy transformation [3], heterogeneous catalysis [4], lithium ion electrode [5], high Tc-superconductors [6], field emission emitters [7-9], magnetic storage media [10], electronics [11], semiconductors [12] etc. The successful preparation of CuO nanowires/ nanorods is believed to enrich our understanding of its fundamental properties, which may lead to enhancement of performance in its applications [13], such as the photocatalytic activity of TiO_2 [14].

Copper and copper oxides can be synthesized, among others, by chemical methods (including solgel, electrochemical deposition and hydrothermal methods) [15-21] and by physical methods (such as chemical vapor deposition and laser ablation) [22]. These methods could be prepared for all kinds of copper oxide micro/nanostructures, including nanoparticles [23], nanowires, nanorods, nanobelts, nanoneedle [24], nanotube, nano cage and complex 3D hierarchical structure, but different shape of copper oxide controllable synthesis reported less.

In the solution-based chemical methods, two typical approaches are used to synthesize copper and copper oxides of well-defined shape and size [25]. In one approach, a capping agent is often used to control the growth direction and size of the product [26-28]. In the other one, a template is used to physically confine the shape and size of the product [29-33]. Because of it is not usually easy to completely remove the template material and other additives used in the synthesis process; the preparation of pure copper oxides of well-defined shape is limited. Similarly, the presence of capping agents used to define the shape of copper oxides may have undesirable effects in the needed application of these copper oxides (e.g., hindrance of the surface for catalysis on Cu/CuO or Cu/Cu_2O thin films) [34].

Different approaches have been used for the synthesis of CuO thin films, like chemical bath deposition [35], from single source precursor [36], spray pyrolysis [37], chemical vapor deposition [38], sputtering [39], spin coating [40], thermal oxidation[41,42] electrochemical deposition, to name a few. Among all these techniques, the electrochemical route for the direct deposition of CuO thin films is less studied, but it can easily be fabricated by the pyrolysis of electrochemically deposited Cu thin film as the precursor [43].

In the present work, we prepared Cu thin film with direct current first, then oxidated it into copper oxide under high temperature. The CuO thin films we have deposited using this particular method came out with monoclinic phase and showed good photocatalytic performance to degrade the methyl blue solution.

2. Experimental

2.1 Materials

All chemicals used in this work were of analytical reagent grade and used as received without further purification. All the aqueous solutions were prepared using distilled water.

Conditions were shown in the following Table 1.

Tabel 1. Material Composition and Electroplating Parameters.

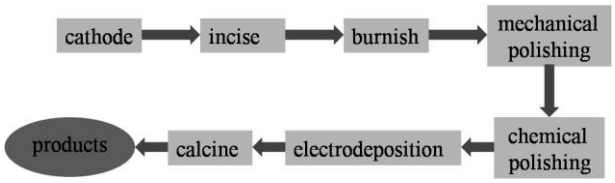
Material Composition and Electroplating Parameters	Numerical
Copper Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$)	25.00 g
Boronic Acid (H_3BO_3)	4.50 g
Saccharin ($C_7H_5NO_3S$)	0.50 g
Sodium Fluoride (NaF)	0.05 g
PH	3.00
Cathode	Cu
Anode	Cu
DC Voltage	2.00V
Electrodeposition Time	30min
Calcine Temperature	700°C
Calcine Time	1h
Electrodeposition Of Temperature	room temperature

2.2 electrodeposition of Cu

The deposition of thin films of metallic Cu on a properly cleaned Cu (which acted as the cathode) was carried out from a copper galvanization solution using direct current and a Cu electrode as the anode. Firstly, 25 g copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 4.5 g boronic acid (H_3BO_3), 0.5 g saccharin ($C_7H_5NO_3S$), 0.05 g sodium fluoride (NaF), respectively, was dissolved in 100 mL distilled water under constant stirring, after that, pour them together with a beaker. Secondly, concentrated sulfuric acid and potassium hydroxide were introduced into the beaker and the PH value of the whole solutions was all adjusted to 3.0. Thirdly, the cathode copper burnished with size from coarse to fine sand paper, then polished it to mirror surface via mechanical polishing, at last, keep it into the solution which contains 5mL concentrated nitric acid and 100mL anhydrous ethanol three to five seconds, rinsed it with distilled water.

2.3 Preparations of CuO

Deposition was carried out by the voltage of 2 V and duration for 30 min. Finally, the deposited Cu films were then annealed at 700 °C for 1 h in muffle furnace, and then to cool naturally, to convert them to CuO. The whole experiments schematic diagram is as following:



2.4 Characterization

The morphology of the copper oxide thin films was observed by scanning electron microscopy (SEM). The as-obtained products were characterized by XRD using a Dmax-3β diffractometer with nickel- filtered Cu K_α radiation. Photo-catalytic properties were tested as followed.

