

# A novel and sensitive amperometric hydrazine sensor based on gold nanoparticles decorated graphite nanosheets modified screen printed carbon electrode



Chelladurai Karuppiah<sup>a</sup>, Selvakumar Palanisamy<sup>a</sup>, Shen-Ming Chen<sup>a,\*</sup>,  
Sayee Kannan Ramaraj<sup>b</sup>, Prakash Periakaruppan<sup>b</sup>

<sup>a</sup> Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC

<sup>b</sup> Post Graduate and Research Department of Chemistry, Thiagarajar College, Madurai-625009, Tamilnadu, India

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## ABSTRACT

A highly sensitive amperometric hydrazine sensor has been developed for the first time using gold nanoparticles (Au-NPs) decorated activated graphite (AG) modified screen printed carbon electrode (SPCE). The preparation of AG and decoration of Au-NPs on AG surface involve simple electrochemical methods. AG/Au-NPs composite modified electrode shows a higher catalytic response and lower overpotential for hydrazine compared to Au-NPs decorated on activated SPCE and/or graphite SPCE. The response of the sensor for hydrazine detection lies within 2 s, indicating an excellent electrocatalytic ability of the composite electrode. The lowest limit of detection (LOD) of  $0.57 \pm 0.03$  nM is able to be achieved using AG/Au-NPs electrode, which is the lowest LOD that has ever been reported in the literature for hydrazine. Under optimum condition, the fabricated AG/Au-NPs composite exhibits a wider linear response for hydrazine detection up to  $936 \mu\text{M}$ . The sensor shows a very good sensitivity along with an excellent operational stability. The sensor proves its superior selectivity even in the presence of 1000 and 200 folds of common metal ions and biologically co-active interfering species.

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## 1. Introduction

Hydrazine is one of the most toxic chemicals, which is known as a neurotoxin, carcinogenic, mutagenic and hepatotoxic substance [1,2]. It has also been widely used as a starting material for the preparation of various materials in agricultural industry and fuel cells [3,4]. Hydrazine is also used as a fuel in certain rockets and spacecrafts [3]. The intermediates of hydrazine have been widely used for the preparation of pesticides, catalyst in polymer industry, corrosion inhibitor and antioxidant [5]. Therefore, the sensitive detection of hydrazine in low concentrations has received much importance in the practical applications. Notwithstanding many methods have been developed for accurate detection of hydrazine that include spectrophotometry, chromatography, titrimetry, chemiluminescence etc [6–10], electrochemical methods are more advantageous vis-à-vis low cost, fast response and high sensitivity. There has always been a great challenge in the electrochemical detection

of hydrazine using un-modified conventional electrodes, such as fouling of signals due to the accumulation of oxidized products of hydrazine and higher working overpotentials.<sup>11</sup> Since the conventional electrodes have shown lower sensitivity along with higher interference effect on the electrode surface, the modified electrodes including carbon nanomaterials, metal nanoparticles, conducting polymers, and metal oxides have been used to reduce the overpotential and also avoid the electrode fouling [11–16].

In recent years, metal nanoparticles have been broadly used for the fabrication of electrochemical sensor and biosensors, in particular, gold nanoparticles (Au-NPs) have received a special interest in the electrochemical sensors owing to its large active sites with high electrical conductivity [17]. In addition, Au-NPs are commonly known as a good electrocatalytic active material for oxidation of hydrazine [18]. Recently nanomaterials have been combined with Au-NPs to advance in the electrochemical detection of hydrazine in terms of sensitivity, limit of detection and overpotential [11,14,19]. The simple and low cost novel nanocomposite materials with advanced properties for the detection of hydrazine will certainly receive further interest to the readers of nano science and analytical chemistry.

\* Corresponding author. Tel.: +886 2 27017147; fax: +886 2 27025238.  
E-mail address: [smchen78@ms15.hinet.net](mailto:smchen78@ms15.hinet.net) (S.-M. Chen).

Currently, electrochemical activation of carbon nanostructures has got much notice and curiosity due to the exceptional electron transfer properties combined with excellent chemical stability [20,21]. The activated carbon nanostructures have more surface defects and fast electron transfer ability compared with un-activated carbon nanostructures [22]. Our previous study demonstrates that electrochemically activated graphite (AG) has more active sites and fast electron transfer ability to the electrode and solution interface than pristine graphite [23]. Since the electrochemical activation of graphite is less expensive and less time consuming one compared with other activation process of graphite reported in the literature [24], herein we have fabricated a novel and sensitive amperometric hydrazine sensor by using Au-NPs decorated AG. As far as we know, Au-NPs have never been decorated on the electrochemically activated carbon nanostructures enrooted for the electrochemical sensors. To the best of our knowledge, that the fabricated composite modified electrode shows the limit of detection (LOD) of  $0.57 \pm 0.03$  nM is the lowest LOD that has ever been reported in the literature for hydrazine detection.

In the present paper, we report on the decoration of Au-NPs on the AG surface used for the sensitive amperometric detection of hydrazine. The fabrication of AG and AG/Au-NPs composite screen printed carbon electrode (SPCE) involves a simple electrochemical method. The fabricated AG/Au-NPs composite modified electrode detects hydrazine at a lower over potential (0.15 V) with high sensitivity than that of Au-NPs decorated on activated SPCE, pristine graphite/SPCE and bare SPCE. The optimization of Au-NPs electrodeposition has also been discussed in detail. The sensor proves its superior selectivity even in the presence of 1000 and 200 folds of common metal ions and biologically co-active interfering species.

