

Fabrication of copper nanoparticles based screen-printed electrodes for electrochemical analysis

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Abstract

This paper is focused on the preparation and characterization of Cu₂O nanoparticles via simple wet chemical route. Samples were characterized by SEM and XRD. These nanoparticles were used for fabrication of screen-printed working electrodes for electrochemical detection of purine bases in DNA.

Keywords: Cu₂O nanoparticles, screen-printed electrode, cyclic voltammetry

Introduction

Cuprous oxide (Cu₂O) is a *p*-type metal oxide semiconductor with a direct band gap of 2.0–2.2 eV. It has attracted increasing interest due to its promising application in magnetic devices, solar energy conversion and catalysts (Huang et al. 2009; Zahmakiran et al. 2009).

New types of solid electrodes are necessary for small device technologies contrary to standard electrochemical analysis, where mercury drop electrodes are commonly used. The performance of solid electrode is determined by its surface modifications to make it sensitive and selective towards a certain analyte, to obtain either chemically or biochemically modified electrodes (Pravda et al. 2001). Solid electrodes can be fabricated by thick-film technology (TFT) process. The advantage of TFT is its flexibility, low production costs, good reproducibility and good electrical and mechanical properties of electrodes.

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Materials and Methods

The preparation method of Cu₂O/CuO nanoparticles is based on the procedure reported in (Luo et al., 2008). Nanoparticles were prepared by two-step synthesis. Copper (II) acetate reacts with sodium borohydride in three-phase system (water – *N,N*-dimethylformamide – cetyltrimethylammonium bromide) at 70°C to produce Cu₂O precursor. Then NaOH solution was added and the precursor was dried to produce Cu₂O/CuO nanoparticles. Prepared nanoparticles were characterized by SEM and XRD.

Two kinds of working electrodes were fabricated using standard TFT process – cermet and polymer. Cu₂O/CuO nanoparticles were well homogenised with 3 wt% of glass frit (in the case of cermet electrode) and suitable vehicle or polymer binder, respectively. Prepared pastes were screen-printed on an alumina substrate and fired. TFT electrodes were made only in the form of working electrode that is commonly a part of three-electrode system.

Electrochemical measurements were performed with AUTOLAB PGS30 Analyzer (EcoChemie, Netherlands) connected to VA-Stand 663 (Metrohm, Switzerland), using a standard cell. A three-electrode system was used, Cu₂O electrode was employed as the working electrode, an Ag/AgCl/3M KCl electrode served as the reference electrode and Pt electrode was used as the auxiliary electrode. Cyclic voltammetry (CV) were carried out in the presence of 0.2 M acetate buffer pH 5.0 and in the presence of 1.10⁻⁴ M adenine. CV parameters: scan rate 100 mV/s, potential range -0.5 to 0.5 V.

Results and Discussion

According to the XRD measurement, we prepared Cu₂O/CuO nanoparticles consisted of 60 % CuO and 40 % Cu₂O. In Figure 1 the differences between fired and non-fired cermet electrodes can be observed. In case of non-fired electrodes the Cu₂O/CuO nanoparticles were covered by vehicle whereas in the case of fired cermet electrode, the organic components were burned out and nanoparticles became naked. In the case of polymer electrode, the nanoparticles remained covered with polymer even fired, so the electrode active area remains minimal (Fig 2).

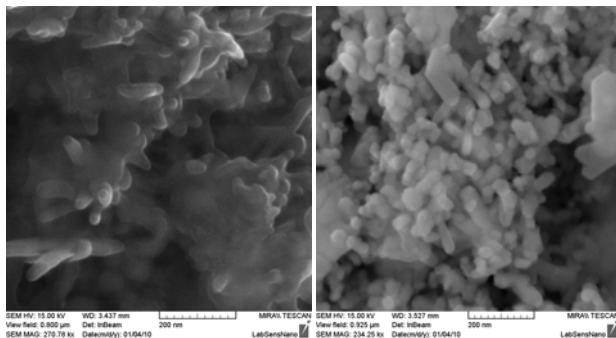


Figure 1: The SEM images of screen-printed cermet paste with $\text{Cu}_2\text{O}/\text{CuO}$ particles before (left) and after (right) firing process.

