Electrochimica Acta 123 (2014) 260–267

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Copper sulfide|reduced graphene oxide nanocomposite for detection of hydrazine and hydrogen peroxide at low potential in neutral medium

Yu Jun Yang [a,*], Weikun Li [b], Xiaoman Wu [a]

[a] School of Chemistry and Chemical Engineering, Xuchang University, Xuchang, Henan, 461000, China
[b] University Library, Xuchang University, Xuchang, Henan, 461000, China

ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 6 January 2014
Accepted 8 January 2014
Available online 23 January 2014

Keywords:
Graphene
Copper Sulfide
Hydrazine
Hydrogen Peroxide
Sensor

ABSTRACT

We report a hydrogen peroxide (H_2O_2) and hydrazine sensor based on novel copper sulfide|reduced graphene oxide (CuS|rGO) nanocomposites, which were synthesized with a facile hydrothermal method. It was discovered that the aggregation of graphene nanosheets could be reduced very significantly by the formation of CuS|rGO composites. The sensor was fabricated by simple casting of CuS|rGO aqueous suspension on glassy carbon electrode (GCE) and its performance was evaluated by cyclic voltammetry and amperometric techniques. It was found that the resulting sensor exhibited good performance toward H_2O_2 detection with wide linear response ranging from 1×10^{-6} to 1×10^{-3} M (R = 0.996) at -0.2 V and low detection limit of 1×10^{-7} M estimated at a signal-to-noise ratio of 3. In addition, the fabricated sensor also exhibited high sensitivity toward the detection of hydrazine with a low detection limit of 3×10^{-7} M, wide linear range from 1×10^{-6} to 1×10^{-3} M (R = 0.999) at 0.4 V. For both analytes, the sensor exhibited good reproducibility, selectivity and stability.

1. Introduction

Graphene (GA), a two-dimensional single-atom-thick conjugated carbon network, has attracted tremendous attention recently [1,2], because of its extraordinary properties, such as excellent electronic conductivity, large specific surface area, strong mechanical strength, and enhanced electrocatalytic activity [3]. The unique nanostructure and properties hold great promise for potential applications in a wide variety of technological fields, for instance, nanoelectronics [4–7], supercapacitors [8–10], batteries [11,12], nanocomposites [13] and sensors [14–18].

Hydrazine is widely used in rocket fuels, fuel cells, pesticides, photography chemicals, weapons for mass destruction, and so on [19,20]. It has been reported that hydrazine is carcinogenic and mutagenic [21,22]. Therefore, it is highly desirable to develop a sensitive method for the effective detection of hydrazine. For the electrochemical determination of hydrazine, the most commonly used electrocatalyst for the electrochemical oxidation of hydrazine are metal or metal alloy nanoparticles such as Au [23–25], Pd [26–28], Co [29], $AuCu_3$ alloy [30], Ag [31] and Pt [32]. FeN4 [33] and CoOOH [34] have also been demonstrated to be effective electrocatalysts for hydrazine detection.

Hydrogen peroxide is a universal molecule and has significant functions as a signaling molecule in the regulation of a variety of biological processes, including aging and carcinogenesis [35]. As such, the accurate determination of hydrogen peroxide is essential in the biological, environmental and clinical fields. Accordingly, many methods have been developed for the highly sensitive detection of hydrogen peroxide. The electrochemical method is a widely used approach by its simplicity and high sensitivity. Different strategies and electrode systems have been explored [36–49]. Till now, there have been several reports on the application of copper chalcogenides such as CuO nanoparticles [42], Cu_2O-rGO nanocomposite [43], Cu_2O nanoparticles[44], Cu_2S nanoparticles [45], Cu_2O microcubes [46] and CuO nanoflowers [47] on the electrochemical determination of hydrogen peroxide.