## 2. Experimental

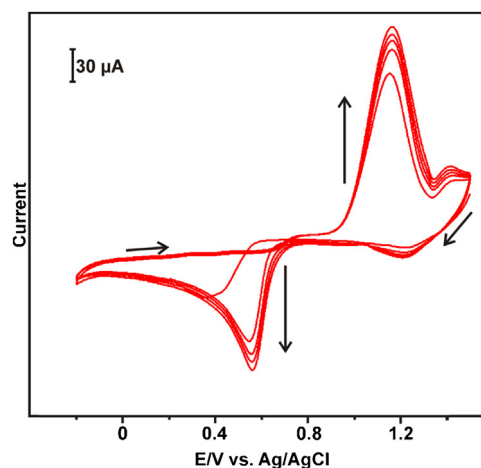
### 2.1. Materials and methods

Raw graphite with an average diameter of about  $>20 \mu\text{m}$  was obtained from Sigma–Aldrich. Screen printed carbon electrode (active surface area =  $0.08 \text{ cm}^2$ ) was purchased from Sensor R&D Co., Ltd., Taipei, Taiwan. Potassium gold (III) chloride trihydrate ( $\text{K}(\text{AuCl}_4 \cdot 3\text{H}_2\text{O})$ ) was purchased from Strem chemicals (USA). Hydrazine was obtained from Sigma–Aldrich and used as received. The supporting electrolyte pH 7 solution (PBS) was prepared using  $0.05 \text{ M Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  solutions and other pH solutions were adjusted with  $0.5 \text{ M H}_2\text{SO}_4$  and  $2 \text{ M NaOH}$ . All other chemicals used were of analytical grade and the solutions were prepared with the help of Millipore water.

All electrochemical measurements were carried out using CHI 750a electrochemical analyzer (CH instruments). Surface morphological studies were carried out using Hitachi S-3000 H scanning electron microscope. Elemental analysis (EDX) was studied using HORIBA EMAX X-ACT energy-dispersive X-ray spectrometer. Electrochemical impedance spectroscopy (EIS) studies were performed using IM6ex ZAHNER (Kroanch, Germany). Amperometric ( $i-t$  curve) measurements were performed using a CHI-750a potentiostat with an analytical rotator. The SPCE was used as a working electrode with Ag/AgCl electrode (Sat. KCl) as a reference electrode and a platinum wire as a counter electrode. All electrochemical measurements were carried out at room temperature and solutions in the electrolyte cell were kept under an inert atmosphere.

### 2.2. Fabrication of AG/Au-NPs composite modified electrode

Prior to the electrochemical pretreatment of the modified electrode, the bare SPCE was first cleaned using bath sonication in ethanol to remove the adsorbed materials onto the electrode



**Fig. 1.** 5 consecutive cyclic voltammograms of Au-NPs electrodeposition on AG modified SPCE in the electrochemical cell containing  $1.3 \text{ mM K}(\text{AuCl}_4) \cdot 3\text{H}_2\text{O} + 0.5 \text{ M H}_2\text{SO}_4$  at the scan rate of  $50 \text{ mV s}^{-1}$ .

surface. The AG modified SPCE was fabricated by our previously reported method [24]. Briefly, first the graphite dispersion was obtained by dispersing graphite flakes in  $10 \text{ mL}$  of DMF ( $10 \text{ mg mL}^{-1}$ ) and followed by successive sonication at room temperature. About  $8 \mu\text{L}$  (optimized concentration) of graphite dispersion was drop coated on the pre-cleaned SPCE and allowed to dry in an air oven. The AG/SPCE was successfully fabricated by immersing the graphite/SPCE into electrochemical cell containing  $0.1 \text{ M PBS}$  and  $\text{KCl}$  solution and applying a constant potential of  $2.0 \text{ V}$  for  $300 \text{ s}$ . The fabricated AG/SPCE was further used for the electrodeposition of Au-NPs. The AG/Au-NPs composite modified SPCE obtained by immersing the AG/SPCE into an electrochemical cell containing  $1.3 \text{ mM K}(\text{AuCl}_4) \cdot 3\text{H}_2\text{O}$  and  $0.5 \text{ M H}_2\text{SO}_4$  solution and 5 successive cycles of CVs were performed in the potential range between  $1.5$  to  $-0.2 \text{ V}$  at the scan rate of  $50 \text{ mV s}^{-1}$ . The AG/Au-NPs composite modified SPCE was gently rinsed with distilled water to remove the loosely bounded Au-NPs. The fabricated AG/Au-NPs composite modified SPCE was used for further experiments and stored at room temperature under dry condition. Graphite and bare SPCE were electrochemically prepared by the same method as mentioned above.

## 3. Results and Discussion

### 3.1. Formation mechanism of Au-NPs on AG surface

Fig. 1 shows the CV response for the electrochemical deposition of Au-NPs on AG surface. The Au-NPs were successfully decorated on AG surface by immersing the AG modified SPCE in the electrochemical cell containing  $1.3 \text{ mM K}(\text{AuCl}_4) \cdot 3\text{H}_2\text{O}$  and  $0.5 \text{ M H}_2\text{SO}_4$ . The Au-NPs were electrodeposited on to the AG surface by 5 potential cycles scanning from  $1.5$  to  $-0.2 \text{ V}$ . In the first negative potential scan, a sharp reduction peak is noticed with an onset potential of  $0.595$ , which is attributed to the well-known three-electron reduction process of Au(III) to form metallic Au-NPs. On the second scan, the onset potential of reduction peak is shifted  $0.727 \text{ V}$  to higher potential in accordance with thermodynamics which predicts an easier growth of previously formed Au-NPs than nucleation of new Au-NPs on the electrode surface. The anodic peak with an onset potential of  $0.9 \text{ V}$  is related to the formation of Au oxides, which is latter on reduced to Au-NPs on the backward scan. This observation is very similar to the previously reported literatures for Au-NPs electrodeposition on glassy carbon electrode [25,26]. The

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