Electrochimica Acta 157 (2015) 183–190

Contents lists available at ScienceDirect

Electrochimica Acta

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

Facile one-pot and rapid synthesis of surfactant-free Au-reduced graphene oxide nanocomposite for trace arsenic (III) detection

Wei-Wei Li[a], Fen-Ying Kong[b,*], Jing-Yi Wang[b], Zhi-Dong Chen[a], Hai-Lin Fang[b,*], Wei Wang[b]

[a] *School of Petrochemical Engineering, Changzhou University,Changzhou 213164, China*
[b] *School of Chemical and Biological Engineering, Yancheng Institute of Technology, Yancheng 224051, China*

ARTICLE INFO

Article history:
Received 28 August 2014
Received in revised form 19 November 2014
Accepted 25 December 2014
Available online 30 December 2014

Keywords:
Graphene
Au nanoparticles
Clean preparation
As (III)
Electrochemical determination

ABSTRACT

A very simple and effective approach of fabricating Au-reduced graphene oxide (Au-RGO) nanocomposite is herein reported. The nanocomposite was synthesized through a one-pot in situ reduction of graphene oxide (GO) and $HAuCl_4$ under ultraviolet (UV) irradiation without using any additional chemical reducing agents, capping agents, stabilizer or surfactant. The surface characterization with various techniques such as UV–vis spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM) showed that GO was effectively reduced and Au nanoparticles with a uniform size were well dispersed on the surface of RGO. This UV light assisted synthesis of Au-RGO nanocomposite is expected to be a universal and clean approach for the formation of various RGO-based nanocomposites. Significantly, the as-prepared nanocomposite possessed high activity in the redox behavior of As (III). Based on the Au-RGO nanocomposite modified electrode, a simple, sensitivity and selective sensing platform for the detection of As (III) was developed. Under optimum conditions, a detection range of 0.3–20 ppb and a low detection limit of 0.1 ppb were obtained, which is found to be well below the World Health Organization (WHO) guidelines of 10 ppb.

1. Introduction

Graphene, the basic building block of all graphitic materials, is a flat monolayer of carbon atoms tightly packed into two dimensional honeycomb lattices [1]. Due to its unique nanostructure and fascinating properties, graphene have become a sensational material in current research [2,3]. The two-dimensional (2D) basal plane structure and high specific surface area make graphene an ideal support material for the deposition of metal nanoparticles [4,5]. Especially, anchor of metal nanoparticles on reduced graphene oxide (RGO) sheets not only assist in keeping the individual sheets well separated but also allow heterogeneous catalytic processes [6,7]. Among various metal nanoparticles, Au nanoparticles are especially attractive owing to their easy preparation, large specific surface area, good biocompatibility and high catalytic activity [8,9]. Based on the unique properties of Au-RGO nanocomposite, considerable efforts have been and still are, devoted to incorporation Au nanoparticles into RGO matrix. However, in previous researches, Au-RGO nanocomposite was synthesis either by applying additional reducing agents or capping reagents (surfactants). Unfortunately, capping reagents can affect the graphene and Au nanoparticles properties and so limit their practical applications. Reducing agents such as hydrogen sulfide, hydrazine, sodium borohydride and hydroquinone are very hazardous. Also, they can introduce additional functional groups during chemical reduction, increasing sheet resistance by scattering electrons [10]. Furthermore, most preparation processes are complicated, time-consuming and need high temperature. To overcome these obstacles, a clean, simple and rapid route to prepare the Au-RGO nanocomposite under mild conditions is great promising.

Inorganic arsenic (As) is a highly toxic substance which is widely distributed in nature, and the contamination of As in water is a major problem in many countries, which has become a challenge for the scientists and the analytical chemists [11–14]. As exists in water mainly in As (V), but can be reduced to As (III) under anaerobic conditions. As (III) is thought to be more toxic than As (V) [15]. Exposure to low-level of As for a long term can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [16,17], The As problem has recently been reviewed [18]. Nowadays, it has been reported that 20 countries in the world

---

* Corresponding authors. Tel.: +86 515 88298186; fax: +86 515 88298186.
E-mail address: kongfy@ycit.edu.cn (F.-Y. Kong).

http://dx.doi.org/10.1016/j.electacta.2014.12.150
0013-4686/

are in risk of being exposed to drinking water with As levels above the World Health Organization (WHO) provisional guideline of 10 ppb [19]. Therefore, to explore a simple, fast and sensitive analytical method for precise monitoring of trace As is urgently needed to avoid their accumulation to a level that imposes great threat on public health [20]. Up to now, many studies and techniques for quantifying such levels of As have been published and developed [21–25]. Among them, the low cost electrochemical techniques such as stripping voltammetry have attracted more attention owing to their favorable portability, short analysis time, high-sensitivity, and suitability for real-time on-site analysis [26–29]. Stripping voltammetry analysis of As has been accomplished based on metallic electrodes such as Ag, Pt, Au, Hg and their modified surfaces. It has been found that Au and Au nanomaterials modified electrodes provide a more sensitive stripping voltammetry response than the others [17,30]. This is mainly due to formation of Au-As intermetallic compounds that can enhance the efficiency for preconcentration of As (0). Recently, some reports demonstrated that Au nanoparticles, supported on carbon substrates could reduce the interference from Cu (II) and allowed the trace determination of As (III) [31,32]. Inspired by these conclusions, we inferred that the Au nanoparticles supported on RGO may be a promising nanomaterial for the highly sensitive and selective determination of As (III).

