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Reduced graphene oxide-supported gold dendrite for electrochemical sensing of acetaminophen

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ABSTRACT

A new nanocomposite was developed based on reduced graphene oxide (RGO) supported gold dendrite and applied for amperometric detection of acetaminophen. The RGO-gold dendrite composite was prepared by self-assembly of poly (diallyldimethylammonium chloride) (PDDA) functionalized gold dendrite and poly (sodium 4-styrenesulfonate) (PSS) functionalized RGO. The composite electrode material was characterized by Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Ultraviolet-vis spectroscopy (UV), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The RGO-gold dendrite composite exhibited enhanced conductivity, catalytic activity and stability for acetaminophen oxidation and determination. The RGO-gold dendrite based electrochemical sensor is competent for detecting acetaminophen with a linear range from 0.07 μM to 3000 μM with a detection limit of 0.005 μM (S/N = 3). Moreover, the sensor was applied for the detection of acetaminophen in tablets and urine samples, which holds great promise in pharmaceutical analysis.

1. Introduction

Acetaminophen is generally employed as a safe and efficient drug to relief fever and pains involve headache, backache and toothache [1]. Rational use of acetaminophen does not induce any toxic and side effect. However, overdoses of acetaminophen cause severe hepatoxicity [2] and nephrotoxicity [3]. The development of rapid, efficient and accurate analytical method for determination of acetaminophen is significant for drug safety. Some methods including spectrophotometry [4], liquid chromatography [5] and capillary electrophoresis [6] have been applied for detection of acetaminophen. These methods exhibited disadvantages of time-consuming extraction process, complicated sample pretreatment or expensive equipment. By comparison, electrochemical sensors have merits of convenient, low cost, fast response, wide linear range and enhanced sensitivity [7,8].

Recent progress revealed electrodes modified with gold nanoparticles exhibits high sensitivity in electrochemical analysis due to its strong catalytic action [9–11]. Traditional preparation methods of gold nanoparticles focused on simple structure such as spheres [12], cubes [13], tetrahedral and octahedral [14]. Gold dendrite with highly branched morphologies has attracted more attention because of larger surface area, more adsorption sites and higher catalytic activity [15]. However, the durability of gold dendrite is reduced by the aggregation owing to the small diameter of nanoparticle and high surface energy [16]. Some composites of gold dendrite including gold dendrite/boron-doped diamond [17], gold dendrite/Fe_3O_4@SiO_2/diazoniabicyclo [18] and Pt/gold dendrite [19] have been employed to solve the problem and exhibited advantages of favorable durability, broad potential window and outstanding catalytic capacity. These efforts demonstrated loading gold dendrite on suitable supporting materials not only improved the durability but also provided better mass transport.

Reduced graphene oxide (RGO) is promising supporting material for nanocatalysts owing to its large surface area, good conductivity and broad potential window [20,21]. Decorating gold dendrite on RGO nanosheets could enhance the detection sensitivity by inducing specific morphology or increasing the electron density in RGO-gold dendrite composite [22]. Whereas, it is still a challenge to synthesize RGO-gold dendrite composite with the increasing requirement of high loading and uniform distribution. Self-assembly has been used as an efficient method to combine RGO to other electrochemical materials [23,24]. For instance, an electrochemical DNA sensor was constructed based on self-assembled composite of RGO and tetraphenylporphyrin [23]. Yt-terbia/RGO composite was prepared by self-assembly and applied to determination of dopamine and uric acid [24]. Therefore, self-assembly can be a practicable method of decorating gold dendrite on RGO nanosheets.

In this work, a novel RGO-gold dendrite composite based electrochemical sensor was prepared for sensitive detection of acetaminophen.

