

ELECTROCHEMICAL FABRICATION OF PEDOT/REDUCED GRAPHENE OXIDE AND ITS POTENTIAL AS AN OXYGEN REDUCTION REACTION CATALYST

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Abstract: A novel reduced graphene oxide-doped poly(3,4-ethylenedioxythiophene) deposited on glassy carbon electrode (GCE) denoted as PEDOT/rGO/GCE was fabricated as a modified electrode to investigate its electrocatalytic performance towards oxygen reduction reaction (ORR). PEDOT/rGO composite was successfully obtained through electropolymerization and a reduction process by cyclic voltammetry (CV). Fourier Transform-Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) were used to physically characterize the PEDOT/rGO composite. FT-IR showed the formation of PEDOT/rGO from the presence of C=C, C-C and C-S thiophene ring bonds. SEM imaging suggested a well-dispersed PEDOT on rGO sheets. The PEDOT/rGO-modified electrode was fabricated using the drop-casting technique. The optimum amount of PEDOT/rGO suspension dripped on the GCE was 15 μ L. Electrochemical behavior of PEDOT/rGO/GCE-modified electrode was determined using CV and electrochemical impedance spectroscopy (EIS) in 1.0 M KCl solution with reference to 5 mM $K_4[Fe(CN)_6]$ redox system. The CV and EIS results showed that modification of the electrode had increased electrical conductivity and decreased resistance. The CV of ORR revealed that both PEDOT/rGO/GCE and rGO/GCE electrodes reflected electronic conductivity. However, PEDOT/rGO/GCE-modified electrode peak current had improved by three-fold compared to bare GCE, indicating a larger surface area to catalyze oxygen.

KEYWORDS: Electrocatalyst, glassy carbon electrode, cyclic voltammetry, oxygen reduction reaction

Introduction

Fuel cells (FCs) have emerged as one of the most promising energy sources owing to its low cost and high efficiency. Recent developments in FCs have led to renewed interest in oxygen reduction reaction (ORR) since this process is one of the key factors that determines the FCs' productivity. ORR occurs via two pathways, either by direct four-electron transfer to produce water or by two-electron transfer to produce hydrogen peroxide. In electrochemistry, the four-electron transfer pathway is most preferable due to higher operation potential and current efficiency in FCs (Viswanathan *et al.*, 2012). To date, commercial electrodes in FCs are usually made of platinum. However, the metal suffers several limitations, such as high cost, poor durability and slow ORR activity. This has led to an urgent need for more abundant, low-cost electrodes with higher activity compared to platinum-based electrocatalysts.

Hence, a wide variety of compounds have been proposed as electrocatalysts for the reduction of oxygen (Ensafi *et al.*, 2016; Kar *et al.*, 2016; Rameshkumar *et al.*, 2015). Among the numerous potential materials, those that are graphene-based have been widely investigated.

Graphene — a single layer of carbon atoms tightly packed into a two-dimensional honeycomb sp^2 carbon lattice — has recently received great attention due to its unique properties, such as a large surface area, stable electrical conductivity, high catalytic activity, low cost and being environmental friendly. Previous research has established that graphene is a suitable material for energy storage (Ahmed *et al.*, 2013; Brownson *et al.*, 2010). The first electrochemical discovery of graphene was by Nai *et al.*, (2008), who used multilayer graphene nanoflake films (MGNFs) for biosensing of dopamine.

However, the difficulty in obtaining defect-free graphene have limited its large-scale synthesis, which is essential for real-life applications. Reduced graphene oxide (rGO) is a graphene derivative which not only compensates for the drawbacks of graphene, but also introduces new properties. The current research involves the utilization of a modified electrode, which was fabricated by introducing the catalysts at the electrode surface and facilitating the electron transfer rate in slow electrochemical reactions (Pauliukaite *et al.*, 2010; Si *et al.*, 2012; Wang *et al.*, 2014). Usage of conductive substrate is one of the strategies to maximize the electroactive surface area and enhance the electrical conductivity of the catalyst.