In this paper, we used ultraviolet (UV) irradiation to produce Au-RGO nanocomposite beginning with $HAuCl_4$ and GO. This UV light assisted synthesis method was simple, clean, fast and effective, allowing Au nanoparticles uniformly anchored on the surfaces of RGO. The reduction of GO and the in situ deposition of Au nanoparticles were achieved in a one-pot process under the ambient condition in the absence of any additional reducing agents, stabilizers or surfactants. Furthermore, the as-prepared nanocomposite showed good disperibility and their electrocatalytic activities were evaluated by the analysis of As (III). The result showed that the prepared electrode had high sensitivity and selective and could be successfully used for the trace detection of As (III) without any interference from Cu (II).

2. Experimental

2.1. Chemical reagents

Graphite powder, Tetrachloroauric acid ($HAuCl_4$) and Sodium arsenite ($NaAsO_2$, 99%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All other chemicals were of analytical grade or better quality and used as received, and Milli-Q ultrapure water (Millipore, $\geq 18\,M\Omega$ cm, USA) was used throughout the experiments. As (III) stock solution ($1.0\,mg\,L^{-1}$) was prepared with $NaAsO_2$ dissolved in 0.1 M aqueous HCl [20] (Caution! $NaAsO_2$ is highly toxic; proper care must be taken in handling.). The As (III) solution was diluted as required before experiments. River water from Yangtze River, drinkingwater, and lake water were collected from the campus of yanchen institute of technology and stored in pre-cleaned polyethylene bottles after filtration. The standard addition method was used to evaluate the As (III) content in the water samples.

2.2. Instrumentation

UV-irradiation was carried out on a UV-illumination system Omni Cure Series 1500 fitted with a UV light filter of 320–500 nm wavelength. UV–vis absorption spectra were measured using a Shimadzu UV-2550 spectrophotometer over the wavelength range from 200 to 800 nm. Fourier transform infrared spectroscopy (FT-IR) experiments were performed on a Tensor 27 FT-IR spectrometer. Transmission electron microscope (TEM) images were acquired on a JEOL JEM-1011 microscope with acceleration voltage of 100 kV. Raman spectra were collected on a LabRAM Aramis Raman spectrometer equipped with a 532 nm laser source. Electrochemical experiments were conducted using a CHI 840C electrochemical workstation with a standard three electrode configuration composed of platinum wire as an auxiliary electrode, Ag/AgCl electrode as a reference electrode, and the bare or modified glass carbon electrode (GCE, 3 mm in diameter) as a working electrode. All experiments were carried out at room temperature (25 ± 2 °C) in air.

2.3. Preparation of Au-RGO nanocomposite

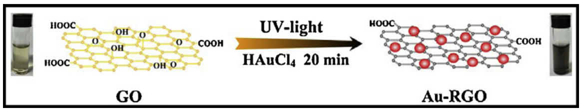
The Au-RGO nanocomposite was synthesized by the one-pot reduction of GO and $HAuCl_4$ under UV irradiation. In a typical synthesis, GO was firstly prepared according to a modified Hummer's method [33]. The freshly prepared GO was dispersed in water by ultrasonication to obtain a yellow–brown aqueous GO solution. After the pH value of the solution was adjusted to 7 by the addition of 0.1 M NaOH solution, 1% $HAuCl_4$ was added and the mixture was stirred for 30 min. Then, the mixture was placed in an optically transparent vial and irradiated with the high intensity UV spot lamp while nitrogen was bubbled through the solution. Here, the blowing nitrogen played twofold role. One is to stir the mixture and ensure a uniform exposure of the GO sheets and $HAuCl_4$ to the UV spot lamp. The other is to deaerate the dispersions and avoid the possibility of re-oxidation by dissolved oxygen molecules. After 20 min of irradiation, the product was separated by centrifugation and washed with water. To end, the sample was re-dispersed in water ($0.5\,mg\,mL^{-1}$) and used for experiment. The as-obtained nanocomposite was found to be very stable for several months. The entire preparation process was achieved as depicted in Scheme 1.

2.4. Fabrication of Au-RGO nanocomposite modified electrode

For the preparation of Au-RGO nanocomposite modified electrode, GCE was carefully polished to a mirror-like smoothness with 0.3 and 0.05 μm alumina slurries on a damp silk cloth, cleaned with ethanol, rinsed with water and dried with nitrogen gas. Subsequently, 5 μL of Au-RGO suspension solution was coated on the clean GCE surface and dried in air for electrochemical studies. The RGO and Au modified GCE was prepared in the same way.

2.5. Analytical procedure

Before electrochemical measurements, the specific modified electrode was transferred to a 5 mL electrochemical cell containing As (III) and kept at −0.4 V vs. Ag/AgCl for 30 s while stirring the solution. Quantitative determinations were then performed in the anodic stripping linear sweep voltammetry (ASLSV) mode. The potential was scanned in the anodic direction from −0.3 to 0.5 V vs. Ag/AgCl. A medium containing 0.2 M HCl was used in the electrochemical experiments. After recording the voltammogram, a preconditioning step (30 s at 0.3 V, with solution stirring) was used to remove the target metals. The renewed electrode was then checked in the supporting electrolyte before the next measurement to ensure that it did not show any peaks within the potential range.



Scheme 1. Schematic illustration for the synthesis of the Au-RGO nanocomposite.