Copper Nanoparticles: Substituted Catalysts of Expensive Platinum for Methanol Oxidation

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This work presents copper nanoparticles as substituted electrocatalysts for oxidation of methanol. Copper nanoparticles were successfully synthesized by a simple electrochemical method and then were characterized by X-ray diffraction and scanning electron microscope. The electrocatalytic properties of the methanol oxidation at this material on the kryptol substrate was investigated at room temperature using cyclic voltammetry, electrochemical impedance spectroscopy and current density-time experiment. The results revealed that copper catalysts presented attractively electrocatalytic activity for methanol oxidation reaction (MOR). Owing to lower production costs of copper, the reported nanostructured copper catalyst is a promising electrode material for direct methanol fuel cells.

Keywords: Copper, Electrochemistry, Nanosize, Methanol oxidation reaction.

INTRODUCTION

Direct methanol fuel cells (DMFC) have been much interest because of their high energy density, low operating temperature and easy fuel handling[1-3]. It is well known that the high costs and severe poisoning are the main barriers for implementation[4-6]. In order to reduce the amount of Pt on the electrodes, a lot of effort has been devoted to developing catalysts, such as increasing the dispersion of the noble metal on different supports[7,8], alloying with other metal[9,10] or mixing with oxides[11,12]. Many metals *e.g.*, Au[13], Pd[14] and Rh[15] have been proposed as alternatives to Pt catalyst. However, these metals were also precious and the usage of them does not help to reduce the costs. Thus, it would be highly desirable to develop a novel metal material, other than precious metal, which has high electrocatalytic properties for methanol oxidation reaction (MOR).

Copper is a very familiar metal with low costs and excellent performance and has been widely used as anode electrode in Li ion batteries[16] and solid oxide fuel cell[17]. It has a potential application as a catalyst for methanol oxidation. Gazdzicki's group[18] reported that copper/Ru(0001) can convert CD_3OH to CO_2, while the electrochemical property had not been studied. Papadimitriou and colleagues[19] obtained Pt-Cu, Pt-Ni and Pt-Co electrode by an electrochemical method and the superior behavior of Pt(Cu) catalysts toward methanol electrooxidation as well as the different behavior of Pt(Ni) and Pt(Co) catalysts were also studied. They reported that Cu, Ni and Co have an influence on methanol dissociative chemisorptions and CO

poison removal at/from the Pt surface. To the best of our knowledge, the related reports are only the above works. Herein, copper nanoparticles were prepared by a simple electrochemical method. The as-prepared products as the catalysts for methanol oxidation reaction as well as their crystallinity, morphology and electrochemical performance were evaluated by X-ray diffraction, scanning electron microscope and electrochemical method, respectively. Electrocatalytic activities of the electrodes based on copper nanoparticles for the electrooxidation of methanol were investigated by means of cyclic voltammetry, electrochemical impedance spectrosco and current density-time experiments. We expect the synthesized copper nanoparticles would have excellent electrocatalytic activities to methanol oxidation reaction

EXPERIMENTAL

Synthesis of copper nanoparticles: All solutions were prepared by analytical grade chemical reagents and double distilled water. Prior to all electrochemical experiments, the solution was degassed by bubbling N_2 for 20 min. Copper particles were electrodeposited on the previous treated kryptol at the potential range from -0.3 V to 0.2 V at 50 mV s^{-1} in a mixed solution of 5 mM $CuSO_4$ and 0.5 M H_2SO_4. The resultant copper electrode were directly used as the working electrode for methanol oxidation.

All electrochemical experiments were carried out in a conventional three-electrode cell by CHI 660D electrochemical work station. A platinum wire and a saturated calomel electrode

(SCE) were used as counter electrode and reference electrode, respectively. A kryptol (electrode geometric area: 0.4976 cm^2) was used as a substrate. The electrocatalytic properties of copper nanoparticles electrode were performed in CH$_3$OH solution. The impedance data were also collected in ac frequency range from 1 Hz to 100 kHz at the open circuit potential of 0.7 V. All the electrochemical experiments were carried out at room temperature.

The products were crapped off the electrode for character. X-ray diffraction (XRD) measurement was performed by a Bruke D8 Advance diffractometer with CuK$_\alpha$ radiation. The morphology of the synthesized nanoparticles was observed on Zeiss scanning electron microscope (SEM, EVO LS-15) at 15 kV.

