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Fabrication of cuprous oxide nanoparticles-graphene nanocomposite for determination of acetaminophen

Hua Yang, Bingdi Liu, Yaping Ding *, Li Li, Xiaoqian Ouyang

Department of Chemistry, Shanghai University, Shanghai 200444, PR China

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ABSTRACT

A glassy carbon electrode modified with cuprous oxide nanoparticles-graphene composite film (Cu_2O/GR) was prepared and applied to detect acetaminophen (AC). Scanning electron microscopy, energy dispersive X-ray spectroscopy and electrochemical impedance spectroscopy were applied for characterization of the proposed electrode. Cyclic voltammetry and square wave voltammetry were used to investigate the electrocatalysis oxidation of AC on Cu_2O/GR. The linearity ranged from 2.0×10^{-8} to 1.3×10^{-6} M with a detection limit of 6.67×10^{-9} M (S/N = 3) and the calculated sensitivity of 14,397.7 μA mM^{-1} cm^{-2}. Under optimal conditions, the sensor displays good stability and satisfactory results in real samples analysis.

1. Introduction

Acetaminophen (AC), paracetamol or *N*-acetyl-p-aminophenol, is an effective, safe and widely used analgesic and antipyretic agent for the relief of pains associated with several parts of the body, such as cancer pain, headache and neuralgia [1,2]. This substance has been long-established and commonly recognized as a good alternative to aspirin in the therapeutic doses [3]. However, several side effects may be caused by overdoses and chronic use of AC, or concomitant use of alcohol or other drugs [4]. Therefore, the need for a simple and efficient method which can detect AC with high selectivity and sensitivity is stringent for pharmaceutical applications to secure human health. Until now, a wide range of analytical techniques has been reported to determine the concentration of AC, including high-performance liquid chromatography (HPLC) [5,6], titrimetry [7], spectrofluorometry [8], electrochemical analysis [9,10], and capillary zone electrophoresis [11,12]. Among all the above, electrochemical methods have been paid great attention owing to their high sensitivity, ease of monitoring, simplicity and low cost.

Recently, to meet the demands of electrochemical sensors, various nanostructured materials have been developed and applied to modify kinds of electrodes. Especially, sensors modified with metallic nanoparticles have attracted extensive attention in electrochemical studies, such as noble metals (Pt, Au), transition metal (Ni, Cu, Zn) and their oxide (NiO, CuO, ZnO) [13–15]. Cuprous oxide (Cu_2O), a p-type semiconductor, is considered as an attractive and promising material due to its relatively narrow band gap (2.0–2.2 eV) [16]. Cu_2O is one of the most attractive inorganic materials and an excellent candidate for catalytic activity, sensing, fuel cells and solar cells [17–21]. Due to the proper redox potentials, non-toxic and low cost, the electrochemical applications of Cu_2O have been reported and applied in various fields [22–24].

Graphene (GR) is a single layer of carbon atoms closely packed into a two-dimensional honeycomb which has attracted tremendous attention in recent years [25,26]. GR possesses numerous unexpected properties, like extraordinary electronic transport properties, large surface area and strong mechanical strength [22]. The distinguished characteristics have made GR gain considerable interests and widespread potential applications in electrochemical supercapacitors [27], fabricated field-effect transistors [28] and chemical sensors [13,29].

Up to now, there are a lot of approaches in preparing metal nanostructures. Especially, electro-deposition can facilely synthesize metal nanoparticles on the surface of conducting substrates and easily control the sizes of the prepared nanoparticles by altering the conditions [30]. Herein, Cu_2O nanoparticles were electrochemically synthesized which present unusual advantages such as electro-catalysis and high effective surface area.

In the present study, an effective electrochemical sensor based on Cu_2O/GR nanocomposite was fabricated by electro-deposition for the electro-catalytic oxidation of AC. This composite material combines the excellent electro-catalytic activity of Cu_2O and electrical conductivity of GR. The modified electrode showed high electro-catalytic activity and sensitivity for the oxidation of AC.

* Corresponding author.
E-mail address: wdingyp@sina.com (Y. Ding).