Only a few published works have dealt specifically with the sensor for the electroanalytical sensing of both hydrazine and hydrogen peroxide [31,34,50–53]. In this study, we demonstrate facile hydrothermal synthesis of copper sulfides|reduced graphene oxide (CuS|rGO) nanocomposites as the electrocatalyst for the ultra-sensitive determination of hydrazine and hydrogen peroxide at a low potential in neutral media. The electrocatalytic performance of CuS|rGO for hydrazine electrooxidation and H_2O_2 electroreduction in neutral media was investigated by cyclic voltammetry (CV) and amperometry. The results exhibited excellent performances, such as fast response, good stability, high sensitivity, and wide linear range for a novel electrochemical

* Corresponding author. Tel.: +86 374 296 8851.
E-mail address: yangyujun@yahoo.com (Y.J. Yang).

0013-4686/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2014.01.046

sensor. To the best of our knowledge, this is the first report on the fabrication of copper chalcogenide modified electrode for the determination of both hydrazine and hydrogen peroxide.

2. Experimental

All chemical reagents used in this experiment were of analytical grade. All solutions were prepared with doubly distilled water. A GCE (Φ 3 mm) was polished with Al_2O_3 powder (0.05 μm), and then cleaned successively with absolute ethanol and doubly distilled water.

The preparation of CuS|rGO nanocomposites was conducted by a facile one-pot hydrothermal method. In a typical synthesis, graphene oxide (GO) powders were initially prepared by a modified Hummers' method [29,30]. 30 mg GO powders were dispersed in 25 mL water under ultrasonic agitation for 2 hours followed by the addition of 1×10^{-4} mol $CuSO_4$ under magnetic stirring to obtain solution 1. Then 1×10^{-4} mol thiourea was dissolved in 25 mL water to obtain solution 2. Solution 1 and solution 2 were mixed together to obtain solution 3. Solution 3 was transferred into a 100 mL Teflon-lined autoclave and heated at 120 °C for 16 hours. The products were then collected, washed with water and ethanol and dried in a vacuum oven at room temperature. The CuS|rGO suspension was obtained by dispersing as-prepared black CuS|rGO powder in 5 mL 0.2% chitosan (CS) (wt%) 1% acetic acid (wt%) solution under ultrasonic agitation for 1 hour. 5 μL CuS|rGO suspension was then cast on GCE and dried at room temperature to obtain the CuS|rGO modified GCE (CuS|rGO|GCE).

Cyclic voltammetric (CV) was performed on CHI 660B (Chenhua, Shanghai). A three-electrode system comprising of a platinum wire as the auxiliary, a saturated calomel electrode (SCE) as the reference and a CuS|rGO|GCE as the working electrode was used for all the electrochemical experiments. The morphology and the crystal structure of the CuS|rGO were observed with a scanning electron microscope (SEM) and an X-ray diffractometer (XRD). The X-ray diffraction (XRD) patterns are obtained by Shimadzu XRD-6000 diffractometer with a Ni filter and Cu Kα radiation (λ = 0.154056 nm). SEM experiments were carried out employing Quanta 200 scanning electron microscope (SEM; FEI Company, Holland). Zeta potential of the CuS|rGO in aqueous phase was measured using a Zetasizer Nano (Malvern Instrumentation, UK). This instrument determines the electrophoretic mobility of the particles automatically and converts it to the zeta potential. The electric field added on the suspension was controlled by the cell voltage of Zetasizer Nano, which was fixed at 80 V. TEM experiments were carried out employing Jeol 100CX II transmission electron microscope (TEM), using an accelerating voltage of 100 kV. The samples used for TEM were prepared by dispersing some CuS|rGO powder in ethanol followed by ultrasonic vibration for 30 min.

