



Electroanalysis of oxygen reduction and formic acid oxidation using reduced graphene oxide/gold nanostructures modified electrode



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ABSTRACT

The preparation of gold (Au) nanostructures electrodeposited on reduced graphene oxide (RGO) modified glassy carbon (GC) electrode and its application towards fuel cell reactions in alkaline medium are reported. The modified electrode was characterized by cyclic voltammetry, reflectance UV–VIS spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. The Au nanostructures deposited RGO modified electrode showed synergistic catalytic behavior towards the electrocatalytic oxygen reduction reaction (ORR). The cyclic voltammogram recorded for the modified electrode revealed a quasi-reversible behavior for ORR and the Koutecky–Levich (K–L) plots showed a two-electron transfer process involved ORR at the modified electrode. The modified electrode also showed a good electrocatalytic activity towards the oxidation of formic acid. Therefore, the present work reports a facile method to fabricate RGO based noble metal nanostructures as electrocatalyst for fuel cell applications.

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1. Introduction

Carbon materials have been widely used in electroanalysis due to their low cost, wide potential window and good electrocatalytic activity [1]. Graphene is one among the variety of carbon materials, extensively studied in various applications in the past few years [2–5]. Graphene finds a wide range of promising applications in solar cells [6], sensors [7], batteries [8] and supercapacitors [9]. Mostly, graphenes are prepared by reducing graphene oxide (GO) using chemical [10,11], electrochemical [12,13], and hydrothermal [14,15] methods. Electrochemical reduction of GO has received more attention in recent years over the other methods since it is a green approach and the thin film of reduced graphene oxide (RGO) can easily be prepared by this method on conducting electrode substrate for electrocatalytic applications [13,16]. The electrochemically reduced GO is confined with less number of oxygen functionalities and is highly conductive than the RGO prepared by other methods [17].

In recent years, the functionalization of graphene nanosheets with various metal, metal oxide and semiconductor nanoparticles to form electroactive hybrid nanomaterials is widely studied [18–20]. Noble metals, especially gold nanoparticles (Au NPs) that have unique optical and electronic properties, are extensively used in various fields like optics, nanoelectronics, biodiagnostics and catalysis. The fabrication of RGO/Au nanocomposite for fuel cell applications received much attention in recent research [16,20–22]. Electrodeposition method is one of the most beneficial approaches for preparing Au nanostructures [23].

By this means, Au nanostructures can be easily synthesized on the RGO modified conducting surfaces, and the morphology of the prepared nanostructures can easily be controlled by changing the conditions of electrochemical deposition.

In this work, we report Au nanostructures electrodeposited on electrochemically reduced GO modified glassy carbon (GC) electrode for electrocatalytic oxygen reduction reaction (ORR) and formic acid oxidation in alkaline medium. The development of Pt alternative electrocatalyst for ORR is highly motivated due to the drawbacks of Pt especially, kinetic limitation for oxygen diffusion rate [24]. The present modified electrode showed the synergistic behavior of RGO–Au nanocomposite towards the electrocatalytic ORR. The modified electrode was also used for the electrocatalytic oxidation of formic acid and it showed a good electrocatalytic activity towards formic acid oxidation. Formic acid oxidation is considered as a promising power source in fuel cells due to their high electromotive force, safety of fuels, limited fuel crossover, and high practical power density at low temperature [25,26]. Therefore, investigation on the electrochemical oxidation of formic acid has received much attention due to its potential application as anodic active species in direct formic acid fuel cell (DFAFC).

2. Experimental

2.1. Materials and Methods

Gold(III) chloride hydrate (HAuCl_4) was purchased from Sigma-Aldrich. Graphite powder was obtained from Alfa Aesar. Sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), formic acid and potassium hydroxide (KOH) were received

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from Merck. All glassware was thoroughly cleaned with aqua regia and rinsed extensively with distilled water before use. The reflectance UV–VIS spectra of the Au nanostructure modified GC electrodes were recorded using an Ocean Optics spectrophotometer. SEM images of the Au nanostructure modified ITO electrodes were collected using a VEGA3 TESCAN and the XRD patterns were obtained with a Bruker AXS D8 Advance. Electrochemical characterization was carried out using a CH Instruments electrochemical workstation (model-760D).

2.2. Preparation of GC/RGO/Au Electrode

Graphene oxide (GO) was prepared from graphite powder by a modified Hummers method [27]. In the typical synthesis, 1 g of graphite was added into 23 mL of 98% H_2SO_4 and the mixture was stirred for 24 h at room temperature. To this solution, 100 mg of NaNO_3 was introduced and the stirring was continued for another 30 min. The mixture was kept below 5 °C in ice bath and 3 g of KMnO_4 was slowly added into the mixture. After heating to 35–40 °C, the mixture was stirred for another 30 min. After that, 46 mL of water was added into the above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of H_2O_2 were added into the mixture to stop the reaction. The unexploited graphite in the resulting mixture was removed by centrifugation and the as-synthesized GO was dispersed in distilled water at a concentration of 0.3 mg mL⁻¹ with the aid of ultrasound for further use. A 5 μL of 0.3 mg/mL GO solution was drop-casted on the GC electrode surface and allowed to dry at room temperature for an hour. The electrode was treated in 0.5 H_2SO_4 by potential cycling between -0.5 and -1 V to form RGO on the electrode surface. At this modified electrode, Au nanostructures were electrodeposited at an applied potential of -0.2 V ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) for 300 s in an electrolyte solution containing 5 mM HAuCl_4 and 0.5 M H_2SO_4 . The prepared modified electrode is represented as GC/RGO/Au.

