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Short Communication

Electrochemical Detection of Dissolved Oxygen in Water using a Composite of Graphene oxide and Platinum Nanoparticles

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In the present study, we report the electrochemical detection of dissolved oxygen in neutral media using graphene oxide-platinum nanoparticles (GO-PtNPs) composite modified glassy carbon electrode (GCE). The GO-PtNPs composite modified electrode was prepared by immersing the GO modified electrode in deoxygenated 0.5 mM K_2PtCl_6 with 0.5 M KNO_3 solution by cyclic voltammetry. As prepared materials were characterized by scanning electron microscopy and elemental analysis. The GO-PtNPs composite modified electrode showed an excellent electrocatalytic activity towards the reduction of oxygen in pH 7.0 solution than that of PtNPs and GO modified electrodes. The GO-PtNPs composite modified electrode was further used for the detection of dissolved oxygen (DO) in water. The electrochemical results revealed that GO-PtNPs composite modified electrode has high precision and accuracy with the results obtained from the commercial oxygen analyzer for the detection of DO in water.

Keywords: Graphene oxide, Platinum nanoparticles, oxygen reduction, electrochemical detection, dissolved oxygen.

1. INTRODUCTION

The carbon nanomaterials-metal or metal oxide nanoparticles composites have shown greater importance in different disciplines including electrocatalysis and oxygen reduction reaction (ORR) [1–4]. Owing to the combined unique properties of carbon nanomaterials with metal nanoparticles have vastly used as an advanced electrocatalyst for different analytes [5–7]. Graphene oxide (GO) is two dimensional, sp^2 carbon nanomaterial and has been received considerable interest in material science due to its high optical transparency, high carrier mobility, and chemical stability [8–10]. Recent reports have shown that the electrocatalytic activity of metal nanoparticles are greatly enhanced in the presence of GO, thus GO is more capable for electron transfer kinetics [11, 12]. On the other hand, platinum nanoparticles (PtNPs) are continuously used as an electrocatalyst for in the field of sensors and fuel cells due to its unique physical and chemical properties [13–15].

Recent years, the researchers are mainly focus on the development of Pt free electrocatalyst for ORR, since ORR is a heart of key factor in fuel cells [16]. However, the developed electrocatalysts so far shown sluggish ORR activity when compared with Pt electrocatalyst [17]. Furthermore, for the industrial applications Pt based electrocatalysts with enhanced catalytic activity has received considerable interest. Hitherto, GO-PtNPs based composite materials have regularly used for different potential applications such as fuel cells, electrochemical sensors, dye sensitized solar cells and energy storage devices [18, 11, 10, 15]. Herein, we have used the combined unique properties of GO-PtNPs composite for ORR and detection of dissolved oxygen in water.

In this communication, the GO-PtNPs composite was prepared by a simple electrodeposition of PtNPs on GO surface. The GO-PtNPs composite modified electrode was used for the ORR and detection of dissolved oxygen in water. The ORR of GO-PtNPs composite electrode was compared with GO and PtNPs modified electrodes; the GO-PtNPs composite electrode shows the enhanced electrocatalytic activity towards ORR when compared with other modified electrodes. The GO-PtNPs composite electrode is also used for the detection of dissolved oxygen in water.

2. EXPERIMENTAL

2.1. Materials and methods

Graphite powder (98.0% purity) and Potassium hexachloroplatinate (IV) (≥99.9% trace metals basis) were obtained from Sigma Aldrich. The oxygen rich natural water was purchased from OXY YOUNG CO. Taipei, Taiwan. The supporting electrolyte 0.05 M pH 7 solution (PBS) was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions in double distilled water. All other chemicals used in this study were of analytical grade and prepared using double distilled water without any further purification.

Electrochemical measurements such as cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed using CHI 750A electrochemical analyzer. Surface morphological studies were carried out using Hitachi S-3000 H scanning electron microscope. The amount of dissolved oxygen in PBS and water were analyzed by SUNTEX 690 Dissolved Oxygen Sensor. Elemental analysis (EDX) was studied using HORIBA EMAX X-ACT energy-dispersive X-ray spectrometer that was attached to Hitachi S-3000 H scanning electron microscope. Glassy carbon electrode with an active surface area of 0.12 cm^2 was used as a working electrode; Ag/AgCl electrode (Sat. KCl) and a platinum wire was used as a reference and counter electrodes, respectively. All electrochemical experiments were performed in room temperature.

