



A novel and green CTAB-functionalized graphene nanosheets electrochemical sensor for Sudan I determination



Yexuan Mao^a, Qiannan Fan^a, Jianjun Li^a, Lanlan Yu^{a,*}, Ling-bo Qu^{a,b,**}

^a College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, PR China

^b School of Chemistry & Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China

ARTICLE INFO

Article history:

Received 5 April 2014

Received in revised form 1 July 2014

Accepted 8 July 2014

Available online 15 July 2014

Keywords:

Hexadecyl trimethyl ammonium bromide

Graphene nanosheets

Sudan I

Food samples

ABSTRACT

Hexadecyl trimethyl ammonium bromide (CTAB)-functionalized graphene nanosheets were synthesized by using a mild and green method and characterized by several techniques, including Fourier transform infrared spectroscopy, transmission electron microscopy, X-ray diffraction spectroscopy and electrochemical impedance spectroscopy. These CTAB-functionalized graphene nanosheets were used as the modified material on electrode to determine Sudan I, which remarkably increased the electrochemical response of Sudan I compared to that on glassy carbon electrode. This increase in electrochemical response is attributed to the long hydrophobic chain in CTAB which facilitates the accumulation of Sudan I and the unique physicochemical properties of graphene nanosheets which also promote the electrochemical response of Sudan I. With the optimized experimental conditions, the anodic peak currents of Sudan I are proportional to its concentration in the range of 0.002–8.0 $\mu\text{mol L}^{-1}$ and 8.0–100.0 $\mu\text{mol L}^{-1}$, and the limit of detection of 0.7 nmol L^{-1} is obtained. This electrochemical sensor shows good repeatability, reproducibility and is successfully applied in the determination of Sudan I in real food samples.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Sudan I which is a kind of industrial synthetic azo dye rather than a food additive, is widely applied in textile, oils, shoes polishing and so forth [1]. The azo structure of Sudan I is possible to lead to carcinogenic property, which has been verified by experiments that these azo dyes may induce tumors in the liver and bladder of mice, rats and rabbits [2,3]. Due to carcinogenic property, Sudan I has been classified as category 3 carcinogens to human beings by International Agency for Research on Cancer [4]. Unfortunately, Sudan I is still illegally added in some daily foodstuffs because of its colorfastness and low cost. Therefore it is urgent to develop a simple and fast method to determine Sudan I especially in foodstuffs.

Up to now, diverse methods are utilized in the determination of Sudan I, such as UV–visible spectrometry [5], high performance

liquid chromatography [6], electrochemical methods [1] and enzyme-linked immunosorbent assay (ELISA) [7]. Electrochemical method is considered as a promising approach in view of its fast response, low instrument and running cost and high sensitivity. In the present study, a simple and sensitive electrochemical sensor was developed based on graphene nanosheets (GNS) to determine Sudan I in foodstuffs.

Graphene, a one atom thick and closely packed two-dimensional honeycomb lattice, recently has attracted a wide interest in many fields such as supercapacitors [8], batteries [9], composites [10] and sensors [11] due to its special electronic, mechanical and thermal properties [12], since the 2010 Nobel Prize was awarded to Andre Geim and Kostya Novoselov [13]. Until now, a lot of efforts were made to obtain this attractive material for various applications. The reported synthesis methods for graphene nanosheets included mechanical exfoliation of graphite [13], chemical reduction of graphite oxide (GO) [14], chemical vapor deposition [15], electrochemical methods [16] and other special technologies [17,18]. Chemical reduction of GO is an efficient approach owing to its special merits, such as low cost, high production and mild condition [19]. In this method, the most used reductant is hydrazine hydrate [20], which is highly toxic, dangerously unstable and harmful to human and environment. In order to decrease the toxicity and danger, a mild and green reducing agent glucose was used to reduce

* Corresponding author at: The College of Chemistry and Molecular Engineering, Zhengzhou University, Kexue Road, Zhengzhou 450001, PR China. Tel.: +86 13525561266.