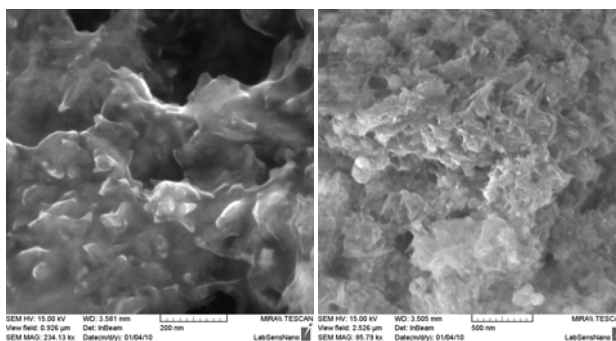


Figure 2: The SEM images of screen-printed polymer paste with $\text{Cu}_2\text{O}/\text{CuO}$ particles before (left) and after (right) firing process.

The electrochemical oxidation of adenine, guanine or other purine derivatives at carbon electrode is well known. Formation of complexes of these compounds with metals including copper has been studied. Species Cu(II) can be reduced to Cu(I) and in the presence of adenine, Cu(I) reacts with adenine to form insoluble compounds that accumulate on the electrode surface (Trnkova et al. 2008) and cause decreasing of current response (Fig 3 and Figure 4).

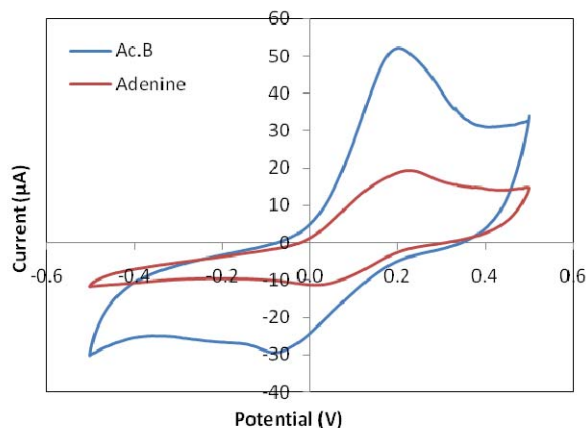


Figure 3: Cyclic voltammogram of cermet electrode with $\text{Cu}_2\text{O}/\text{CuO}$ particles after firing process.

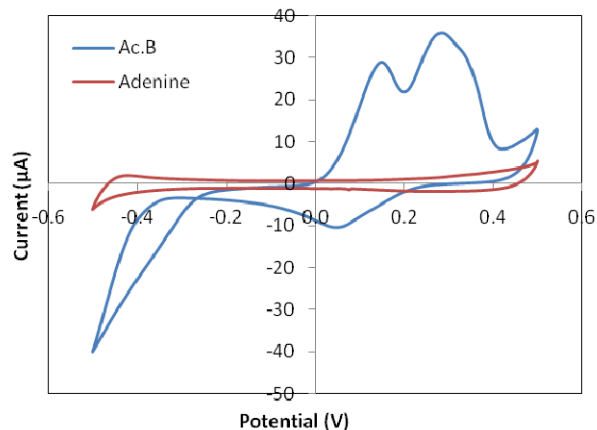


Figure 4: Cyclic voltammogram of cermet electrode with $\text{Cu}_2\text{O}/\text{CuO}$ particles before firing process

The polymer electrode gives bad response due to the polymer binding material that covers $\text{Cu}_2\text{O}/\text{CuO}$ nanoparticles which lead to electrode active area decreasing.

Conclusion

$\text{Cu}_2\text{O}/\text{CuO}$ nanoparticles for preparation of thick film pastes were prepared. Prepared pastes were screen-printed on previously prepared electrode substrate. These electrodes were successfully used as the working electrodes for electrochemical detection of adenine.

Acknowledgement

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