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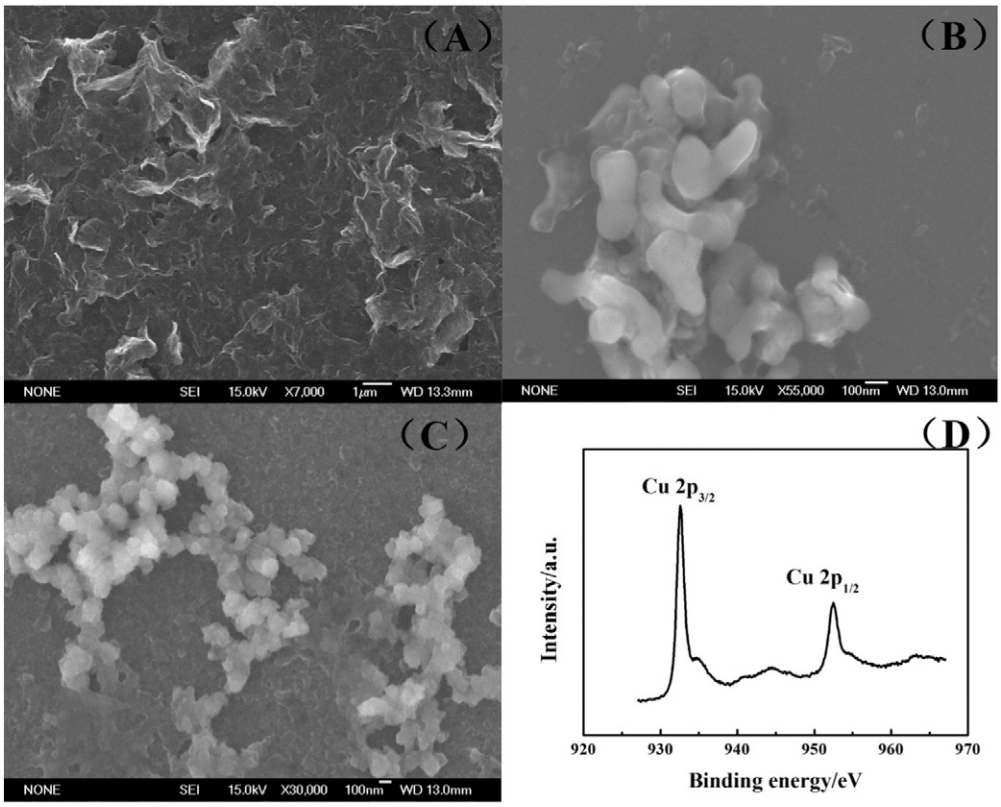

Fig. 1. SEM image of GR (A), Cu_2O (B), Cu_2O/GR (C) and XPS survey spectra of Cu_2O (D).

2. Experimental

2.1. Chemicals

All chemicals and reagents employed in this work were of analytical grade and used without further purification. GR was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). AC, ascorbic acid (AA), dopamine (DA), cysteine, phenylalanine and leucine were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution (PBS) with different pH values were prepared by mixing stock solutions of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 (Shanghai Chemical Reagent Co., Ltd.,) and double distilled water was used throughout the experiment. All electrochemical experiments were carried out at 25 ± 0.1 °C.

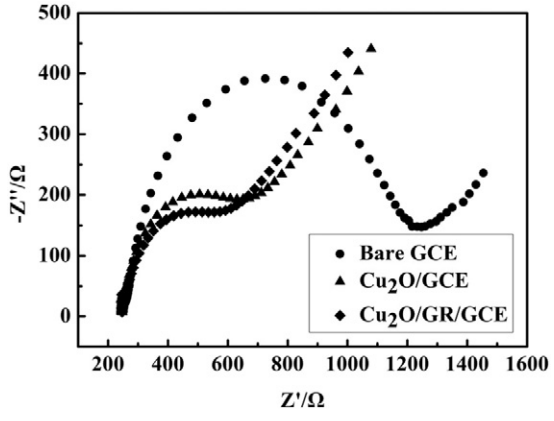

Fig. 2. Nyquist plot of EIS for bare GCE(●), Cu_2O/GCE(▲), Cu_2O/GR/GCE(◆)in 5.0 mM $Fe(CN)_6^{3-/4-}$ + 0.1 M KCl.

2.2. Apparatus

All the electrochemical measurements including cyclic voltammetry (CV), square wave voltammetry (SWV), chronoamperometry and electrochemical impedance spectroscopy (EIS) were performed with a CHI 660D electrochemical workstation (Chenhua Corp., Shanghai, China). A conventional three-electrode system was employed comprising a glassy carbon electrode (GCE, 3 mm in diameter) coated with Cu_2O/GR film as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode as the reference electrode. Scanning electron microscopy (SEM) images and Energy Dispersive X-ray spectroscopy (EDS) were carried out using a scanning electron microscope (JSM-6700F, 15.0 kV). X-ray photoelectron spectroscopy (XPS) analysis was carried out on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer).

2.3. Fabrication of modified electrodes

The bare GCE was firstly polished on chamois leather with 0.05 μm α-Al_2O_3 to a mirror-like surface and then rinsed with water. Then, the electrode was washed with ethanol and double distilled water for 5 min in an ultrasonic bath, respectively.

200 μL of 1 mg mL^{-1} GR was added to 10 mL 0.1 M KCl to form a homogeneous suspension with ultrasonication for 15 min. The GCE was immersed in above solution by electro-depositing at a potentiostatic potential of 1.8 V for 400 s. The electro-deposition of Cu_2O was similar to the literature [31]. Solid sodium hydroxide was slowly added to 25 mM $Cu(NO_3)_2$ aqueous solution in ice bath till clarification of the solution. Then the GR/GCE or GCE was respectively placed in the prepared