Among the conductive materials, conducting polymer is a common material used as modified electrodes to achieve desired properties. Several studies have demonstrated that the incorporation of graphene sheets with conducting polymers may enhance its electrochemical characteristics in terms of energy storage capacity and electrical conductivity (Al-mashat *et al.*, 2010; Biswas & Drzal, 2010). Among the conducting polymers, Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of most promising because of its unique properties, such as stability, strong electrical conductivity, remarkable capacitive behavior and mechanical flexibility (Choe *et al.*, 2015). In this study, a novel composite electrode consisting of rGO and PEDOT (PEDOT/rGO) as an electrocatalyst is synthesized through electropolymerization and reduction techniques. The electrochemical activity of PEDOT/rGO fabricated on glassy carbon electrode (GCE) is further investigated using cyclic voltammetry and electrochemical impedance spectroscopy with $K_4[Fe(CN)_6]$ as the electrolyte in KCl solution.

Materials and Methods

Instruments

Scanning electron microscopy (SEM) image was obtained on Scanning Electron Microscopy

JEOL JSM 6360LA at the operational voltage of 5 kV. Fourier Transform Infrared Spectroscopy (FTIR) spectra of the composite were recorded on a Perkin Elmer 100 by using potassium bromide (KBr) in the spectral range of 2000 cm^{-1} – 450 cm^{-1} .

Electrochemical measurements were carried out on Potentiostat/Galvanostat Autolab PGSTAT302N coupled with three-electrode system controlled by NOVA 1.10 software. A bare or modified glassy carbon electrode (3 mm in diameter) was used as a working electrode. Ag/AgCl (saturated KCl) electrode and platinum wire electrode were used as a references electrode and auxiliary electrode, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were performed using Autolab FRA32M controlled fitness of NOVA 1.10 software in 5.0 mM $K_4[Fe(CN)_6]$ solution containing 1.0 M KCl. All the potentials recorded were relative to Ag/AgCl (saturated KCl). The frequency range is 1-100,00 Hz with the direct potential set 0.20 V.

Preparation of GO

GO was obtained through oxidation of graphite powder from modified Hummers method (Hummers & Offeman, 1958). Briefly, 3 g of graphite powder and 1.5 g of $NaNO_3$ was mixed with 50 ml concentrated H_2SO_4 and stirred at room temperature. Then, 3 g of $KMnO_4$ was added in a mixture and stirred in ice bath (0-10°C). 46 mL of distilled water was added into above mixture with stirring above 98°C. The reaction was stopped by added 15 mL of 30% H_2O_2 . Finally, the mixture was washed with 5% of HCl and distilled water for several times, followed by centrifugation, filtration and drying to obtained graphene oxide powder.

Preparation of PEDOT/rGO Nanocomposite

20 mg of GO was dispersed in 30 mL of acetonitrile (MeCN) by sonication. Then, 20 μ L of EDOT solution was added into the mixture under rapid stirring. The resulting product of

EDOT/GO was centrifuged and washed with ethanol and distilled water. Finally, it was dried at 50°C for 24 hours. To produce PEDOT/rGO, 20 μL of EDOT/GO suspension (1mg/mL) was coated on GCE surface. After drying at room temperature, the EDOT/GO/GCE was electrochemically reduced and polymerized by 15 successive cycles of cyclic voltammetry. The product of PEDOT/rGO was smoothly scratched out from GCE surface and kept for further experiment.

Preparation of Electrode

GCE surface was pre-polished with 1 μm of alumina/water slurry, then rinsed with distilled water and sequentially sonicated in water and acetone for 5 minutes before used. For electrochemical measurements, rGO and PEDOT/rGO composites were prepared in distilled water (1 mg/mL) by under sonication. 15 μL of composite was dropped onto GCE surface by drop casting technique. All the electrochemical experiments were performed in 5.0 mM of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution containing 1.0 M KCl solution.

