Dissolved oxygen detection by galvanic displacement-induced graphene/silver nanocomposite

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Abstract. This paper proposed a simple, efficient and sensitive electrochemical sensor for dissolved oxygen (DO) detection based on a galvanic displacement synthesized reduced graphene oxide–silver nanoparticles (RGO/Ag) composite modified grassy carbon electrode (GCE). The synthesized RGO/Ag nanocomposite was characterized by UV–vis spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results indicate the graphene oxide (GO) has been successfully reduced during the galvanic displacement process and the average size of Ag nanoparticle is 52 nm. The RGO/Ag nanocomposite-modified GCE showed a significant enhancement of DO detection compared with bare and RGO-modified GCEs. Moreover, the proposed DO sensor also exhibited an excellent repeatability, reproducibility and anti-interference ability.

Keywords. Nanocomposite; graphene; dissolved oxygen; sensor.

1. Introduction

Oxygen reduction reaction has been of great importance in many fields such as food industry, fuel cells, batteries, metal corrosion, bioscience and biotechnology. For example, dissolved oxygen (DO) is an indicator of water quality. Furthermore, careful controlling and monitoring the oxygen level also play an important role in the food industry and clinical analyses. Thus, the evaluation of the amount of DO in aqueous systems is essential for many fields. Up to now, several methods have been developed for DO detection such as titration,¹ colorimetry,² fluorescence,³ chemiluminescence⁴ and electrochemical sensor.^{5–9} Among these analytic approaches, the electrochemical sensor has received lots of attention due to its fast speed, low cost, low detection limit and high accuracy. However, direct detection of DO at commercial electrode needs a high potential. Therefore, many different methods have been developed for electrode surface modification and improving electrons transfer efficiency between DO and electrode surface. Rahim *et al*⁵ demonstrated a DO sensor based on the electrode modified by cobalt (II) phthalocyanine immobilized carbon ceramic mesoporous SiO₂/C.

Graphene, a newly developed form of carbon, has attracted increasing attention in recent times due to its unique physical and electrochemical properties. In electrochemistry field,

using graphene as modifier showed potential advantages of high surface area, ease of processing and safety.¹⁰ Besides, graphene has a large theoretical surface area (2630 m² g^{−1}) and superior electrical conductance (64 mS cm^{−1}).^{11,12} Moreover, graphene also exhibits a large potential window, low charge-transfer resistance and fast electron transfer rate. Many reports also pointed out that graphene could enhance the electrocatalytic performance of noble metal nanoparticles.^{13,14} In recent times, as a typical nanomaterial, silver nanostructures are also studied for detecting DO.⁹ Therefore, attempting to combine the graphene with Ag nanoparticles is expected to generate a suitable electrode material for DO sensing application.

In this context, we report the development of a DO sensor based on the galvanic displacement-induced reduced graphene oxide/silver nanocomposite (RGO/Ag). The RGO/Ag nanocomposite was characterized by UV–vis spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). RGO/Ag nanocomposite-modified glassy carbon electrode (GCE) was then fabricated for DO determination.

2. Experimental

2.1 Materials

AgNO₃, uric acid (UA), 3-hydroxytyramine hydrochloride (DA) and glucose were purchased from Sigma-Aldrich. Graphene oxide powder was purchased from JCNANO, Inc. All other chemicals used were analytical grade reagents

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without further purification. The O_2 -saturated phosphate buffer solution (PBS) was produced by bubbling PBS with O_2 gas for 15 min, in which the DO concentration was 250 μ M. Milli-Q water (18.2 M Ω cm) was used throughout the experiment.

2.2 Synthesis of RGO/Ag nanocomposite

RGO/Ag nanocomposite was prepared via the galvanic displacement method. In a typical experiment, 10 ml of $AgNO_3$ solution (20 mM) was firstly mixed with 2 ml of graphene oxide (GO) dispersion (1 mg ml $^{-1}$) under vigorous stirring. Then, a piece of Cu foil (1 cm $\times$ 1 cm) was polished with sandpaper and then immersed into the mixture. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave. The autoclave was heated to 120°C and maintained for 2 h in an oven, after that it was naturally cooled down to the room temperature. Gray sediment was collected and centrifuged to obtain RGO/Ag nanocomposite.