2.2. Preparation of GO-PtNPs composite

Graphite oxide was prepared by according to our previous reported method [**19, 20**]. As prepared graphite oxide was further purified using HCl and water and dried in air over. The GO aqueous dispersion was prepared by dispersing graphite oxide (1 mg mL^{-1}) into the water with aid of sonication. About 8 µL of GO was drop coat on the GCE surface and dried at room temperature. As prepared GO modified GCE was transferred into the electrochemical cell containing N_2 saturated 0.5 mM of K_2PtCl_6 with 0.5 M KNO_3 solution and followed by 10 successive CV cycles in the potential range between 0.7 to -0.6 V at the scan rate of 50 mVs^{-1}. Finally, the PtNPs were electrochemically deposited on GO modified GCE. The fabricated GO-PtNPs composite modified electrode was gently rinsed in double distilled water to remove free PtNPs from the composite. For compassion, PtNPs and GO modified GCEs were prepared by the similar method as mentioned above without GO and PtNPs.

3. RESULTS AND DISCUSSION

3.1. Characterization of GO–PtNPs composite

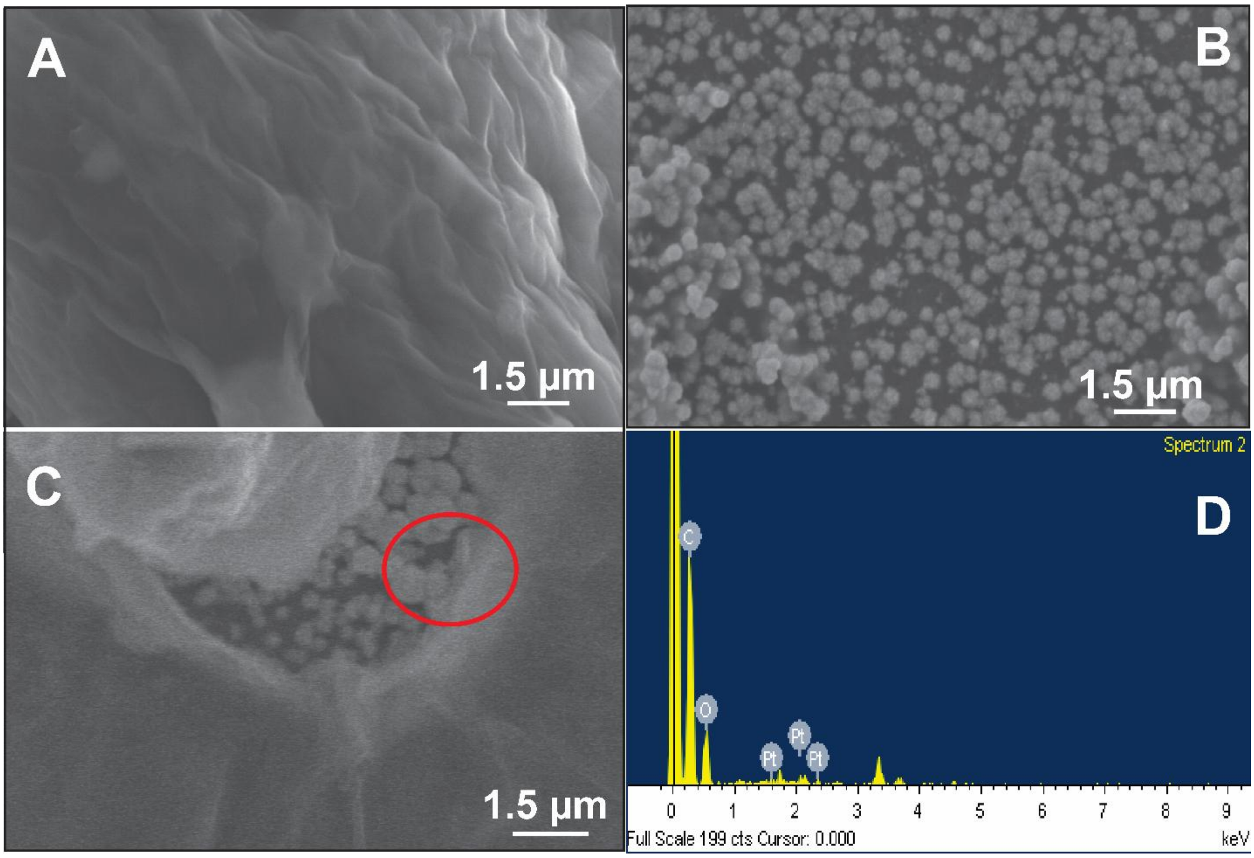

Figure 1. The SEM images of GO (A), PtNPs (B) and GO-PtNPs composite (C). D) EDX profile of GO-PtNPs composite.

