



CuO nanoparticles incorporated in hierarchical MFI zeolite as highly active electrocatalyst for non-enzymatic glucose sensing



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ABSTRACT

A hierarchical MFI zeolite, with typical micro/meso bimodal pore structures, was prepared by desilication method. CuO nanoparticles (NPs) were incorporated into the hierarchical MFI zeolite by impregnation method. CuO/hierarchical zeolite composites were characterized by X-ray diffraction, transmission electron microscopy and nitrogen sorption. It is shown that the CuO nanoparticles are mostly dispersed in the mesopores with remaining of the crystallinity and morphology of the host zeolite. CuO nanoparticles located in hierarchical zeolite exhibit the excellent electrocatalytic performances to oxidation of glucose in alkaline media. The electrocatalytic activity enhances with increasing the loading content of CuO from 5% to 15%. The composites were fabricated for nonenzyme glucose sensing. Under the optimal conditions, the sensor shows a wide linear range from 5×10^{-7} to 1.84×10^{-2} M with a low detection limit of 3.7×10^{-7} M. The sensor also exhibits good repeatability, long-term stability as well as high selectivity against interfering species.

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1. Introduction

Nowadays, the fast determination of glucose is considered to be important in wide areas of food industry, biotechnology and clinical diagnostics. Especially for the patients with diabetes mellitus, the regular test of glucose level is also necessary, which demands glucose sensors with high sensitivity, good reliability and excellent selectivity. Glucose oxidase (GOD)-based electrochemical biosensors have been proved to be a powerful device for glucose determination thanks to the high selectivity, sensitivity and low detection limit. However, due to the intrinsic feature of enzymes, there are some drawbacks in the GOD-based biosensors, such as poor reproducibility, thermal and chemical instability [1,2]. Therefore, the non-enzymatic glucose biosensors based on metal nanoparticles (Au, Pt, Pd, Cu, Ni), metal oxides (Co_3O_4 , CuO, NiO) or alloys (Pt/Pb, Pt/Au, Au/Ag) [3–10] have received more and more attentions. Non-enzymatic glucose biosensors alleviated the

problems of enzyme-based biosensors such as insufficient stability, lower reproducibility, thermal and chemical instability, sensitivity to temperature, pH and humidity. Hence it will probably become the fourth generation glucose sensors for the future analytical applications.

Non-enzymatic glucose biosensors are based on the glucose oxidation catalyzed by a variety of electrocatalysts. Therefore, the preparation of electrocatalysts with high performance is crucial for improving sensitivity, selectivity and reliability of sensors. Copper oxide (CuO) nanoparticles, as a well-known p-type semiconductor, has gained increasing attention due to its low production cost, high stability, good electrical conductivity and easy availability, and more importantly, CuO nanoparticles possess the excellent electrocatalytic activity to reduction of H_2O_2 and oxidation of glucose as well as purine and amino acid [9,11–15]. Except that, a series of CuO nanocomposites based on various substrates have been developed for non-enzymatic glucose sensors [16–18]. In recent years, some novel host materials, such as graphene, carbon nanotubes, ordered mesoporous silica-based materials, etc., are widely applied as hosts for electrocatalysis and further construction of biosensors owing to their large surface area and good biocompatibility [19–22].

In this work, hierarchical zeolite, another novel type of silica-based matrix, was prepared by desilication of microporous MFI

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zeolite in alkaline media [23]. As we know, microporous MFI zeolite has definite shape and unique crystal structures, but usually it cannot be applied for construction of biosensors due to the smaller pores (<1 nm). The desilication method by base leaching has already been proved to be able to create extra mesopores (10–30 nm) in addition to the intrinsic micropores [24]. The hierarchical zeolite is highly desired in catalysis fields [25] and is becoming attractive in biosensing application. This type of hierarchical zeolite with micro/meso pore structures not only possesses mesopores induced by desilication, but also offers the interconnected three-dimensional pore systems. The larger mesopores are favorable for biomolecules immobilization or high loading of nanoparticles, and the interconnected three-dimensional pore structures can provide a convenient and fast pathway for mass transfer. Recently, Ren and co-authors [26] dispersed gold nanoparticles (AuNPs, 3–20 nm) into the hierarchical zeolite, which was used as a novel matrix for the immobilization of hemoglobin protein to construct H₂O₂ biosensor.

Herein, we incorporated high content of CuO nanoparticles (~15%) in hierarchical MFI zeolite by the simple wet impregnation method. The CuO/hierarchical zeolite composites were applied as highly reactive electrocatalyst for glucose oxidation and further constructed a non-enzymatic glucose biosensor. The sensor exhibits the excellent performance such as high sensitivity, low detection limit and good selectivity.

2. Experimental

2.1. Synthesis of CuO incorporated hierarchical porous MFI zeolite composites

The parent MFI zeolite used in this work is commercially available with a nominal Si/Al ratio of 50. The hierarchical MFI zeolite with micro/meso pore structures (denoted as meso-MFI), were prepared by treatment of microporous MFI zeolite in NaOH solution as described in detail elsewhere [23]. The incorporation of CuO NPs was performed by impregnation of 1.0 g meso-MFI zeolite into 10 g of Cu(NO₃)₂ aqueous solution with different concentrations at 90 °C over 3 h under stirring. The mixtures were then slowly dried at 60 °C for 6 h. Subsequently the solid sample were annealed in air at 550 °C for 5 h, which was labeled as meso-MFI-xCuO, in which x represents the mass ratio of CuO to zeolite powder.