2.3 Characterization

The morphology and crystal formation of the RGO–Ag nanocomposite were characterized using a scanning electron microscope (SEM, S-4700, Hitachi High Technologies Corporation, Japan) and a X-ray diffractometer (D8-Advance XRD, Bruker, Germany) with Cu K α radiation, respectively. Raman spectroscopy was performed at room temperature using a Raman Microprobe (Renishaw RM1000) with 514 nm laser light. For electrochemical experiments, a GCE was polished with alumina–water slurry followed by rinsing with ethanol and water. For the electrode surface modification, 5 μ l of catalyst dispersion (1 mg ml $^{-1}$) was dropped onto the GCE and dried at room temperature. Electrochemical measurements were performed on a CH Instruments 660A electrochemical Workstation (CHI-660 A, CH Instruments, Texas, USA) using a three-electrode system. A platinum wire was used as the auxiliary electrode and an Ag/AgCl (3 M KCl) as the reference electrode. The specific DO concentration in the cell was controlled by using N_2

bubbling with different time intervals. The DO concentration was monitored during the whole experiment by using the dissolved oxygen meter.

3. Results and discussion

Figure 1a shows the SEM image of the synthesized RGO/Ag nanocomposite. It can be clearly seen that the RGO/Ag nanocomposite was successfully synthesized via the galvanic displacement. The RGO sheets show a corrugated structure. The Ag nanoparticles are decorated on the both sides of RGO sheet, which could effectively prevent the stacking of RGO sheets.¹⁵ Figure 1b displays the size distribution of Ag nanoparticles. The average size of Ag nanoparticle formed via the galvanic displacement is calculated as 52 nm. EDX analysis was conducted to obtain elements information about RGO/Ag nanocomposite (figure 2a). The spectrum presents the existence of C, O, Ag and Cu. The EDX measurement also shows that the Ag loading of RGO/Ag nanocomposite is about 70.57%.

The reduction of GO and formation of Ag were confirmed by UV–vis spectroscopy. Figure 2b displays the UV–vis spectra of GO and RGO/Ag nanocomposite. The spectrum of GO displays a characteristic peak at 236 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the C=C bonds, while the RGO/Ag nanocomposite shows a peak at 259 nm corresponding to the excitation of π -plasmon of graphitic bond.¹⁶ This red-shift indicates the reduction of GO during the galvanic displacement. Moreover, a clear broad absorption peak located at 385 nm was observed in the spectrum of RGO/Ag nanocomposite due to the surface plasmon resonance absorption of Ag nanoparticles.

The reduction of GO was also confirmed by the Raman spectroscopy. As shown in figure 3, the spectrum of GO exhibits two characteristic bands at 1572 and 1335 cm $^{-1}$, which was assigned to the graphite (the G band, first-order scattering of E_{2g} phonons by sp 2 carbon atoms) and diamondoid (the D band, breathing mode of κ -point photons of A_{1g} symmetry) bands, respectively.¹⁷ The intensity ratio between the D band and the G band (I_D/I_G) increases from

Figure 1. (a) SEM image of RGO/Ag nanocomposite and (b) particle size distribution of Ag nanoparticles.

Figure 2. (a) EDX spectrum of RGO/Ag nanocomposite and (b) UV-vis spectra of GO and RGO/Ag nanocomposite.

Figure 3. Raman spectra of GO and RGO/Ag nanocomposite.

Figure 4. XRD pattern of RGO/Ag nanocomposite.