2.3. Electrochemical Studies

All the electrochemical studies were performed in a single compartment three-electrode cell using a CH Instruments electrochemical workstation at room temperature. GC electrode (3 mm diameter) was polished with alumina slurry (0.05 μm), cleaned by potential cycling between +1 and -1 V in 0.1 M H_2SO_4 before the experiments and used as working electrode. A platinum wire and calomel electrode were used as counter and reference electrodes, respectively. The electrochemical measurements for ORR were carried out in O_2 saturated 0.5 M KOH solution. Differential pulse voltammograms (DPVs) were recorded using an increment potential of 4 mV, pulse amplitude of 50 mV, pulse width of 0.05 s, sample width of 0.02 s and a pulse period of 0.2 s. For the ORR studies at the rotating disk electrode (RDE), the working electrode was scanned cathodically at a scan rate of 50 mV s^{-1} with varying rotation speed from 500 to 3000 rpm in O_2 -saturated 0.5 M KOH aqueous solution.

3. Results and Discussion

3.1. Formation of Au Nanostructures on GC/RGO Modified Electrode

TEM image of the prepared GO sheet is shown in Fig. S1. The GO solution drop-casted GC electrode was subjected to the potential cycling in 0.5 M H_2SO_4 between the potential window of -0.5 and -1 V (Fig. 1A). The appearance of a reduction peak at -0.89 V during the first cycle indicated the reduction of functional groups present in GO and subsequent formation of RGO [28]. The electrodeposition of Au nanostructures was carried out at an applied potential of -0.2 V on RGO modified GC electrode for 300 s. Because of the presence of RGO support, the nucleation of Au nanostructures on GC/RGO is expected to be different when compared to that on bare GC. The cyclic voltammograms of bare GC, GC/RGO, GC/Au and GC/RGO/Au electrodes recorded

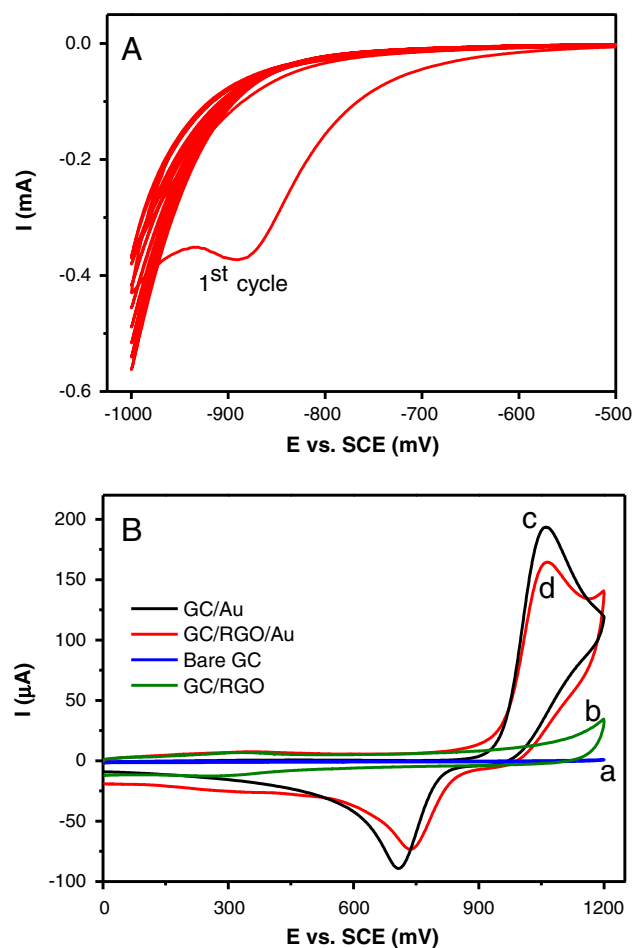


Fig. 1. Continuous cyclic voltammograms (10 cycles) recorded for GC/GO modified electrode in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} (A). Single cyclic voltammogram recorded for bare GC (a), GC/RGO (b), GC/Au (c) and GC/RGO/Au (d) electrodes in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} (Au was electrodeposited at -0.2 V for 300 s) (B).

in 0.5 M H_2SO_4 are shown in Fig. 1B. Both the Au modified electrodes showed characteristic oxidation peaks for gold oxide in the anodic sweep and the corresponding reduction peaks during the cathodic sweep (Fig. 1B(c and d)). These voltammetric features confirmed the formation of nanostructured Au on GC and GC/RGO electrodes during electrodeposition [29] and the nanostructures are in good electrical contact with the electrode surface. From the voltammograms the electrochemically active surface areas (EASAs) of the Au modified electrodes were calculated by using the charges corresponding to the reduction of Au oxide [29]. The EASAs of GC/Au and GC/RGO/Au modified electrodes were calculated as 0.2432 and 0.1834 cm^2 , respectively using the following equation.

$$\text{EASA} = Q/Q^*$$

where, Q is the charge required for the reduction of Au oxide monolayer and Q^* is the calibration factor with a value of 390 $\mu\text{C}/\text{cm}^2$ for Au [29]. However, no voltammetric features were observed for bare GC and GC/RGO electrodes in 0.1 M H_2SO_4 (Fig. 1B(a and b)).

To exemplify the influence of pH on the reduction potential of gold oxide, the cyclic voltammetric characteristics of the GC/RGO/Au modified electrode were studied at different pHs (Fig. 2). As the pH of the solution was varied from 3 to 8, the gold oxide reduction peak potential shifted negatively (Fig. 2A) and revealed a linear relation (Fig. 2B). The pH dependent cathodic peak potential showed Nernstian behavior with a slope of 72 mV/pH, which is close to the reported value of

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