



One-pot synthesis of reduced graphene oxide/zinc sulfide nanocomposite at room temperature for simultaneous determination of ascorbic acid, dopamine and uric acid



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ABSTRACT

With graphene oxide, zinc sulfate, sodium thiosulfate and thioglycerol (TG) as starting materials, reduced graphene oxide/zinc sulfide nanocomposite (rGO/ZnS) was successively synthesized with a facile one step method under ambient conditions. Thiosulfate was not only the sulfur source for the synthesis of ZnS but also the reducing agent for the reduction of graphene oxide (GO). TG was used not only as the catalyst for the hydrolysis of thiosulfate but also the catalyst for the reduction of graphene oxide (GO). Hexadecyl trimethyl ammonium bromide (CTAB) functionalized rGO/ZnS (CTAB/rGO/ZnS) was used as a novel electrode modifier for the simultaneous determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA). The combination of reduced graphene oxide (rGO) and ZnS nanoparticles endows the biosensor with large surface area, good biological compatibility, electricity and stability, high selectivity and sensitivity. In the threefold co-existence system, the linear calibration plots for AA, DA and UA were obtained over the range of 50.0–1000 μM , 1.0–500 μM and 1.0–500 μM with detection limits of 30 μM , 0.5 μM and 0.4 μM , respectively. In addition, the biosensor was applied to the determination of AA, DA and UA in urine samples by using standard addition method with satisfactory results.

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1. Introduction

Dopamine (DA), ascorbic acid (AA) and uric acid (UA), usually coexisting in biological matrixes, were considered as crucial molecules for physiological processes in human metabolism [1–6]. Simultaneous determination of AA, DA and UA is important for investigating their physiological functions and diagnosing diseases.

In the past few decades, electrochemical techniques have been employed in the detection of small biomolecules such as AA, DA and UA because of their high sensitivity, rapid response, simple operation and low expense [7]. However, the oxidation potentials of these electroactive species are too close to be determined separately at bare glassy carbon electrode (GCE). Carbon based nanomaterials [8–20], polymers [21–25], noble metals [26–33], metal oxides [34–39], metal hydroxides [40,41] and metal complexes [42,43] have been used as effective electrode modifiers for the simultaneous determination of AA, DA and UA. Metal sulfide nanomaterials have been employed in the electrochemical sensing of AA [44,45], tryptophan [46] and dopamine [47]. However, to the best of our

knowledge, the application of metal sulfide in the simultaneous determination of AA, DA and UA has never been reported.

Due to its unique properties such as large surface-to-volume ratio and high electrical conductivity, graphene has become the research focus in fabricating electrochemical biosensors recently. The graphene/nickel hydroxide nanocomposite [40], graphitic carbon nitride nanosheets doped graphene oxide [15], rGO/Au nanoplates composite [30], hemin functionalized GO [12], CTAB functionalized GO/multiwalled carbon nanotube composite [18], overoxidized polyimidazole/graphene oxide copolymer [25] have been employed in the simultaneous determination of AA, UA and DA. Although much effort has been devoted in resolving the overlapping oxidation peaks of these species, developing a facile and sensitive analytical method is still a challenge.

In this work, a one-step method was developed to synthesize zinc sulfide/rGO nanocomposite under ambient conditions. Thiosulfate was used as both the sulfur source for the synthesis of ZnS and the reducing agent for the reduction of GO. TG not only catalyzes the hydrolysis of thiosulfate to release S^{2-} but also the reduction of GO. It was found out that ZnS nanoparticles were distributed on the graphene sheet. The rGO/ZnS was further modified with CTAB and used to construct sensing interface to achieve simultaneous detection of DA, AA and UA. Due to the combination of

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the advantages of rGO and ZnS nanoparticles, the sensor exhibited excellent catalytic activity to DA, AA and UA, which could facilitate the discrimination of species with similar redox potentials. The attractive performances of the proposed method and its potential merits are presented in details.

2. Experimental

2.1. Reagents and materials

All chemical reagents were of analytical grade and used as received. Uric acid (UA) and thioglycerol (TG) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Ascorbic acid (AA) and dopamine (DA) were purchased from Sinopharm Chemical Reagent Co. Ltd. 0.1 M pH 7.0 phosphate buffer solution was prepared using 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4 . Twice-distilled water was used throughout the experiment.

2.2. Preparation of GO

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer's method [48]. In brief, 2 g graphite powder and 1 g sodium nitrate were mixed together followed by the addition of 23 mL of concentrated H_2SO_4 with an ice bath under vigorous stirring. After 1 h, 6 g KMnO_4 was added gradually into the above solution while maintaining the temperature below 20 °C. After removing the ice bath, the mixture was stirred at 35 °C for 18 h and the resulting solution was diluted by the gradual addition of 240 mL water under vigorous stirring. To ensure the complete consumption of KMnO_4 , 30% H_2O_2 (5 mL) was added into the mixture. The resulting mixture was subjected to centrifugation and the obtained precipitate was washed with HCl and H_2O respectively, followed by filtration and drying.

