



# 3,4-Ethylenedioxythiophene functionalized graphene with palladium nanoparticles for enhanced electrocatalytic oxygen reduction reaction



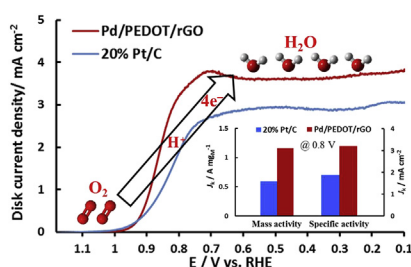
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## HIGHLIGHTS

- Synthesis of Pd/PEDOT/rGO with well dispersed PdNPs.
- Higher ORR due to intermolecular charge-transfer between graphene & PdNPs via PEDOT.
- ORR possess 4-electron pathway with lower  $\text{H}_2\text{O}_2$  & faster electron transfer kinetic.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Poly(3,4-ethylenedioxythiophene) functionalized graphene with palladium nanoparticles (denoted as Pd/PEDOT/rGO) has been synthesized for electrochemical oxygen reduction reaction (ORR) in alkaline solution. The structural features of catalyst are characterized by scanning electron microscopy, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The TEM images suggest a well dispersed PdNPs onto PEDOT/rGO film. The ORR activity of Pd/PEDOT/rGO has been investigated via cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) techniques in 0.1 M KOH aqueous solution. Comparative CV analysis suggests a general approach of intermolecular charge-transfer in between graphene sheet and PdNPs via PEDOT which leads to the better PdNPs dispersion and subsequently superior ORR kinetics. The results from ORR measurements show that Pd/PEDOT/rGO has remarkable electrocatalytic activity and stability compared to Pd/rGO and state-of-the-art Pt/C. The Koutecky–Levich and Tafel analysis suggest that the proposed main path in the ORR mechanism has direct four-electron transfer process with faster transfer kinetic rate on the Pd/PEDOT/rGO.

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## 1. Introduction

The electrocatalytic oxygen reduction reaction (ORR) has attracted extensive interest in the field of electrochemical energy storage and conversion [1,2]. Typically, because of the slow reaction kinetics on the cathode, various metal nanoparticles (NPs) have

been used to catalyze ORR. The Pt-based materials are usually used as the electrocatalysts in fuel cells (FCs), which are limited by cost and durability issues [3]. Consequently, recent efforts have focused on the discovery of electrocatalysts with various Pd-metals alloy or metal-free for ORR [4–6]. Among the various candidates for the replace of Pt-based catalysts, Pd is the most attractive one for it. It has already been established that the Pd is a promising electrocatalyst because it is cheaper and higher resistance to CO poisoning than Pt and is high electroactive for FCs [7–9]. Moreover, most

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researchers have been interested in the fabrication and application of PdNPs due to strong catalytic effect in both reduction and oxidation reaction [10].

Graphene sheets are highly conductive and 2D flat lattices consisting of a monolayer of  $sp^2$ -hybridized carbon atoms which have been attracted a great deal of research interest due to high electrical conductivity and electron mobility, large surface area, long-term stability and unique mechanical flexibility [11–13]. Graphene has already been used in various fields, especially in sensors [14,15], capacitor [16] and ORR catalysts [4–6,17–19]. The graphene sheets could be readily synthesized by reducing the oxygen functional groups present on the surface of graphene oxide (GO) that has a layer structure with oxygen-containing functional groups such as hydroxyl, epoxide and carboxyl groups on planes and edges [5]. Chemical reduction of GO (hereafter rGO) is cost-effective approach for large scale production, which includes non-covalent and covalent functionalization of rGO [5,20].

The reasons for the spectacular applications of thiophene compounds are related to their good environmental stability in both neutral and doped states, and their structural versatility, which has provided opportunities for improving their electrical properties [21]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most excellent conducting polymers which has unique properties such as, high electrical conductivity, stability, good capacitive behavior and mechanical flexibility [10,21–25]. The EDOT, as monomer has strong electron donating ability and small steric interaction between repeating units in polymers [24,25]. However, PEDOT functionalized carbon materials including graphene have already been widely investigated and shown quite impressive results in the field of FCs catalysis due to excellent combination of properties and easy preparation [21,22].

Based on the above discussion, the PdNPs decorated PEDOT functionalized rGO (Pd/PEDOT/rGO) has been synthesized via a chemical process, which has the following merits: (a) the Pd/PEDOT/rGO is easily synthesized by a wet-chemical process; (b) the rGO can be easily functionalized with PEDOT into rGO via non-covalent approach; after noncovalent functionalization, the PEDOT/rGO has got smooth surface and increased sulfur content which may leads to well set PdNPs; and (c) the Pd in Pd/PEDOT/rGO can be electrochemically utilized in maximum due to well dispersion with smaller in NPs size. The electrochemical behavior of Pd/PEDOT/rGO for ORR has been investigated using cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) techniques in 0.1 M KOH solutions. The results prove that the Pd/PEDOT/rGO fabricated glassy carbon electrode (GCE) has superior electrocatalytic activity for ORR than that of PEDOT/rGO, Pd/rGO and Pt/C.