3. Results and Discussion

Chemical reduction of graphene oxide (GO) has been widely employed to synthesize graphene. However, the reduced species of GO tend to generate irreversible agglomerates and even restack to develop graphite, because of π–π stacking interactions and highly cohesive vander Waals energy. Thus, chemical modification of graphene becomes essential to improve its stability and introduce special functionalities. We found out that the as-prepared CuS|rGO can be easily dispersed in water and the CuS|rGO suspension is highly stable without the aid of any surfactant. As shown in Fig. 1, no precipitate can be observed after storing the CuS|rGO aqueous suspension for one week at ambient conditions. However, it is very difficult to disperse rGO, which is synthesized by the chemical reduction of GO, in water even under ultrosonic agitation for 2 hours while the obtained rGO aqueous suspension can't remain stable for 2 hours (Fig. 1). We measured the zeta potential of our aqueous dispersions of CuS|rGO in an effort to explain the stability of such dispersions. It is not surprised to find out that the CuS|rGO is negatively charged. We found negative zeta potentials of 57-62 mV for CuS|rGO. The range of zeta potential (57-62 mV) is ideal for stabilizing conventional colloidal particles. The colloids with zeta potentials higher than 40 mV (negative or positive) are defined to have "good stability." [54] Our aqueous dispersion of CuS|rGO show good stability. Thus, it can be concluded that the aggregation of graphene nanosheets could be reduced by the formation of CuS|rGO composites.

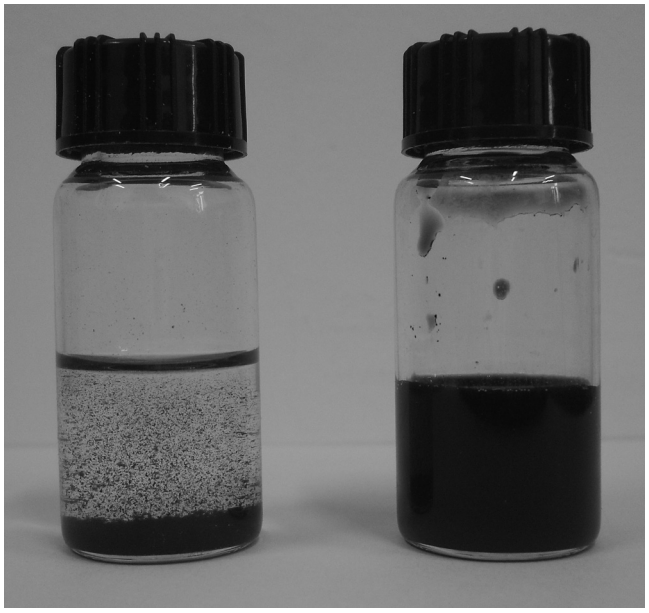

Fig. 1. Photo images of rGO (left) and CuS|rGO (right) aqueous suspension after being stored at ambient conditions for one week.

The XRD patterns of the synthesized rGO (Fig. 2, curve a) and CuS|rGO sample (Fig. 2, curve b) clearly shows two sets of diffraction peaks, indicating that the sample is a composite material containing both rGO and CuS. All of the diffraction peaks marked with star could be correctly indexed as hexagonal covellite CuS (space group: *P*63|*mmc*), with the following lattice parameters $a = 0.3791$ and $c = 1.6744$ nm, which are in good agreement with the standard

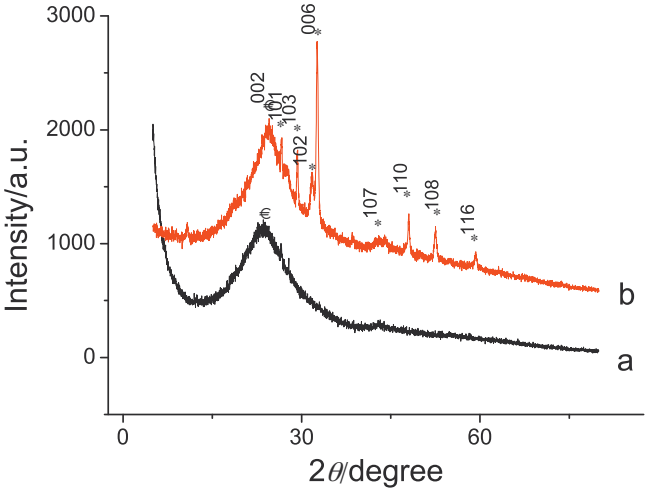

Fig. 2. Powder XRD patterns of the as-prepared rGO (a) and CuS|rGO composite (b).