PL studies Room temperature photoluminescence spectra were carried out on a fluorescence spectrophotometer (LS-55) using Xe lamp with excitation wavelength of 325 nm.

Photo-decomposition test The methyl blue solution of 12 mg/L was pour into the beaker. The Cu thin films were immersed in the solution. It was illuminated by a high pressure mercury lamp (160 W) under 15 cm vertical distance.The absorbance of methyl blue solution was measured by a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

3. Results and discussion

3.1 XRD analysis

The XRD pattern of Fig. 1 (a) corresponds to the as deposited film and matches well with the standard diffraction pattern of metallic Cu (PDF 04-0836) with diffraction from (200) and (111) crystal plane, indicating the cubic nature of the deposited material, the rest of the peak is likely to be impurities. According to the XRD results in Fig. 1 (b), both tenorite CuO and cuprite Cu_2O were found to exist in the synthesized microstructure, which can be seen in Fig. 1b. The Cu film, when annealed in air at 700℃ for 1 h in muffle furnace, produced CuO with monoclinic phase (JCPDS card No. 05-0661, a=0.4684 nm, b=0.3425 nm, c=0.5129 nm and β=99.47), as reflected by its XRD pattern and the positions of the diffraction planes are in good agreement with the literature value, all the diffraction peaks of Cu_2O prepared in this experiment can be indexed to the cubic phase structured Cu_2O (JCPDS card No. 05-0667, a=0.42696 nm), as reflected by its XRD pattern and the positions of the diffraction planes have good agreement with the literature value. They were with high crystallization. The product appeared characteristic peaks of copper oxide at the 2 theta of 29.5920°, 36.4404°, 42.3208°, 52.4698°, 61.3816°, corresponding to the different planes of cuprous oxide. The intensities of characteristic peaks of Cu_2O are stronger than CuO, which can be attributed to the negative influence of O_2. The peaks of (220) crystal planes of Cu_2O are very adjacent to the peaks of (-113) crystal planes of CuO, therefore, the peaks of the (220) plane of Cu_2O and (-113) plane of CuO are overlapped together, which is clearly shown in Fig. 1b.

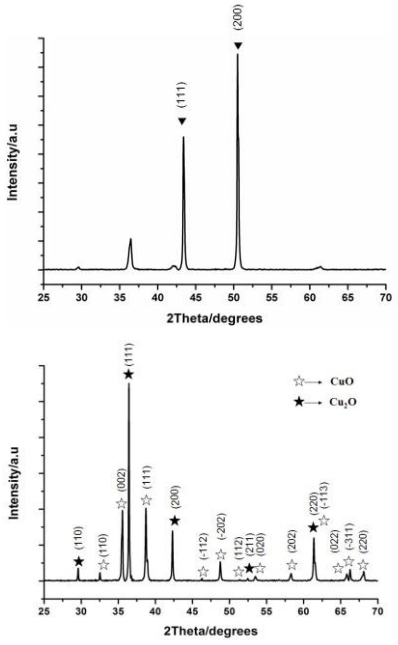


Fig. 1. XRD patterns for (a) electrodeposited Cu; (b) CuO thin film.

3.2 Surface morphology by SEM

Fig. 2 shows the SEM morphologies of the CuO thin film. Clearly, the CuO particles are Mosaic together. The CuO thin films are composed with CuO particles, the average diameter of such CuO particles were found to be about 20 μm. Containing lots of Cubic phase of Cu_2O, the microstructure present spherical particles. The particles are composed with flake copper oxide, whose diameter is about 2~3 μm. These flakes were monoclinic phase of CuO. Synthesis of the copper oxide is composed of a large number of micro balls set each other. Micro balls were made up of many flakes, with smaller size, well-distributed. The annealing has two effective functions, to convert Cu to CuO or Cu_2O and to change the morphology from cubic to Monoclinic.

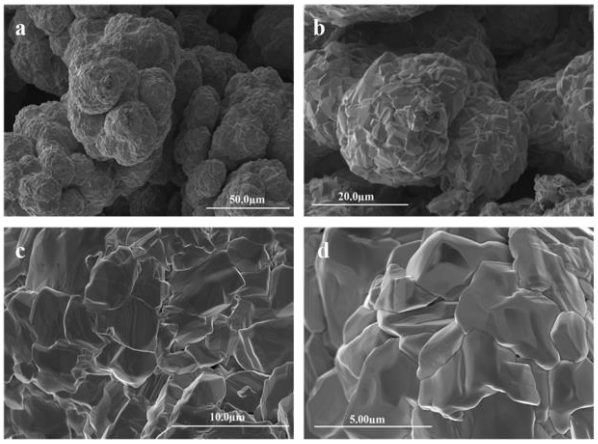


Fig. 2. SEM micrographs of the CuO thin film.