Electroreduction of Oxygen

For ORR activity, cyclic voltammetric experiments were carried out on a modified

PEDOT/rGO/GCE in 50 mL 0.1 M KOH earlier deaerated by purging N_2 . Later, similar experiments were done by purging O_2 gas. These were scanned several times in the applied potential range of -1.1 to 0.2 V to obtain stable responses.

Results and Discussion

Preparation of Composite

All the catalyst were reduced and polymerized through electrochemical technique. It is because of this technique is more simple, low cost, time consuming and promote to green route compared to chemical technique (Pumera, 2010). In the electrochemical technique, hydrogen ion in electrolyte plays a key role to reduced oxygen functional group of GO and polymerized EDOT monomer to PEDOT (Zhou *et al.*, 2009). This technique was confirmed by cyclic voltammetry where it was done by using 100 mV/s scan rate in 1.0 M of KCl solution for 15 scan cycles.

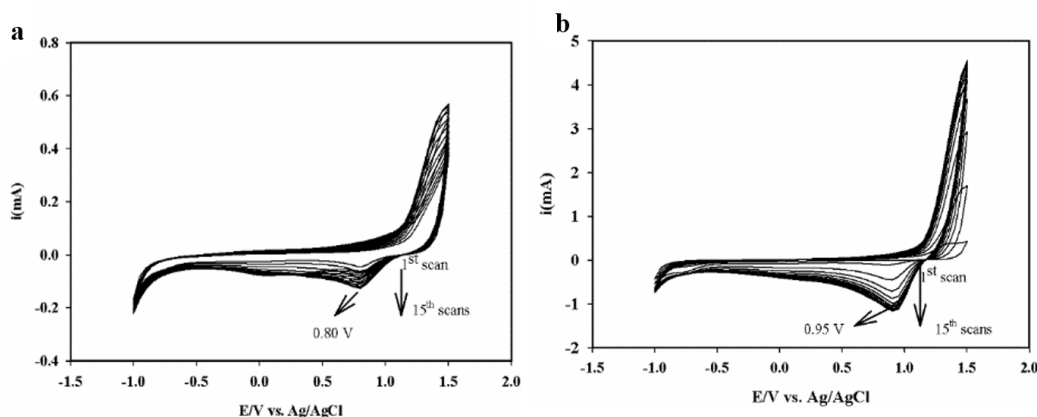


Figure 1: Cyclic voltammogram of (a) reduction of GO; (b) polymerization of EDOT/GO in 1.0M of HCl at a potential range between -1V and 1.5V at 100 mV/s scan rate.

As can be seen from Figure 1a, the large cathodic current peak of reduction GO was appears at 0.8 V with a starting potential of 0.6 V, indicates that the reduction of the surface oxygen groups (Guo *et al.*, 2009). For the polymerization of EDOT monomer (Figure 1b), the peak current appears at 0.95 V due to the doping/undoping of PEDOT. The increase of the cathodic current with the continual CV scans indicate the increasing of reduction and polymerization of composites. Additionally, the potential for both reactions are similar reflects the stability of electrode.

Physical Characterization of Composite

The surface morphology of composites were characterized by using SEM to observe the

surface of structure modification. As shown in figure 2a, the SEM image of rGO before doped with EDOT monomer has smooth-like structure. After the doping and polymerization of EDOT monomer (figure 2b), the surface of PEDOT/rGO becomes rougher and more crumpled suggested the doping of PEDOT on rGO sheets. The morphology of PEDOT/rGO promote the ions of electrolyte diffuse on the surface composite where it favorable for high sensitivity of modified electrode.