RESULTS AND DISCUSSION

X-ray diffraction analysis: Fig.1 shows the X-ray diffraction spectra of the prepared copper particles. From Fig.1, it can be seen that the obtained powders were pure copper, because all diffraction peaks matched well with the cubic crystal structure (JCPDS file No.85-1326, Fd3m). According to the Scherrer's equation: $D = \kappa\lambda/(\beta_{1/2}\cos\theta)$, the average particles diameter of as-prepared copper particles is 35 nm.
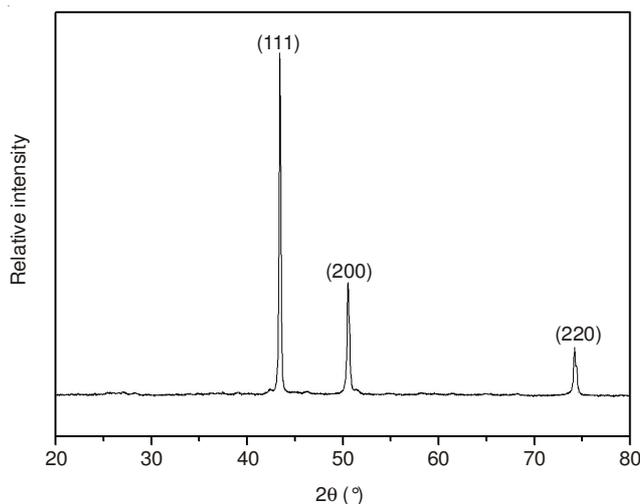
Fig. 1. X-ray diffraction patterns of pure copper

Scanning electron microscope images: The scanning electron microscope micrographs of the synthesized copper nanoparticles are illustrated in Fig. 2. The resultant samples are aggregated in Fig. 2a. However, the samples can be clearly seen in the scanning electron microscope with octahedral morphologies and the average diameter of these nanoparticles are about 50-60 nm (Fig. 2b), which bigger than and not much different from the analysis by X-ray diffraction.

Cyclic voltammetrys (CVs) for the oxidation of methanol: Fig.3 provides the cyclic voltammetrys of kryptol electrode and copper nanoparticles electrode in 0.5 mol L^{-1} H$_2$SO$_4$ and 1 mol L^{-1} CH$_3$OH solution. The shapes of the cyclic voltammetry curves are very similar to that of previously reported with other anode materials[20]. The anodic peaks for methanol oxidation reaction appears on both anodes in the forward and reverse sweeps. According to Fig. 3b, we notice that there

is methanol oxidation peak of pure copper electrode while the methanol oxidation peaks of kryptol electrode (Fig. 3a) cannot be seen obviously, which implies that the kryptol substrate only plays a conductor role in the resultant electrode and copper nanoparticles can be used as catalyst for the methanol oxidation.
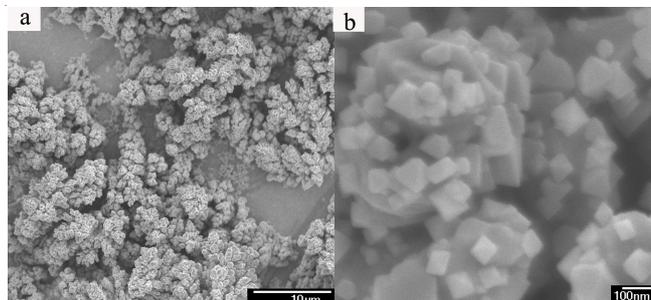
Fig. 2. TEM morphologies of Copper nanoparticles
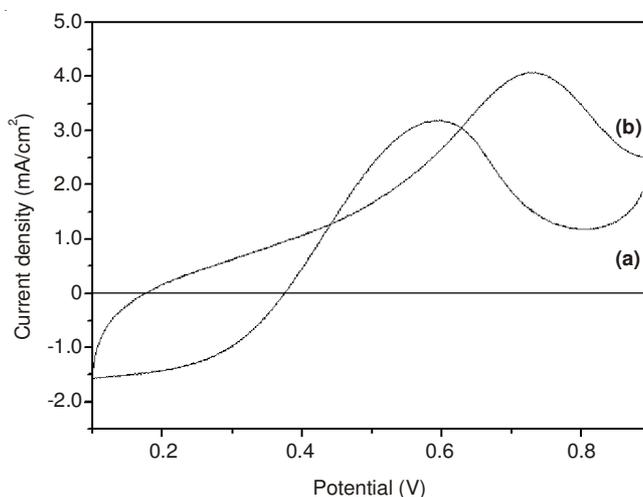
Fig. 3. Cyclic voltammograms for (a) kryptol and (b) copper electrode in 0.5 mol/L H$_2$SO$_4$ + 1 mol/L CH$_3$OH solution obtained at 0.05 V/s.