The surface morphology of GO, PtNPs and GO-PtNPs were evaluated by SEM. Fig. 1 shows the SEM images of (A) GO, PtNPs (B) and GO-PtNPs (C). The SEM image of GO shows a crumpled morphology with an enfolding of many GO nanosheets together. On the other hand, an urchin type morphology was observed for electrochemically prepared PtNPs, which is resulting from the association of PtNPs one over another. The average diameter of PtNPs was found in the range of 40 to

62 nm. Fig. IC clearly reveal that PtNPs are uniformly decorated on the GO sheets, which indicates the formation GO-PtNPs composite. In addition, the surface morphology of PtNPs was unchanged in GO-PtNPs composite and is good agreement with the SEM image of PtNPs (Fig. 1B). The results confirm the formation of GO–PtNPs composite. The presence of PtNPs was further confirmed by EDX analysis and results are shown in Fig. 1D. It can be seen that the C, O and Pt were clearly seen on the EDX of GO-PtNPs composite. The SEM and EDX results confirm the formation of GO-PtNPs composite.

3.2. Oxygen reduction reaction of different modified electrodes

The electrocatalytic activity of different modified electrodes towards the ORR was studied by CV using 0.1 M phosphate buffer solution, potential sweeping between 0.6 to -0.4 V at a scan rate of 50 mV/s. Fig. 2a shows the ORR of GO in 0.1M phosphate buffer solution and it has no activity towards ORR, however many of carbonaceous materials familiar with oxygen reduction reaction particularly for 2e$^-$ pathway [21].

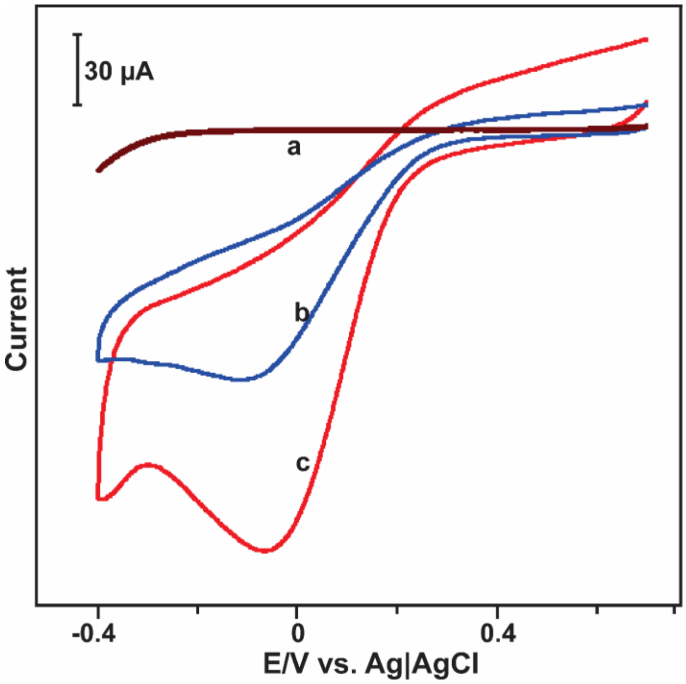

Figure 2. Cyclic voltammetric response of GO (a), PtNPs (b) and GO-PtNPs (c) modified GCEs in oxygen saturated PBS at a scan rate of 50 mV s^{-1}.

The 2e$^-$ pathway experiences via anthraquinone functional group on carbon materials, though nitrogen doped graphene follows 4e$^-$ pathway [22]. Here the incorporation of GO is to enhance the electrocatalytic activity of PtNPs and also increases the electroactive surface area, besides that, the adsorption of dissolved oxygen is high for GO compare to bare PtNPs modified electrode. The ORR curve of bare PtNPs and GO–PtNPs composite modified electrodes are shown in Fig. 2b and c, here the onset potential of two materials are more or less same but GO–PtNPs reveals highest diffusion rate compare with PtNPs modified electrode because the PtNPs influences the GO where the dissolved oxygen is adsorbed. The objective of this ORR reaction in buffer solution is to determine the efficiency of GO–PtNPs composite.

To validate the activity of ORR, the GO–PtNPs composite was subjected to nitrogen and oxygen atmosphere. The GO–PtNPs composite exhibit only the capacitance behavior in nitrogen atmosphere (Fig. 3a) and also there is minimal Pt response, in oxygen atmosphere (Fig. 3b). It also shows the strong oxygen reduction peak at the potential of 0.35 V vs Ag/AgCl. This study concludes the efficiency and activity of GO–PtNPs composite towards ORR in oxygen saturated buffer solution.