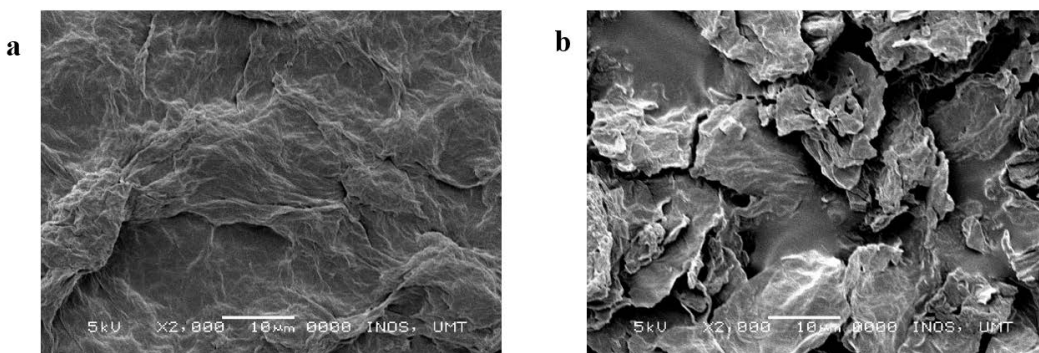


Figure 2: the SEM image of (a) rGO and (b) PEDOT/rGO.

Figure 3 shows the FT-IR spectra of rGO and PEDOT/rGO composites. The rGO spectrum had less oxygen functional group, indicating that rGO had been completely reduced. The three peaks appeared at 1630 cm^{-1} , 1408 cm^{-1} and 903 cm^{-1} , which could be attributed to the C=C and C-O bond of carboxylic acid, and the C=C bond of alkene.

For PEDOT/rGO, the peaks at 1628 cm^{-1} and 1215 cm^{-1} were due to the vibration of the C=C

and C-C stretching of the quinonoid structure and thiophene ring, respectively. The presence of a strong bond at 1091 cm^{-1} indicated the formation sulfoxide (S=O) bonds, while the peak at 983 cm^{-1} was related to the C-S bond in the thiophene ring. The series of the band indicated that PEDOT had been doped on rGO sheets.

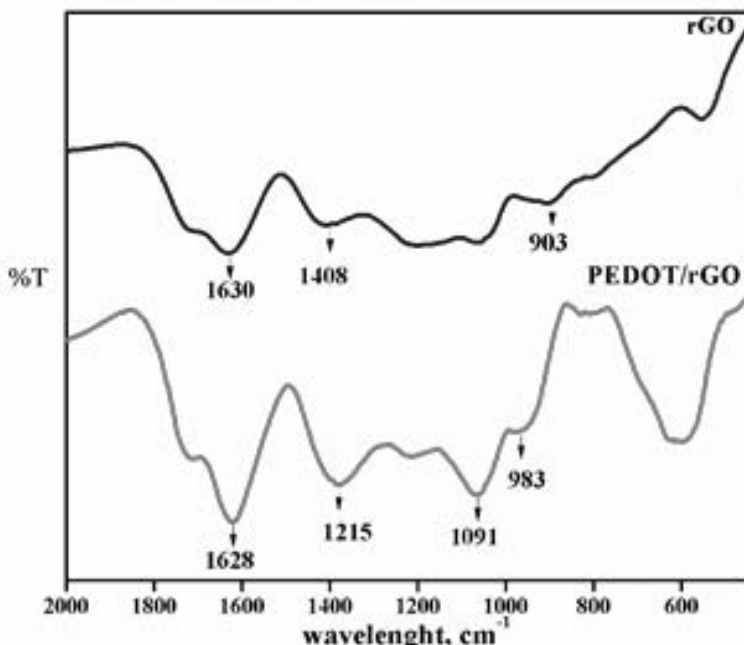
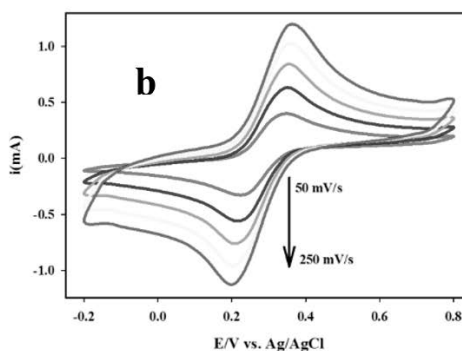
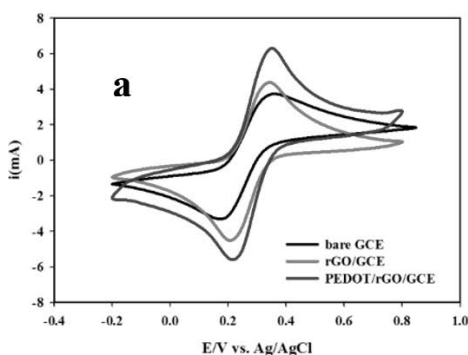