2.2. Fabrication of modified carbon paste electrode

The modified carbon paste electrode was prepared as follows: 50 mg meso-MFI-xCuO composites, 0.5 g carbon graphite and 0.4 g liquid paraffin were uniformly mixed and carefully grounded in an agate mortar. The resulting homogeneous pastes were then packed into a cavity (3 mm diameter) at the end of a glass tube. Electrical contact was made by a fine copper wire contacted to one side of the carbon paste. The resulting carbon paste electrode was finally polished and smoothed on a weighting paper.

2.3. Apparatus and measurements

Powder X-ray diffraction measurements were performed with a Rigaku D-MAX/IIA X-ray diffractometer in a scanning range of 5–70° (2θ) at a rate of 4° (2θ)/min with Cu Kα radiation. Transmission electron microscope (TEM) images were obtained on a JEOL 2011 instrument. Nitrogen sorption isotherms were carried out on a Micromeritics ASAP2020M+C instrument. All electrochemical experiments were performed on CHI 660C electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode system, where the modified carbon paste electrodes as working electrode, a platinum wire as auxiliary electrode and a

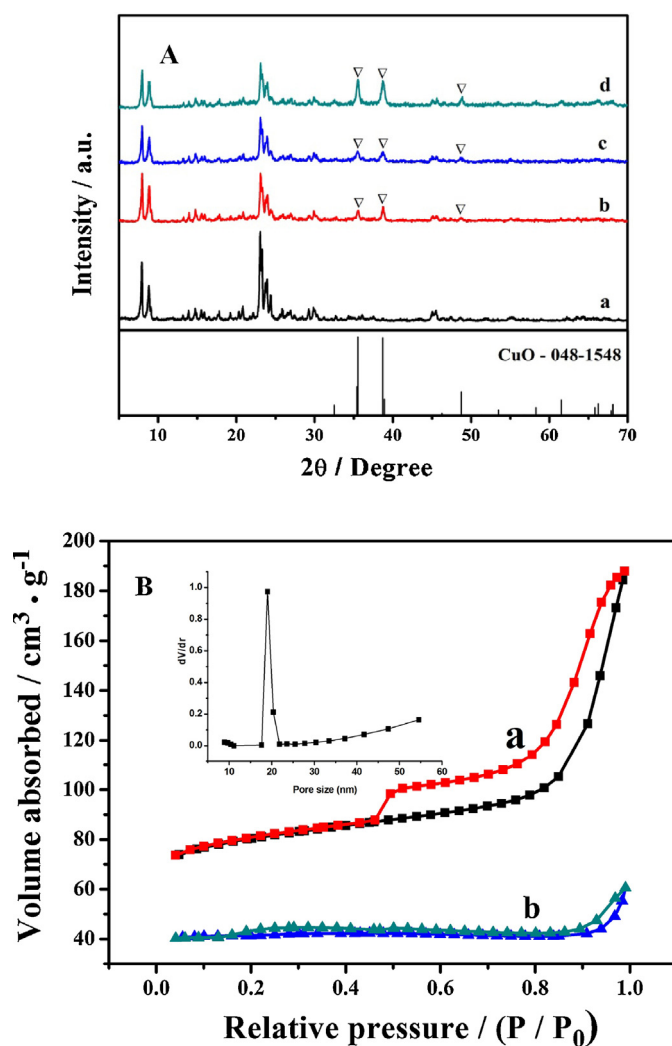


Fig. 1. (A) XRD patterns of meso-MFI samples after loading 0% CuO (a), 5% CuO (b), 10% CuO (c) and 15% CuO (d). (∇ denoted as the diffraction peaks of CuO.) (B) N₂ sorption isotherms of meso-MFI before (a) and after (b) loading 15% CuO. The inset is pore size distribution of meso-MFI.

Ag/AgCl (3 M KCl) electrode as reference electrode. All solutions in the cell were deoxygenated by highly purified nitrogen gas for at least 15 min prior to experiments and a nitrogen atmosphere was then kept over the solution during measurements.

3. Results and discussion

3.1. Characterization of meso-MFI-xCuO composites

The X-ray diffraction patterns of meso-MFI zeolite after loading different content of CuO were shown in Fig. 1A. Compared with meso-MFI zeolite (curve a in Fig. 1A), all meso-MFI-xCuO composites can keep the typical MFI crystal structure after CuO NPs are incorporated into the hierarchical zeolite, except for the slight decreasing of peak intensity. In contrast with the standard diffraction patterns for CuO (JCPDS 045-0937), the diffraction peaks at 35.5°, 38.7° and 48.7°/2θ (denoted as the symbol of ∇) for meso-MFI-xCuO composites are assigned to that of monoclinic CuO crystals. Furthermore, the diffraction intensity of CuO increases as the loading of CuO NPs in meso-MFI zeolite from 5% to 15% (curves b–d in Fig. 1A).

N₂ physical sorption analysis is used to evaluate pore structures of meso-MFI zeolite before and after the incorporation of CuO.

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