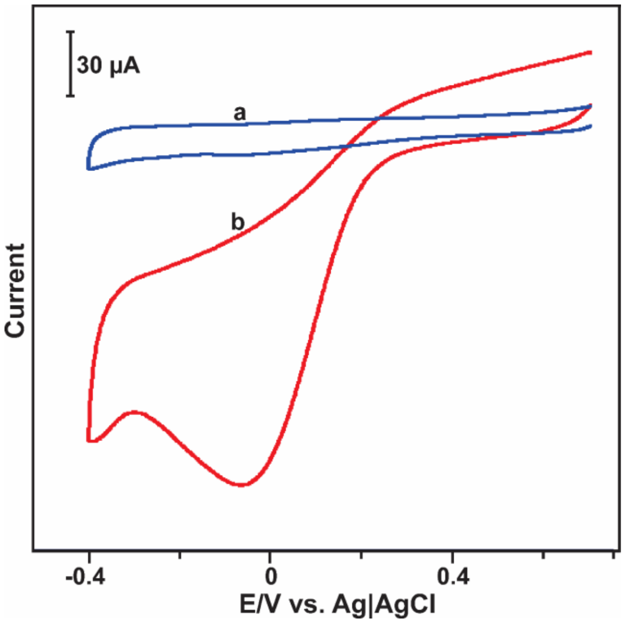

Figure 3. Cyclic voltammetric response of GO-PtNPs modified GCE in N_2 (a) and O_2 (b) saturated PBS at a scan rate of 50 mV s^{-1}.

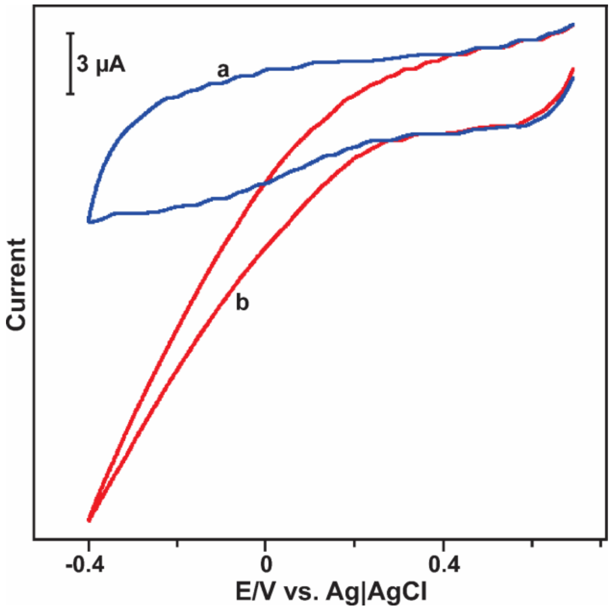

Figure 4. Cyclic voltammetric response of GO-PtNPs modified GCE in O_2 saturated drinking water at a scan rate of 50 mV s^{-1}.

The objective of this work mainly concentrates on the electrochemical detection of oxygen in drinking water, hence we studied the ORR in real sample. Fig. 4a shows that the ORR of GO–PtNPs composite modified electrode in nitrogen saturated drinking water, there are no reduction peaks were observed, though it reveals tiny amount of current due to the adsorbed oxygen at electrode surface. Fig. 4b shows that the strong oxygen reduction peak in drinking water, but the steady state polarization is not so good compare to buffer solution because of the ions movement in drinking water is very lower than buffer solution. The result clearly shows that GO–PtNPs composite modified electrode has high electrocatalytic activity towards the reduction of dissolved oxygen water and can be used for the detection of dissolved oxygen in water.

In order to detect the amount of dissolved oxygen in drinking water, LSV was performed in the potential range between 0.7 to –0.4 V at a scan rate of 50 mV/s. The amount of dissolved oxygen was pre-determined by the commercial oxygen analyzer and un-known amount of oxygen was determined using LSV by GO-PtNPs modified electrode. The obtained results were summarized in Table 1. The Table 1 clearly shows that the proposed GO-PtNPs composite modified electrode has high accuracy for the detection of dissolved oxygen in water, and the results are comparable with the results obtained from the commercial oxygen analyzer. The result clearly indicates that the GO-PtNPs modified electrode can be used for sensitive detection of dissolved oxygen in drinking water.

Table 1. Detection of oxygen content in drinking water using GO–PtNPs modified electrode by this electrochemical method.

Sample	Detected by commercial O_2 analyzer ($mg\ mL^{-1}$)	Detected by this electrochemical method ($mg\ mL^{-1}$)	Accuracy (%)	RSD (%)
Drinking water	10.5	9.4	89.5	5.3
	13.2	11.8	89.4	5.9

4. CONCLUSIONS

In conclusion, we demonstrated a simple electrochemical fabrication of GO–PtNPs composite modified electrode by electrodeposition of PtNPs on GO surface. The GO–PtNPs composite modified electrode was used for the application to ORR and detection of dissolved oxygen in water. The SEM image of GO–PtNPs composite modified electrode clearly showed that PtNPs were uniformly deposited with a size of 40 to 62 nm on GO surface. The GO–PtNPs composite modified electrode showed superior electrocatalytic activity towards ORR than that of electrodes modified with PtNPs and GO. The GO-PtNPs composite modified electrode also shower its potential application towards the detection of dissolved oxygen in water.

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