Figure 3: FTIR spectra of rGO and PEDOT/rGO.

Electrochemical Characterization of Composite

The electrochemical behavior of composites were observed by recording of CV in the presence of $K_4[Fe(CN)_6]$. The redox couple of $K_4[Fe(CN)_6]$ was chosen as a marker to characterize electron transfer of modified electrode due to the sensitivity to the surface chemistry and close to the quasi-reversible of carbon-based electrode (Jiang *et al.*, 2012). Figure 4(a) shows the electrocatalytic activity of modified electrode

in 5.0 mM $K_4[Fe(CN)_6]$ containing 1.0 M KCl solution at a scan rate 100 mV/s. From the results obtained, it is clear that PEDOT/rGO/GCE showed the largest peak current compared to rGO/GCE and bare GCE, indicates PEDOT/rGO/GCE is electroactive and large effective surface which provide a sufficient reaction site to accelerate electron transfer of $K_4[Fe(CN)_6]$ (Yusoff *et al.*, 2014). The peak separation is less than 200 mV for both oxidation and reduction peak is indicative of the good reversibility of electrode processes.



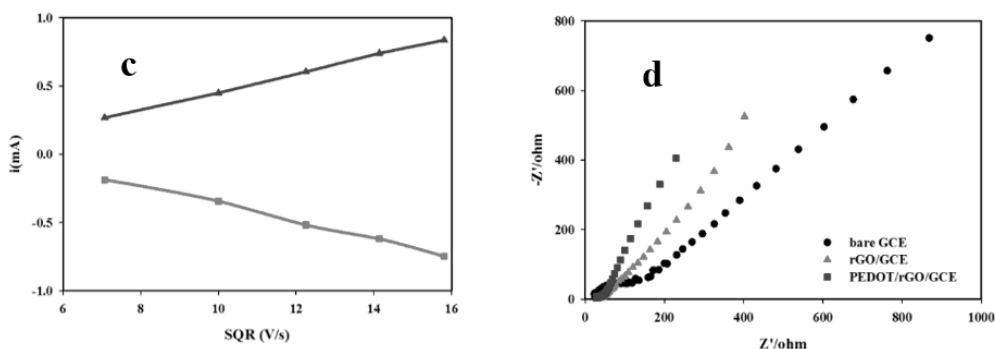


Figure 4: (a) CVs of bare GCE, rGO/GCE and PEDOT/rGO/GCE electrode; (b) CVs of PEDOT/rGO/GCE-modified electrode at different scan rate; (c) plot of anodic and cathodic peak currents vs. the square root of the scan rate; (d) Nyquist plot of 0.2V for the modified electrode. Electrolyte: 5.0 mM $K_4[Fe(CN)_6]$ in 1.0M KCl solution.

The effects of scan rate towards PEDOT/rGO/GCE-modified electrode surface was also investigated (Figure 4b). It could be seen clearly that the peak current of oxidation and reduction at the electrodes was increasing linearly with the square root of scan rate (Figure 4c). The diffusion coefficient value (D) of $1.17 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, derived from the slope of the peak current, proved that the electrode process was diffusion-controlled. This results suggested that the modified electrode behavior was controlled by electron transfer and confirmed that it was stable.

