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Short communication

The fabrication of silver ion implantation-modified electrode and its application in electrocatalytic oxidation of formaldehyde

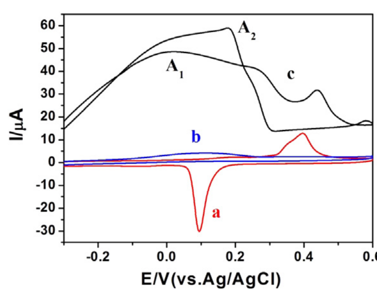
Yanan Yu [b], Mingzhe Jia [b], Huifeng Tian [b], Jingbo Hu [a, b, *]

[a] Key Laboratory of Beam Technology and Material Modification of Ministry of Education, Beijing Normal University, Beijing 100875, PR China
[b] College of Chemistry, Beijing Normal University, Beijing 100875, PR China

HIGHLIGHTS

- A novel process for the fabrication of a silver-nanoparticle-modified electrode using ion implantation.
- The zero-valent state of AgNPs exhibit well catalytic performance and stability towards the electro-oxidation of formaldehyde.
- AgNPs/ITO electrode may be a promising anode electrode material for the direct formaldehyde fuel cells (DFFCs).

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we present a novel process for the fabrication of a silver-nanoparticle-modified electrode using silver ion implantation. This method is facile, low-cost and environmental friendly without the use of any linking chemicals. The modified electrode was verified by scanning electron microscope (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectra (EIS) and cyclic voltammetry (CV). The AgNPs formed on the electrode are in the zero-valent metallic state with a size distribution in the range of 3–6 nm. The modified electrode shows prominent electrocatalytic activity towards the oxidation of formaldehyde with long-term stability and could be useful in fuel cells.

1. Introduction

The electrochemical oxidation of small organic molecules such as methanol, ethanol, formic acid and formaldehyde have been investigated intensively for the development of direct fuel cells due to the relative ease of storage and handling as well as high energy density [1–6]. Several reports have been published on the electrochemical oxidation of methanol and many of them were carried out on noble metal electrodes [7–11]. In recent years, there has been increasing interest in the electrochemical oxidation of formaldehyde [12–15].

Noble metals such as Pt and Pd are initially good catalysts for the electro-oxidation of small organic molecules. Numerous reports have been published on the oxidation of formaldehyde and most of them are carried out on Pt or Pd catalyst [6,16,17]. However, the high cost of noble metals inhibits their application in fuel cells. Therefore, the effort to finding out an abundant, inexpensive and efficient electrocatalytic material as the substitute for noble metal catalysts is of great significance. Ag is much cheaper than Pt and Pd. It has the highest electrical conductivity among the metals and silver nanoparticles (AgNPs) have been explored traditionally to be

* Corresponding author. College of Chemistry, Beijing Normal University, Beijing 100875, PR China.
E-mail address: hujingbo@bnu.edu.cn (J. Hu).

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employed as catalysts in various reactions [18–20]. In recent years, there are myriads of methods to prepare AgNPs, such as chemical reduction [21], electrochemical deposition [22], drop casting [23] and metal-vapor synthesis [24]. Nevertheless, it is still expected that the less use of stabilizers and binding reagents would improve the performance of the modified electrode significantly in the consideration of the negative effects brought by these chemicals.

Ion implantation is a kind of material surface modification technique, which provides practical and excellent electrode materials with long-term stability. By this method, we can modify the metallic nanoparticles on the substrate and control their size just by the implantation condition. In addition, the process is facile, low-cost and eco-friendly without the use of any other chemicals [25–30]. In our previous reports, we have prepared several metal-nanoparticle-modified electrodes successfully by ion implantation [7,31,32]. These electrodes exhibited very low background current and excellent electrochemical stability, even after ultrasonic treatment, indicating the high stability of the nanoparticles on the surface. Indium tin oxide (ITO) was chosen as the electrode substrate due to its wide electrochemical working window and stable electrochemical properties [33–36]. In addition, it can be available at a very low cost from industrial mass production.

In this paper, our group describes a new method to prepare AgNPs modified ITO electrode (AgNPs/ITO) by silver ion implantation. The prepared AgNPs on the ITO electrode surface are free from any chemical reagents surrounding or binding to them. The AgNPs/ITO electrodes were used for the electrocatalytic oxidation of formaldehyde and exhibited remarkable catalytic activity with good stability.

2. Experimental

2.1. Reagents

ITO glass was purchased from Beijing Tsinghua Engineering Research Center of Liquid Crystal Technology. All chemicals were of analytical grade and used as purchased without further purification. All measurements were performed at room temperature. All solutions were prepared with triple distilled water.