Combining XRD and SEM results, we can make a conclusion that the obtained products are of microstructures with tenorite CuO and cuprite Cu_2O. Therefore, the micron copper oxide can be obtained by electrodeposition.

3.3 PL spectra

To investigate the optical properties of the Copper oxide thin films, their PL spectra are measured at room temperature under the excitation wavelength of 325 nm with a Xe lamp. Fig. 3 shows the PL spectra of copper oxide powder. There are two strong peaks in the PL spectra, a strong emission at around 544 nm and another strong emission at around 489.2 nm. This result is in well agreement with the previous conclusion. Due to the content of Cu_2O is more than the CuO, therefore, the stronger emission of 544.0 nm belongs to Cu_2O, the weaker emission of 489.2 nm belongs to CuO. The peak position is blue-shifted intensely in comparison to the bulk CuO, the strong emission has slight blue shift in

comparison to the bulk Cu_2O. Significant amount of quantum confinement effect arises due to the presence of Cu_2O in the material, leading to the blue-shifted in the PL spectra.

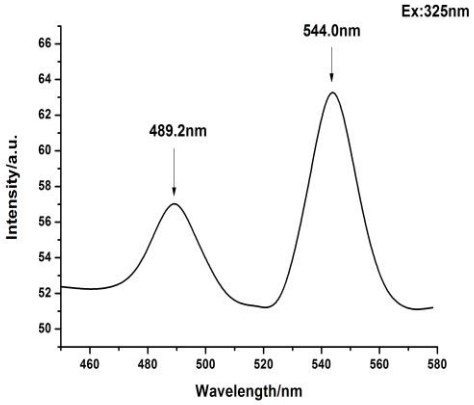


Fig. 3. Room-temperature PL spectra of copper oxide thin film.

3.4 Photo-decomposition test

Methyl blue in aqueous solution containing CuO/ Cu_2O after 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min and 240 min, under UV light, degradation rate respectively for 25.54%, 45.26%, 63.27%, 78.22%, 88.03%, 89.17%, 90.28% and 90.46%. That CuO/ Cu_2O have the photocatalytic performance can be seen in Fig. 4. The degradation experiments of methyl blue revealed that the photocatalytic performance of the copper oxide powder is good. After 180 minutes, the degradation of methyl blue reaches to 90%.

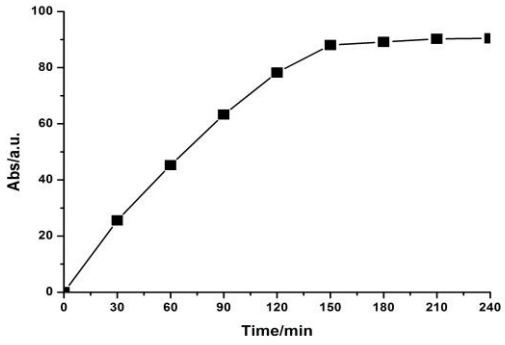


Fig. 4. Photo-catalytic activity of the CuO/ Cu_2O.

The above results indicate that the electrodeposition process had a great effect on the relative intensity and position of typical PL properties of CuO/ Cu_2O. So, the PL properties of the microstructures can be tuned by this approach. The degradation experiments of methyl blue revealed that the photocatalytic performance of the copper oxide thin film can reach to 90% Aafter 180 minutes.

4. Conclusion

Photocatalytically active CuO thin films were prepared by annealing a precursor Cu thin film deposited by an electrochemical technique. The grains were found to change their shapes from cubic to monoclinic as the effect of annealing. The high surface to volume ratio puts its signature in the good photocatalytic behavior. About 90% degradation was achieved after 180 min of exposure. This indicates that, such films could find potential application as a photocatalyst for waste water treatment.

In brief, we can summarize our results in the following four points. (1) CuO with monoclinic phase and Cu_2O with cubic phase can be Synthesised by this method of electrodeposition. (2) Annealing provides an effective approach for preparing a photocatalytic CuO through Cu, which is formed in the electrodeposition process. (3) The present preliminary work has demonstrated that when electrodeposition of Cu was annealed at 700 °C for 1 h in muffle furnace, a composite structure is produced during Annealing. CuO/ Cu_2O exhibit high efficient photocatalytic properties, such as, high photo-decomposition properties. (4) Electroplating parameters is often used to adjust to control the growth direction, size and the morphology of the product.

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