0.92 in GO to 1.09 in RGO/Ag nanocomposite, which is due to the decrease of average size of sp^2 domains by reduction of GO.¹⁸

Figure 4 presents the XRD pattern of galvanic displacement synthesized RGO/Ag nanocomposite. As shown in the figure, the diffraction peaks at 36.41° , 42.67° , 62.93° and 75.91° are assigned to the (200), (220), (311) and (222) silver face-centred-cube (fcc) crystal diffractions (JCPDS file no. 04-0783), respectively. Besides Ag peaks, additional peak appears at 26.2° , which is ascribed to the partial RGO sheets restacking into an ordered crystalline structure.¹⁹

Figure 5 gives a comparison among the cyclic voltammograms (CVs) of bare, RGO and RGO/Ag nanocomposite-modified GCEs in 0.1 M N_2 saturated PBS. No obvious redox peaks were observed for the bare and RGO-modified GCEs. However, the RGO-modified GCE showed a much higher current response over the scan range, indicating the RGO-modified GCE owned a larger surface area. In contrast, a well-defined redox peak was observed for RGO/Ag nanocomposite-modified GCE with the anodic peak potential at 0.47 V and the cathodic peak potential at 0.07 V, which correspond to the one-electron redox process of Ag nanoparticles.^{20,21}

The electrochemical performance of the RGO/Ag nanocomposite towards detecting DO was investigated.

Figure 6 displays the cyclic voltammograms (CVs) of bare, RGO and RGO/Ag nanocomposite-modified GCEs in pH 7.0 PBS with the absence and the presence of saturated O_2 . It can be seen that no electrode response was observed for RGO/Ag nanocomposite-modified GCE with the absence of O_2 . However, in the presence of 250 μM DO, well-defined reduction peaks were observed on the bare, RGO and RGO/Ag nanocomposite-modified GCEs with reduction potential at -0.62 , -0.53 and -0.26 V, respectively. Moreover, it illustrated a significant current enhancement on the RGO/Ag nanocomposite-modified GCE. The increasing peak current and lowering peak potential indicate that RGO/Ag nanocomposite can effectively catalyse the electrochemical reduction of DO due to a synergistic effect. The RGO sheets not only serve as an excellent electron transfer mediator, but also act as a platform for Ag nanoparticle leading to their enhanced catalytic performance.

The mechanism of oxygen reduction usually involves two steps and four electrons.²² The first step is the reduction of O_2 to H_2O_2 and OH^- . The second step is the reduction of H_2O_2 to OH^- . The formula can be expressed as follows:

Figure 5. Cyclic voltammograms of bare, RGO- and RGO/Ag-modified GCE in N_2 saturated PBS. Scan rate 50 mV s^{-1} .

Figure 6. Cyclic voltammograms of bare, RGO- and RGO/Ag-modified GCE in O_2 -saturated or normal PBS. Scan rate 50 mV s^{-1} .

Figure 7. Cyclic voltammograms of RGO/Ag-modified GCE in PBS for different DO concentrations (from the top 1, 5, 10, 20, 30, 40, 50, 60, 70 and $80 \mu\text{M}$). Scan rate 50 mV s^{-1} .

However, only one sharp reduction peak was observed on the RGO/Ag nanocomposite-modified GCE. It indicates a fast and efficient four electrons reaction of DO reduction that occurred on RGO/Ag nanocomposite-modified GCE, which is consistent with that of other silver-based material modified electrode reported previously.^{9,23,24} The formula can be expressed as follows:

Figure 8. Cyclic voltammograms of the RGO/Ag-modified GCE at scan rate of $20\text{--}200 \text{ mV s}^{-1}$ in PBS containing $50 \mu\text{M}$ DO. Inset: plots of peak current vs. the square root of the scan rate.

Figure 9. Amperometric response of the RGO/Ag-modified GCE with different concentrations of DO in PBS. Measured at 0.3 V . Inset: calibration curve at a concentration range of $0\text{--}120 \mu\text{M}$.

The electrocatalytic activity of RGO/Ag nanocomposite-modified GCE for various DO concentrations was then evaluated and is as shown in figure 7. It can be clearly seen that the electrocatalytic current responses gradually increase along with the increment of DO concentration in the range from 1 to $80 \mu\text{M}$.

In order to further understand the electrochemical behaviour of proposed DO sensor, RGO/Ag-modified GCE was examined to investigate the relationship between the peak current and the scan rate. Figure 8 shows the CVs of RGO/Ag nanocomposite-modified GCE in 0.1 M PBS containing $50 \mu\text{M}$ DO by controlling the scan rate from 20 to 200 mV s^{-1} . As shown in figure 8, the reduction peak current increase with the increase of the scan rate. The current responses also been found linearly dependent on the square root of scan rate from 20 to 200 mV s^{-1} (inset of figure 8), indicating that the reduction of DO at electrode surface is controlled by diffusion. The corresponding linear regression can be expressed as $I_{pa}(\mu\text{A}) = -1.9677v^{1/2}(\text{mV s}^{-1})^{1/2} + 2.31904$ ($R^2 = 0.991$).