** Corresponding author at: The College of Chemistry and Molecular Engineering, Zhengzhou University, Kexue Road, Zhengzhou 450001, PR China. Tel.: +86 037167756886; fax: +86 37167756886.

E-mail addresses: yulanlan@zzu.edu.cn, shitouzhen@126.com (L. Yu), qulingbo@zzu.edu.cn (L.-b. Qu).

GO and obtain graphene nanosheets in the present study. To prevent the aggregation of bulk-quantity graphene nanosheets due to the strong π - π stacking interaction between different nanosheets, poly(*N*-vinyl-2-pyrrolidone) (PVP) was used as the stabilizer to disperse GNS. Furthermore, hexadecyl trimethyl ammonium bromide (CTAB) is also used for the construction of electrochemical sensors. CTAB is a positively charged detergent with a long hydrophobic chain, which may facilitate the accumulation of Sudan I. By functionalizing the graphene nanosheets with CTAB, it is possible to increase the sensitivity for Sudan I determination. Therefore, in this study a CTAB-functionalized GNS electrochemical sensor was developed and used for the determination.

2. Experimental

2.1. Reagents and apparatus

All chemicals and reagents were of analytical grade and were used without further purification. Natural graphite flakes (99%) with the average diameter of 200 mesh were purchased from Sigma-Aldrich (Shanghai, China). GO was prepared from natural graphite powder through a modified Hummers method [21]. Sudan I, CTAB, glucose and PVP (K30, $M_w = 30,000$ – 4000) were purchased from Sinopharm Chemical Reagent Co. Ltd. The stock solution of Sudan I (1.0 mmol L^{-1}) was prepared with anhydrous ethanol. A mixture of 0.1 mol L^{-1} HCl and anhydrous ethanol with a ratio of 1:1 was chosen as the supporting electrolyte (containing 0.1 mol L^{-1} KCl).

Infrared spectra data were collected on a NEXUS-470 Fourier transform infrared (FTIR) spectrometer (Thermo Electron). The images of transmission electron microscopy (TEM) were obtained with a JEM-2100 high-resolution transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) spectra data were obtained on X'PertPRO (Holand) using $\text{Cu K}\alpha$ (1.5406 \AA) radiation. RST5000 electrochemical station (Suzhou Risetech Instrument Co. Ltd., Suzhou, China) was employed for all the voltammetric measurements. A conventional three-electrode system was used, including a bare glassy carbon electrode (4 mm in diameter) as the working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire electrode as the auxiliary electrode. All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution every day.

2.2. Synthesis of CTAB-functionalized GNS

GNS were synthesized according to the previous literature with slight modification [22]. Firstly, 15 mg GO were exfoliated by ultrasonication in a water bath for about 1 h and a homogeneous graphene oxide aqueous dispersion (0.25 mg mL^{-1}) was obtained. Secondly, 200 mg of PVP was added into the above solution, followed by stirring for 12 h. Thirdly, 200 mg glucose was added into the above mixture and stirred for about 30 min. Then, $400 \mu\text{L}$ of ammonia solution (25%, w/w) was added into the above dispersion. After being vigorously stirred for a few minutes, the mixture was gently stirred for 60 min at 95°C . Finally, the resulting stable black dispersion was centrifuged (12,000 rpm) and washed with water for three times. The obtained GNS was redispersed in water before further use.

The PVP/GNS was functionalized with CTAB by the following procedure. 3 mL of 1 mg mL^{-1} PVP/GNS was dispersed in 12 mL aqueous solution containing 0.625 mol L^{-1} KCl and 1.25 mg mL^{-1} CTAB. After mixing, the mixture was ultrasonicated for 3 h to obtain a homogeneous black dispersion. The composite was subsequently centrifuged (12,000 rpm) and washed with water for three times.