Table 1 shows the relationship between the square root of scan rate and peak current. From this table, it could be concluded that the correlation coefficient (R_2) would increase as the composite deposited on GCE. It was because of the increase in the composite's surface area that the diffusion of electrons on the surface of the electrode would increase. Moreover, as the scan rate increased, the value of peak current (I_p) of anodic and cathodic also increased, indicating that the rate of electron charge transfer had increased (Yusoff *et al.*, 2013).

Table 1: Relationship between scan rate and peak current.

Composite	V	$v^{1/2}$	Peak current(μA)		R_{pa}^2 vs $v^{1/2}$	R_{pc}^2 vs $v^{1/2}$	Slope (I_{pa})	Slope (I_{pc})	E_{pa} (mV)	E_{pc} (mV)	ΔE
			Anodic	cathodic							
Bare GCE	50	7.07	280	-230	0.9788	0.9858	21.34	-22.21	346.3	177.2	169.1
	100	10.0	370	-320							
	150	12.25	430	-390							
	200	14.14	480	-460							
	250	15.8	530	-510							
rGO	50	7.07	200	-210	0.9959	0.9907	59.85	-52.22	319.3	231.9	87.4
	100	10.0	430	-450							
	150	12.3	590	-610							
	200	14.1	710	-720							
	250	15.8	820	-830							
PEDOT/rGO	50	7.07	390	290	0.9991	0.9958	64.98	-64.18	352.5	224.4	128.1
	100	10.0	620	530							
	150	12.3	830	690							
	200	14.1	1020	959							
	250	15.8	1170	1300							

EIS is a powerful technique to evaluate the characteristics of electron transfer between an electrolyte and modified electrode surface (Yang & Gunasekaran, 2013). Figure 4(d) shows the Nyquist plot of an electrode with different modifications. The semicircle portion at high frequencies could be attributed to the charge transfer process being equivalent to the charge transfer resistance (R_{ct}), and a linear portion at low frequencies corresponded to kinetics of the diffusion process.

From the Nyquist diagram, bare GCE plots show higher R_{ct} of semicircle plot, pointing to very low resistance of electron transfer in the redox probe. However, R_{ct} decreased when PEDOT/rGO was deposited on bare GCE, exhibiting a linear graph. The results

demonstrated that PEDOT/rGO/GCE had higher conductivity and more surface area for electron transfer between electrolytes in the solution and electrode surface.

Oxygen Reduction Reaction

Figure 5 shows the ORR onsets of all composites. PEDOT/rGO/GCE showed greater enhanced catalytic activity towards reduction of O_2 . The cathodic peak of PEDOT/rGO/GCE was $-0.45V$. The cathodic peak current (I_p) of PEDOT/rGO/GCE increased for three times compared to bare GCE, implying that the modified electrode had larger surface area to catalyzed O_2 . However, bare GCE and rGO/GCE had a low response towards ORR.

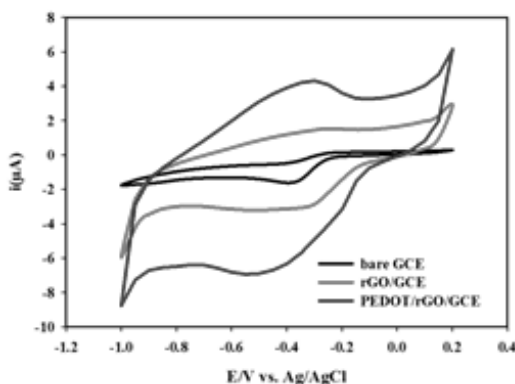


Figure 5: CVs of ORR in O_2 saturated 0.1 M KOH solution of modified electrode.

Conclusion

A simple PEDOT/rGO/GCE was fabricated to catalyze ORR in 0.1M KOH solution that was saturated with oxygen. The composite was prepared using a green synthesis drop-casting technique on GCE, followed by electropolymerization and reduction by CV. The PEDOT/rGO/GCE-modified electrode showed excellent catalytic activity towards ORR. Future research could focus on the application of PEDOT functionalized rGO on GCE as a cathode in FCs.

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