## 2. Experimental

### 2.1. Instruments

Scanning electron microscopy (SEM) images were carried out on JSM-7500F field emission scanning electron microanalyzer (JEOL, Japan) at an operational voltage of 15 kV. The field emission transmission electron microscopy (FE-TEM) and energy-dispersive X-ray spectroscopy (EDX) observations were carried out in a JEM-2100F microscope at 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a MultiLab 2000 (Thermo Electron Corporation, England) with a 14.9 keV Al K $\alpha$  X-ray source. A three-electrode potentiostat (CHI 700C Electrochemical Workstation, USA) in a grounded Faraday cage was used for voltammetric measurements. A Pt wire was used as an auxiliary electrode. A calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) in 3 M Cl solution was used as a reference electrode.

The potential of the Ag/AgCl reference electrode is corrected with the reversible hydrogen electrode (RHE), in 0.1 M KOH,  $E_{(RHE)} = E_{(Ag/AgCl)} + 0.982$  V. The current densities were normalized with respect to the geometrical surface area of electrodes. An RRDE was employed as a working electrode. An EG&G Model 636 RRDE system and a CHI 700C electrochemical workstation were used for hydrodynamic voltammetry.

### 2.2. Preparation of catalysts

#### 2.2.1. Electrochemical preparation of PEDOT/rGO

GO was prepared by oxidizing graphite according to the improved Hummers method [5,26–28] using graphite powder (325-mesh) from Aldrich (see Supporting information). Then, 20 mg GO powder was dispersed in 30 mL acetonitrile (MeCN) with 10 min ultrasound agitation, then 20  $\mu$ L EDOT (Aldrich) was added to the solution under stirring and keep as it is for 15 h. After that, it was centrifuged and washed with DW (distilled water) and ethanol several times. Finally, the resulting product (EDOT/GO) was dried at 50 °C in a vacuum oven for 24 h. The GC plate (area 1 cm<sup>2</sup>) surface was coated with a 100  $\mu$ L EDOT/GO suspension (1 mg/mL DW). After drying at RT, EDOT/GO/GCE was electrochemically polymerized and reduced by ten successive cycles of CVs in an electrochemical cell containing 1 M KCl solution over a potential range of  $\pm 1.5$  V at a 100 mV s<sup>-1</sup> scan rate (Fig. S1). The PEDOT/rGO/GCE was washed with DW before and after each electrochemical experiment.

#### 2.2.2. Preparation of Pd/PEDOT/rGO

To make Pd/PEDOT/rGO, 5 mg PEDOT/rGO powder [collected from 100  $\mu$ L PEDOT/rGO coated GC plate (area 1 cm<sup>2</sup>) by smooth scratching] and 2.5 mL of 10 mM K<sub>2</sub>PdCl<sub>4</sub> (Aldrich) solution was dispersed by sonication in 10 mL ethanol–water (1:1, v/v ratio) solution. Subsequently, 0.1% NaBH<sub>4</sub> (2 mL) solution was added in a drop wise manner and was stirred for 3 h at RT with continuous magnetic stirring. Finally, the resulting product was filtered, washed three times with DW and dried in a vacuum oven at 70 °C for 12 h (Scheme 1). For comparison, the electrochemically reduced rGO (without EDOT and PdNPs) and Pd/rGO (without EDOT) have been employed toward ORR.

#### 2.2.3. Electrode preparation

For the electrode preparation, rGO, Pd/rGO, PEDOT/rGO or Pd/PEDOT/rGO suspensions in DW (1 mg/mL) were prepared by introducing a predetermined amount of the corresponding samples under sonication. The 10  $\mu$ L and 16  $\mu$ L portions of the each suspension was then dropped onto the surface of GCE (0.0707 cm<sup>2</sup>) and RRDE GC disk (0.1962 cm<sup>2</sup>) electrodes, respectively, that were prepolished with a 0.05  $\mu$ m alumina suspension on a polishing cloth (BAS, USA). The resulting catalysts-coated GCE was washed with DW before and after each experiment. All the experiments were performed at RT in 0.1 M KOH solution, which were purged with O<sub>2</sub> or Ar for 20 min prior to each measurement. For comparison, the 16  $\mu$ L of 20 wt% Pt/C was also casted onto RRDE GC disk electrode from 1 mg/mL ethanol solution. The metal loading was calculated as 14.10, 15.65  $\mu$ g<sub>Pd</sub> cm<sup>-2</sup> and 16.30  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup> for Pd/PEDOT/rGO, Pd/rGO and Pt/C, respectively.

## 3. Results and discussion

### 3.1. Characterization

The surface morphology of rGO, PEDOT/rGO and Pd/PEDOT/rGO were characterized by SEM and TEM, respectively, which are usually employed to observe the surface structure modification and

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