Electrochemical impedance spectroscopy (EIS) of copper electrode: Fig. 4 gives the electrochemical impedance spectroscopy of copper electrode in 1 mol/L CH$_3$OH + 0.5
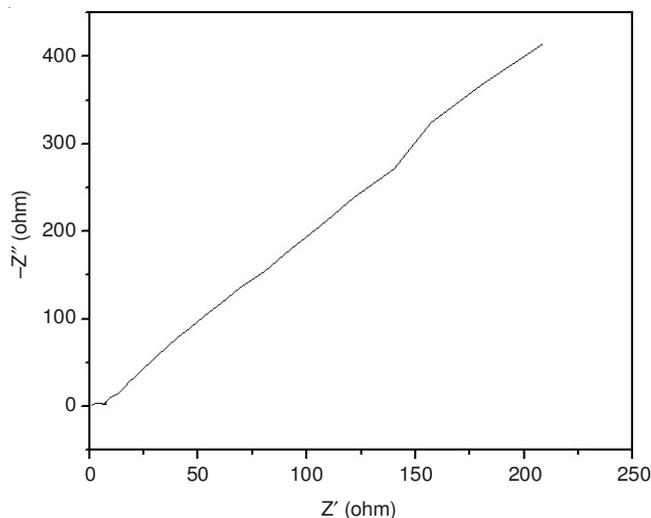
Fig. 4. EIS of copper electrode in 1mol/L CH$_3$OH + 0.5 mol/L H$_2$SO$_4$ aqueous solution

mol/L H_2SO_4 aqueous solution. As can be seen, the impedance spectra display the characteristics of a depressed semi-circle in the high frequency region and a straight line with a slope of nearly 45° in the low frequency region. This demonstrates that a fast charge transfer in the electrode/solution interface.

i-t curve: After the anodic peak current reached its highest value, the copper electrode was electrolyzed in the same solution at the potential of 0.7 V for 10 min. The typical current-time curves of copper electrodes in 1M CH_3OH + 0.5 M H_2SO_4 solution at an anodic potential of 0.7 V are shown in Fig. 5. This potential was chosen because it was close to the oxidation potential of methanol from cyclic voltammetrys (Fig. 3). It can be seen that the samples show a current decay in current-time measurements. There is an initial current drop, followed by a slower decay. It can be supposed from the figure that the electrode is relatively endurable for intermediate production.
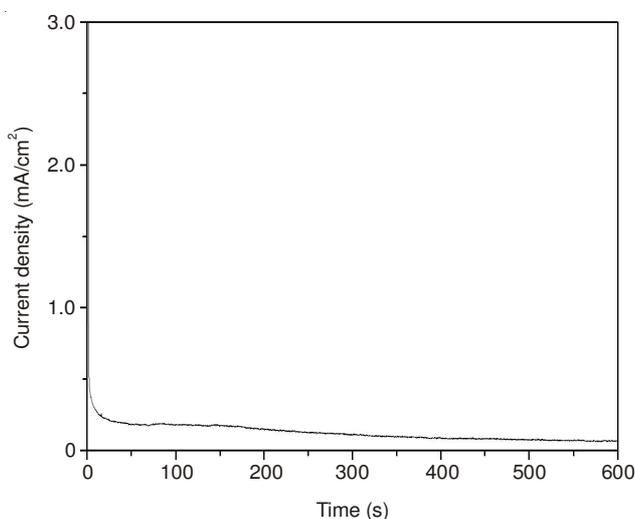
Fig. 5. Current-time curves at 0.7 V for Copper electrode in 1M CH_3OH and 0.5M H_2SO_4

Conclusion

The copper nanoparticles electrode was successfully synthesized by the electrochemical method. The results of cyclic voltammetry measurement imply an obvious electrocatalytic activity for methanol on the copper nanoparticles electrode. Together with the low cost of copper, the copper nanoparticles electrodes are expected to be a promising candidate as electrodes materials of direct methanol fuel cells.

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