Amperometric measurements were performed in a PBS at applied potential of -0.26 V for DO determination. Figure 9 shows the typical amperometric response upon successive

Table 1. Comparison of different electrochemical sensors for the determination of DO.

Electrode	Method	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	Detection limit (μM)	Reference
Silver nanodendrites/GCE	I-T	0.169	0.043	Zhang <i>et al</i> ⁹
SiO ₂ /SnO ₂ /MnPc/GCE	DPV	0.147	0.7	Santos <i>et al</i> ⁶
β CDSH/FeTMPyP/CDAuNP/GCE	IT	0.1	0.625	Damos <i>et al</i> ²⁵
Poly-L-lysine/GCE	DPV	0.174	3	Luz <i>et al</i> ²⁶
GNP-f-CNT/GCE	LSV	—	3.125	Tsai <i>et al</i> ⁷
Nickel-salen/platinum electrode	I-T	—	0.5313	Martin <i>et al</i> ²⁷
RGO/Ag/GCE	I-T	0.205	0.031	This work

Table 2. The responses of common interference on the RGO/Ag-modified GCE.

Interference species	Response ratio (%)	Interference species	Response ratio (%)
Na ⁺	2.14	NO ₃ ⁻	3.52
Mg ²⁺	3.22	SO ₄ ⁻	2.07
Cu ²⁺	1.21	AA	1.55
NH ₄ ⁺	0.87	UA	3.69
Fe ³⁺	0.66	Glucose	2.11

additions of DO at RGO/Ag nanocomposite-modified GEC. The profile suggests that the RGO/Ag nanocomposite-modified GCE responds rapidly after the addition of DO and attains a steady-state current within 5 s. A linear relationship between the current response and the DO concentrations was observed in the range from 1 to 120 μM with a correlation coefficient of 0.997. The sensitivity and detection limit was 0.205 $\mu\text{A } \mu\text{M}^{-1}$ and 0.031 μM , respectively. The comparative study (table 1) indicates that the proposed sensor could be applied for detecting the DO content sensitively.

The repeatability of proposed DO sensor was tested by five different RGO/Ag nanocomposite-modified GCEs towards 50 μM DO. The RSD of current responses was 4.12%, suggesting an acceptable reproducibility of the proposed fabrication method. The repeatability of the proposed sensor was investigated by eight successively detections of 50 μM DO. The RSD of current responses was 6.22%, indicating a good reproducibility. The effects of common interference species on proposed DO sensor has also been investigated. In total, 0.5 mM of Na⁺, Mg²⁺, Cu²⁺, NH₄⁺, Fe³⁺, NO₃⁻, SO₄⁻, AA, UA and glucose was added into 50 μM DO during the amperometric test at the applied potential of -0.26 V. As shown in table 2, the observed influences are less than 4%. Therefore, the fabricated DO sensor can tolerate high concentrations of interfering species.

4. Conclusion

This paper demonstrated that a RGO/Ag nanocomposite was synthesized by the simple galvanic displacement method using GO, AgNO₃ and Cu foil as raw materials. The

synthesized RGO/Ag nanocomposite was characterized by UV-vis spectroscopy, Raman spectroscopy, XRD and SEM. The RGO/Ag nanocomposite-modified GCE was studied for the analytical determination of DO in aqueous solutions. The RGO/Ag-modified GCE showed a high current response with a positive reduction potential (-0.26 V) when compared to the reduction on the bare GCE- and RGO-modified GCE. Under optimized conditions, the detection limit and sensitivity of the proposed DO sensor are 0.031 μM and 0.205 $\mu\text{A } \mu\text{M}^{-1}$, respectively. The proposed DO sensor also exhibited excellent repeatability, reproducibility and anti-interference ability.

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