2.3. Preparation of rGO/ZnS nanocomposite

rGO/ZnS nanocomposite was prepared by following steps: 30 mg GO was dispersed into 10 mL water under ultrasonic agitation for 1 h. 1×10^{-4} mol ZnSO_4 was dissolved into the GO suspension under ultrasonic agitation for 1 h. Then 1×10^{-3} mol $\text{Na}_2\text{S}_2\text{O}_3$ and 109 mg TG was dissolved into the GO suspension under magnetic stirring. The reaction was carried out for 24 h under hard stirring under ambient conditions. The obtained black suspension of rGO/ZnS was centrifuged at 4000 rpm and the precipitate was washed with water for several times.

2.4. Preparation of CTAB/rGO/ZnS nanocomposite

The produced rGO/ZnS was re-dispersed into 10 mL water under ultrasonic agitation for 20 min and 85 mg CTAB was dissolved into the ZnS/GO suspension under ultrasonic agitation for 1 h. 10 mL absolute ethanol was added into the obtained suspension of CTAB modified ZnS/GO (CTAB/rGO/ZnS) to facilitate the precipitation of CTAB/rGO/ZnS. The suspension was let stand for 12 h and allowed to separate into layers. The CTAB/rGO/ZnS suspension was centrifuged and the obtained precipitate was washed with absolute ethanol for several times to remove excess amount of CTAB. Finally the produced CTAB/rGO/ZnS was dried in vacuum oven at room temperature for 12 h.

2.5. Fabrication of the sensor

The GCE ($\Phi = 3$ mm) was firstly polished successively with 0.3 and 0.05 μm alumina slurry to obtain a mirror-like surface, then rinsed with double distilled water and ethanol in ultrasonic bath to remove the physically absorbed substance. To construct

the CTAB/rGO/ZnS modified GCE, 5 mg CTAB/rGO/ZnS was dispersed into 10 mL 0.2% chitosan 1% acetic acid solution under ultrasonic agitation for 2 h. Finally, 5 μL of the CTAB/rGO/ZnS suspension was dropped onto the surface of the GCE to fabricate CTAB/rGO/ZnS/GCE. Subsequently, it was dried in air at room temperature. For comparison, 5 mg rGO/ZnS were dispersed into 10 mL 0.2% chitosan 1% acetic acid solution and 5 μL of the rGO/ZnS suspension was dropped onto the surface of the GCE to fabricate rGO/ZnS/GCE.

2.6. The physical and electrochemical measurements

Cyclic voltammetry (CV) was performed on CHI 660E (Chenhua, Shanghai). A three-electrode system was used for the electrochemical experiments. A platinum wire, a saturated calomel electrode (SCE) and the modified GCE were used as the counter electrode, reference electrode and working electrode, respectively. Infrared spectra (IR) were recorded with a Fourier transform infrared (FT-IR) spectrophotometer (Vector 22, Bruker, Germany). The morphologies of the CTAB/rGO/ZnS/GCE and rGO/GCE were observed with a scanning electron microscope (SEM) (Quanta 200 scanning electron microscope, FEI Company, Holland). The crystalline structures of the pristine graphite, GO, rGO and CTAB/rGO/ZnS were investigated with an X-ray diffractometer (XRD) (Shimadzu XRD-6000 diffractometer with a Ni filter and $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$)).

3. Results and discussion

In this experiment, thiosulfate was used as the sulfur source for the synthesis of ZnS as well as the reducing agent for the reduction of GO. However, both the hydrolysis of thiosulfate and the reduction of GO cannot happen without the addition of TG. TG not only catalyzes the hydrolysis of thiosulfate but also the reduction of GO by thiosulfate.

It is well known that a $\text{S}_2\text{O}_3^{2-}$ ion can hydrolyze to release a S^{2-} anion [49], which reacts with Zn^{2+} to produce zinc sulfide. However, in a system containing only zinc sulfate, sodium thiosulfate and water, the hydrolysis of thiosulfate is an extremely slow process at ambient conditions. With the addition of TG, $\text{S}_2\text{O}_3^{2-}$ immediately decomposed to free S^{2-} ions, which reacted with Zn^{2+} ions to produce white ZnS precipitate. At the same time, in a system containing only zinc sulfate, TG and water, no ZnS can be produced no matter how long the reaction time is. In our previous research, we adopt the method of Ni et al. to ascertain the decomposition product of $\text{Na}_2\text{S}_2\text{O}_3$ [50]. After metal sulfide precipitate was centrifuged off, 1 mL dilute mixed solution of $\text{Ba}(\text{NO}_3)_2$ and HNO_3 was dropped into the system. A white precipitate was produced immediately which indicates that SO_4^{2-} was produced during the hydrolysis of $\text{Na}_2\text{S}_2\text{O}_3$ [51].

The catalytic effect of TG on the hydrolysis of thiosulfate has been discussed in our previous research [51,52]. The reactions can be written as follows:



Although a lot of research has been carried out to investigate the catalytic effect TG, the role of TG played in step 1 of the proposed mechanism is still not clear. Our recent study indicated that, under the catalysis of TG, the rate of the hydrolysis of thiosulfate increased as the solution pH increased [51]. This discovery suggests a possibility that step 1 of the proposed mechanism is promoted under base condition.

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