Finally, the CTAB-functionalized GNS were redispersed in 3 mL water (about 1 mg mL^{-1}). The whole procedure was shown in Fig. 1.

2.3. Preparation of the modified electrode

Prior to the surface coating, the bare GCE was polished with $0.05 \mu\text{m}$ alumina slurry and then ultrasonicated in absolute ethanol and doubly distilled water, respectively. The cleaned GCE was dried with high-purity nitrogen steam for next modification. $10 \mu\text{L}$ of CTAB-functionalized GNS (0.1 mg mL^{-1}) dispersion was dropped onto the GCE surface and dried under an infrared lamp. Finally, the modified electrode was obtained. A certain volume of Sudan I stock solution was transferred into the cell (the volume is 10 mL) containing 5 mL HCl (pH 1.0, containing 0.1 mol L^{-1} KCl), and then the three-electrode system was installed. After an accumulation of 300 s on open circuit, the cyclic voltammograms were recorded from 0.00 V to 1.10 V (vs. SCE) at scan rate of 0.10 V s^{-1} . Before or after every measurement, the potential scan was repeated successively for three times in a blank solution for the electrode surface regeneration. The electrode was cleaned by doubly distilled water. The soluble oxygen was not removed in all the measurements, because it does not affect. All the electrochemical measurements were conducted at room temperature (about 25°C).

2.4. Sample preparation

In this study, the chosen food samples were ketchup, chili powder, duck egg yolk, chili sauce. They were purchased from a local market and treated as below. In brief, 2.0 g food samples were mixed with 50 mL absolute ethanol for 1 h. After vacuum filtration, liquid was collected and proper amount of the sample solution was transferred to the cell for voltammetric determination.

3. Results and discussion

3.1. Characterization of CTAB-functionalized GNS

Fig. S1 shows the photographs of aqueous dispersions (0.25 mg mL^{-1}) of GO before and after the reduction with glucose (see Supplementary data). The color of the solution changed from brown to dark before and after reaction, which indicated that GO has been reduced to GNS to some extent.

The reduction of the oxygen containing groups in GO by glucose was further testified by FTIR spectroscopy (Fig. S2, see Supplementary data). The FTIR spectrum of GO displays a strong absorption band at 1717 cm^{-1} owing to the C=O stretching and the absorption at 3388 cm^{-1} , 3125 cm^{-1} and 1384 cm^{-1} indicates the presence of O–H. The absorption at 3388 cm^{-1} and 3125 cm^{-1} are attributed to free state O–H and associating state O–H, respectively. The absorption of GO also indicates the presence of C=C ($\nu_{\text{C=C}}$ at 1616 cm^{-1}) and C–O ($\nu_{\text{C-O}}$ at 1105 cm^{-1}). After the reduction of GO, the characteristic absorption bands of oxide groups ($\nu_{\text{O-H}}$, $\nu_{\text{C-O}}$, $\nu_{\text{C=O}}$) decrease dramatically, which further verifies that GO has been reduced to GNS. Fig. S3 displays the typical TEM images of GNS at different magnifications (see Supplementary data). Some corrugations and scrolling at the edge of GNS, and also some amorphous materials loaded on the GNS are observed, which may be ascribed to the effect of functionalization of CTAB on GNS.

To further verify the formation of GNS, XRD was performed to characterize the crystal structure of GNS. As shown in Fig. S4, pristine graphite shows a sharp peak at 27.0° with interlayer space (d-spacing) of 0.33 nm (Fig. S4a, see Supplementary data). However the feature diffraction peak of exfoliated GO appeared at 11.9° is found with d-spacing of 0.74 nm (Fig. S4c, see Supplementary data). This value is much larger than that of pristine graphite, which is attributed to the introduction of oxygen containing functional

Download English Version:

<https://daneshyari.com/en/article/7146969>

Download Persian Version:

<https://daneshyari.com/article/7146969>

[Daneshyari.com](https://daneshyari.com)