Au-Pt bimetallic nanoparticles decorated on sulfonated nitrogen sulfur co-doped graphene for simultaneous determination of dopamine and uric acid

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A B S T R A C T

In this work, a novel nanohybrid (AuPtNPs/S-NS-GR) of well-defined Au-Pt bimetallic nanoparticles (Au-PtNPs) decorated on sulfonated nitrogen sulfur co-doped graphene (S-NS-GR) was developed. Firstly, nitrogen sulfur co-doped graphene (NS-GR) was synthesized by one-step thermal annealing method. Secondly, phenyl SO_3H- group was introduced onto the surface of NS-GR via diazotization reaction, which could provide more binding sites for the formation of metal nanoparticles. Finally, Au-Pt bimetallic nanoparticles were anchored on the surface of S-NS-GR by using electrochemical deposition. The prepared material was characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy and electrochemical impedance spectra (EIS). In addition, the electrocatalytic activity towards dopamine (DA) and uric acid (UA) was systematically studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Under optimum conditions, the linear ranges for the detection of DA and UA were 1.0×10^{-8} – 4.0×10^{-4} M and 1.0×10^{-6} – 1.0×10^{-3} M with the limits of detection (LOD, S/N = 3) of 0.006 μM and 0.038 μM, respectively. Furthermore, the modified electrode was applied to real sample analysis.

1. Introduction

Dopamine (DA) and uric acid (UA) always coexist in the extracellular fluids of the central nervous system and serum in mammals, which play very important roles in human metabolism [1]. As one of the important and representative catecholamine neurotransmitters, DA plays a significant role in central nervous, renal and hormonal systems [2]. The abnormal levels of DA are the symptoms of some neurodegenerative diseases like Alzheimer's and Parkinson's [3]. UA, another important biological substance in body fluid, is usually considered as the final product of purine metabolism in the human body [4]. The abnormal levels of UA in human body fluid might lead to the occurrence of gout, hyperuricemia or Lesch-Nyhan syndrome [5]. Considering the importance of DA and UA in physiology and pathology, it is necessary to develop highly efficient and sensitive methods to detect them. In recent years, many approaches have been developed, including spectrophotometric [6], chemiluminescent [7], fluorescent [8] and liquid chromatographic [9,10]. Although these methods exhibit high sensitivity and selectivity, there are many disadvantages as follows: the use of a large quantity of solvent, troublesome and time consuming

pretreatment, high running cost [11]. Compared with other techniques, the electrochemical methods [12–14] are more accessible for dopamine and uric acid sensing and quantification due to their low price, fast response, trouble-free operation, and good stability [15].

Graphene (GR), a two-dimensional nanomaterial consisting of a single layer of sp^2 network of carbon atoms, has received considerable interests for potential applications in many technological fields for its very large 2D electrical conductivity, large surface area and low cost [16]. In recent years, both theoretical and experimental studies have revealed that chemical doping of GR with heteroatoms including N [17], B [18] and S [19] is an effective method to realize new functions of material [16]. For example, N-doping can induce a negative charge with respect to the delocalized sp^2-hybridized carbon framework, resulting in enhanced electron transfer ability as well as improved electrocatalytic activity [20]. While S-doping can change the electronic structure of GR by means of affecting π electrons in the carbon lattice [21]. Moreover, co-doped GR by two elements with different electronegativities can give rise to a unique electron distribution and then result in a synergistic effect [22]. For instance, Kannan et al. [23] reported that N and S co-doped graphene nanosheets synergistically

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enhanced the photovoltaic performance for counter electrodes in dye-sensitized solar cells. However, like GR, N and S co-doped graphene (NS-GR) is hydrophobic and tends to agglomerate irreversibly which limits its further application. To overcome its poor processability, the phenyl SO$_3$H- group was covalently grafted onto the surface of NS-GR via diazotization reaction in this work. The experimental results revealed that sulfonated nitrogen sulfur co-doped graphene (S-NS-GR) exhibited excellent dispersivity in water. Meanwhile, the introduction of phenyl SO$_3$H- group onto the surface of the material cannot only facilitate the homogeneous distribution of metal nanoparticles and reduce the metal average particle size but also strengthen the interaction of the metal atoms with the functional groups [24].

Noble metal nanoparticles such as Au [25], Ag [26], Pt [27], Pd [28], Au-Ag [14], Au-Pt [29], and Pt-Pd [30], have been widely synthesized and used as sensing materials in electrochemical sensors. It was reported that metal nanoparticles not only maximize the availability of nano-sized electroactive surface area for electron transfer but also provide better mass transport of reactants to the electrocatalyst [31]. Compared to monometallic nanoparticles, the bimetallic nanoparticles provide a much better catalytic performance and promote electron transfer via their synergistic effects in electrochemistry [32]. For example, Jiang et al. [33] reported a sensitive electrochemical sensor for simultaneous determination of ascorbic acid (AA), DA and UA based on Au@Pd-reduced graphene oxide nanocomposites. Especially, Liu et al. [29] presented a nanocomposite composed by Au-Pt hybrid bimetallic nanoclusters anchored at graphene oxide-electrochemically reduced graphene oxide (GO-REGO). In their work, a much wider linear range for the simultaneous detection of DA and UA was achieved with the synergistic electrocatalytic effect of Au-Pt bimetallic nanoclusters and GO-REGO.

Encouraged by the works mentioned above, a novel nanohybrid (AuPtNPs/S-NS-GR) of well-defined Au-Pt bimetallic nanoparticles (AuPtNPs) supported on sulfonated nitrogen sulfur co-doped graphene (S-NS-GR) was developed in this study. The electrochemical activity of DA and UA on the surface of AuPtNPs/S-NS-GR was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques, and the proposed method was applied to simultaneous determination of DA and UA real sample.