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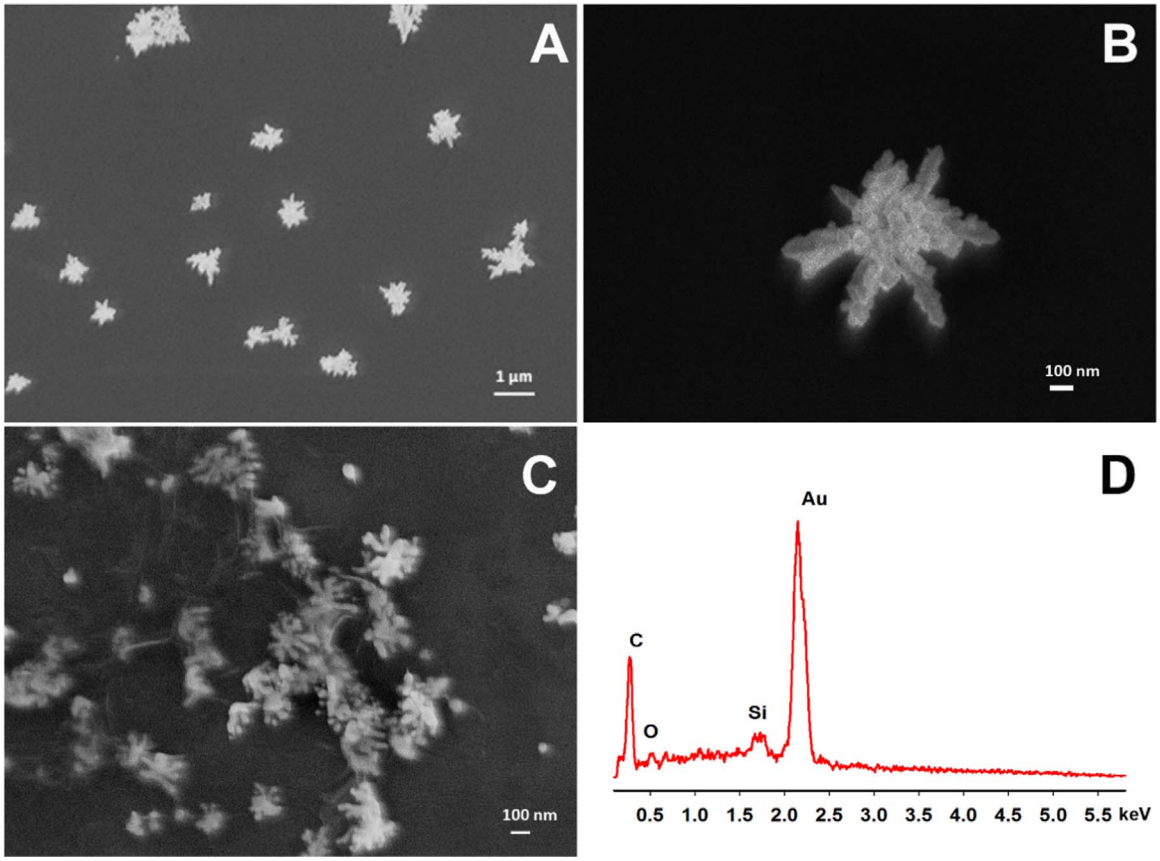

Fig. 1. SEM images of the gold dendrite in low magnification (A), high magnification (B), RGO-gold dendrite composite (C), and the EDS spectrum of RGO-gold dendrite (D).

The composite was prepared by self-assembly of poly (diallyldimethylammonium chloride) (PDDA) functionalized gold dendrite and poly (sodium 4-styrenesulfonate) (PSS) functionalized RGO. The RGO-gold dendrite composite exhibited enhanced sensing performance for acetaminophen compared respectively with RGO and gold dendrite, due to its large electrochemical active surface area, outstanding conductivity and catalytic capacity. The excellent sensing performance along with the applicability in tablets and urine samples enabled this RGO-gold dendrite composite an effective and promising hybrid electrode material for electrochemical sensors.

2. Experimental section

2.1. Reagents and apparatus

Natural graphite was purchased from Tingdao Hengrui Industrial, China. $HAuCl_4 \cdot 4H_2O$ was purchased from Aladdin reagent China. PDDA (M_w = 400,000–500,000, 20% in water) and PSS were purchased from Aldrich. Acetaminophen was purchased from Aladdin Reagent, China.

The RGO-gold dendrite composite was characterized by Scanning electron microscopy (SEM, Hitachi S-4800), energy dispersive X-ray spectroscopy (EDS), Ultraviolet-vis spectroscopy (UV, UV-1700 Shimidazule), X-ray diffraction (XRD, CuKα radiation, D/max2550VB, Rigaku), Raman spectroscopy (532 nm radiation, Renishaw inVia Raman Microscope, UK) and X-ray photoelectron spectroscope (XPS, ESCALAB-MKII 250 photoelectron spectrometer, VG Co.). Cyclic voltammetric and amperometric tests were constructed on a CHI 660E electrochemical workstation (Chen Hua Instrument Co., Ltd, Shanghai, China).

2.2. Preparation of PDDA functionalized gold dendrite

100 μL PDDA was added into 10 mL $HAuCl_4$ (0.5 mM) solution. Then 0.1 mL freshly prepared ascorbic acid (100 mM) was drop-wise added and stirred for 2 min. The reaction was controlled at 30 °C throughout the process. The resultant product was purified by centrifugation (11,000 rpm, 10 min) and washed with water (3 times).

2.3. Preparation of PSS functionalized RGO

Graphene oxide (GO) was prepared from graphite using the modified Hummers method [25]. 200 mg PSS was mixed with 50 mL GO suspension (0.1 mg/mL) and sonicated for 30 min. Then, 2 mL hydrazine hydrate was dropped in and the dispersion was refluxed for 2 h at 95 °C in oil bath. The resultant product was isolated by centrifugation (11,000 rpm, 20 min), and the excess PSS was removed by centrifugation and washed with water (3 times).

2.4. Preparation of RGO-gold dendrite composite

The RGO-gold dendrite composite was prepared by a facile self-assembly method. The PDDA-gold dendrite was mixed with PSS-RGO under stirring for 1 h at room temperature. The precipitate was collected and dispersed in water.

The as prepared RGO-gold dendrite composite was modified on the electrode. Before modification, the glassy carbon electrode (GCE) was polished with 0.3 μm alumina slurry and washed with 1:1 nitric acid, ethanol and distilled water, respectively. Then, 6.0 μL RGO-gold dendrite composite was cast on the processed bare electrode.