2.2. Preparation of the AgNPs/ITO electrode

Ion implantation was carried out using a Beijing Normal University (BNU) metal vapor vacuum arc (MEVVA) implanter. Silver ions with 10 KeV at the fluences of 1.0×10^{17} ions cm^{-2} were implanted onto the pretreated ITO surface, forming the AgNPs/ITO electrode. According to our experience, the fluence and energy we used could implant the maximum amount of AgNPs on the substrate and retain the electrical conductivity of the electrode. The electrode was washed with distilled water and ethanol for several times before used.

2.3. Apparatus

The structure and morphology of the electrode were characterized by scanning electron microscope (SEM) (Hitachi X650, Japan). Tapping mode atomic force microscope (AFM) images were recorded by using a Nanoscope Instrument (Vecco). X-ray photoelectron spectroscopy (XPS) measurement was performed on an AXIS Ultra spectrometer (Shimadzu, Japan). All electrochemical measurements were carried out on a CHI660D electrochemical workstation (CH Instrument Inc, USA). A conventional three-electrode system was employed with a bare or modified ITO electrode ($A = 75$ mm^2) as the working electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and a platinum wire electrode as the auxiliary electrode.

3. Results and discussion

3.1. Characterization of AgNPs/ITO electrode

3.1.1. SEM images of AgNPs/ITO electrode

Fig. 1 (A) shows the structure of the bare ITO electrode surface. As seen in this image, there are some spherical-shaped grains on the bare ITO electrode surface. After ion implantation, we can observe a distinct change in the surface as a result of the formation of AgNPs (Fig. 1(B)). It shows clearly that the spherical-shaped grains disappeared and the highly dispersed AgNPs with diameters between 3 and 6 nm emerged on the modified electrode.

3.1.2. AFM studies of AgNPs/ITO electrode

Fig. 2 illustrates the three-dimensional view of the tapping mode image of the bare ITO (A) and the AgNPs/ITO (B). From AFM measurement, it is given that the surface roughness (Rrms) of the bare ITO and the AgNPs/ITO is 1.76 and 1.36, respectively. As can be seen from the figure and Rrms data, the bare ITO surface is so coarse, but the AgNPs/ITO electrode surface becomes smoother after silver ion implantation. The results confirm the morphological change of the ITO after ion-implantation, which might be attributed to the creation of a new interface after bombardment by heavy ions [28,37].

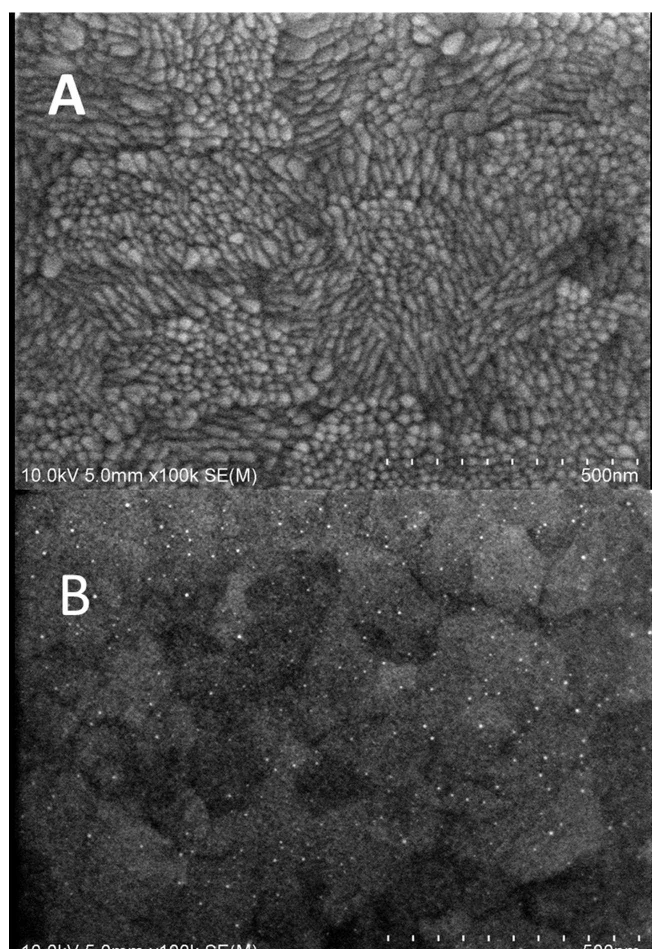

Fig. 1. SEM images of the bare ITO (A) and the AgNPs/ITO (B).