2. Experimental

2.1. Reagents and materials

Graphite was purchased from Shanpu Chemical Co., Ltd. (Shanghai, China). Cysteine, sulfanilic acid and hypophosphorous acid were supplied by Aladdin Chemistry Co., Ltd. (Shanghai, China). Chloroauric acid (HAuCl$_4$·4H$_2$O), chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O), sodium nitrite (NaNO$_2$) and dopamine were from Aladdin Chemistry Co., Ltd. (Shanghai, China). Uric acid was obtained from Alfa Aesar Chemical Co., Ltd. (Tianjin, China). Phosphate buffer solutions (PBS, 0.1 M) with different pH values were prepared by mixing stock solutions of 0.1 M K$_2$HPO$_4$ and 0.1 M KH$_2$PO$_4$, and adjusting the pH value with 1.0 M KOH or 1.0 M H$_3$PO$_4$. All other chemicals were of analytical grade and were used without further purification. Double distilled water and nitrogen gas (99.99%) was used for all experiments. All experiments were performed at room temperature.

2.2. Instruments and measurements

Electrochemical experiments and measurements were performed at a CHI660E electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three electrode system. A bare or modified glassy carbon electrode (GCE, CHI104, Φ = 3 mm, Gaoss Union Co., Ltd., Wuhan, China) was employed as the working electrode, a platinum column as the counter electrode, and an Ag/AgCl electrode (saturated KCl) as the reference. Differential pulse voltammetry (DPV) was

performed from 0.1 to 0.8 V with the amplitude of 50 mV and pulse width of 100 mV. Electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potentials and were performed in 5 mM Fe(CN)$_6$$^{3-/4-}$ (1:1) mixture containing 0.1 M KCl and a sinusoidal potential modulation with an amplitude of ± 5 mV and a frequency from 10^5 to 0.1 Hz was superimposed on the formal potential of the Fe(CN)$_6$$^{3-/4-}$ redox couple at 0.40 V vs. Ag/AgCl (saturated KCl). The nitrogen and sulfur co-doped graphene was prepared by a SK-G05123K Tube Furnace (Tianjin Zhonghuan Test Electrical Furnace Co., Ltd., Tianjin, China). The scanning electron microscopy (SEM) image was collected on a JSM-5600LV at 5.0 kV. Energy-dispersive X-ray spectroscopy (EDS) was collected on an Aztec-X-80 scanning electron microscopy (Japan) equipped with an energy dispersive X-ray spectroscopy detector. Raman spectra were obtained by in Via Renishaw confocal spectroscopy (Britain) with 633 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was made based on PHI-5702 (USA).

2.3. Synthesis of nitrogen and sulfur co-doped graphene (NS-GR)

Nitrogen and sulfur co-doped graphene (NS-GR) was prepared by a free catalyst thermal annealing method using green material cysteine as the nitrogen and sulfur source [17,34]. The graphene oxide (GO) was prepared from natural graphite flakes by the modified Hummers' method [35]. In a typical procedure, the mixture of GO and Cysteine was grinding in a mortar using pestle for 3 h with a weight ratio of 1:10. Subsequently, the mixture was increased to 600 °C at a heating rate of 3 °C min^{-1} in the center of a corundum tube with a flow of argon (Ar). After the temperature was maintained for 2 h, the furnace was cooled to room temperature slowly under Ar ambient, and then the final product of nitrogen and sulfur co-doped graphene (NS-GR) was obtained.

2.4. Sulfonation of NS-GR

Sulfonated nitrogen and sulfur co-doped graphene (S-NS-GR) was synthesized through diazotization reaction according to the literature [36]. Briefly, 1.04 g of 0.03 M sulfanilic acid was ultrasonically dispersed in 60 mL of 1 M HCl aqueous solution in a round-bottom flask. The flask was then transferred to an ice water bath, and the temperature was controlled at 3–5 °C with continuous stirring. 6 mL of 1 M NaNO$_2$ aqueous solution was added into admixture by drop. A clear solution was obtained after all the addition of NaNO$_2$. After stirring for another 1 h at the same temperature, a white precipitate was formed. This was filtered and washed with a copious amount of double distilled water.

The obtained white precipitate was transferred to a round-bottom flask and dissolved in 24 mL of ethanol and water (1:1) mixture maintained at 3–5 °C with continuous stirring. Then, 30 mg of NS-GR was added to the above mixture, maintaining the same temperature. Subsequently, 20 mL of 50 wt% H$_3$PO$_2$ aqueous solution was added dropwise, and the mixture was stirred for another 3 h. The obtained sulfonated nitrogen and sulfur co-doped graphene (S-NS-GR) was washed with amount of double distilled water and dried under vacuum at 60 °Cfor 12 h.

2.5. Preparation of modified electrodes

The bare GCE (Φ = 3 mm) was polished successively using 0.3 mm and 0.05 mm Al$_2$O$_3$ washed thoroughly with ethanol and water in an ultrasonic bath, dried by high-purity nitrogen (N$_2$) blowing. As showed in Scheme 1, 5 μL of 1 mg mL^{-1} S-NS-GR dispersion was dropped on the pretreated GCE and dried at room temperature to form S-NS-GR/GCE. The modified electrode was immersed into an electrochemical cell containing 1.0 mM HAuCl$_4$ and 2.0 mM H$_2$PtCl$_6$ with 0.1 M KCl. The electrodeposition of Au-Pt bimetallic nanoparticles was performed using cyclic voltammetry (CV) with a potential range of 1.0 to −1.0 V for 3 cycles at scan rate of 100 mV s^{-1}. After rinsed with double