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# Synthesis of Pd nanoparticles supported on PDDA functionalized graphene for ethanol electro-oxidation

Yanfang Fan, Yanchun Zhao<sup>\*</sup>, Duhong Chen, Xiao Wang, Xinglan Peng, Jianniao Tian<sup>\*</sup>

Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), College of Chemistry and Pharmacy, Guangxi Normal University, Guilin 541004, PR China

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## ABSTRACT

We described a facile and eco-friendly method for preparation of Pd nanocomposites (Pd-PDDA/RGO), which possesses a low Pd metal percent (20 wt%) and a mean size of 3.9 nm. The reaction was carried out at room temperature using Pd nanoparticles anchored on reduced graphene oxide (RGO) with the assist of poly(diallyldimethylammonium chloride). The Pd nanoparticles were well distributed without obvious aggregation. The Pd-PDDA/RGO nanocomposites exhibit higher electrocatalytic activity and stability for the electro-oxidation of ethanol than Pd/RGO, Pd-PDDA/MWCNTs (multi-walled carbon nanotubes) and Pd-PDDA/XC-72 carbon black. The peak current density for ethanol oxidation of Pd-PDDA/RGO is 1.38, 1.60 and 2.40 times stronger than that of Pd/RGO, Pd-PDDA/MWCNTs and Pd/XC-72, respectively.

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## Introduction

Direct alcohol fuel cells (DAFCs) have attracted tremendous attention as power sources for portable electronic devices. Among various types of DAFCs, direct methanol and ethanol fuel cells (DMFCs and DEFCs) are promising power sources due to their high energy density, low pollutant emission, low operating temperature, and easy handling [1]. Especially, DEFCs has the advantages of low toxicity, high energy density, good stability and easy storage [2]. Furthermore, ethanol is a green and renewable resource that can be easily obtained in large amounts from agricultural products or biomass by

fermentation [3,4]. Despite these advantages, the low efficiency of ethanol oxidation has greatly limited the development of DEFCs. Therefore, it is a challenge for the commercialization of DEFCs to develop a highly-active anode catalyst [5–7].

Palladium is an effective anode catalyst for the ethanol oxidation reaction in alkaline DEFCs. As noble metal catalyst, Pd has two significant advantages as compared with the Pt. Firstly, According to reports in the literature [8–10], Pd shows both higher catalytic activity and better stability for the oxidation of methanol and ethanol in alkaline medium. Masel et al. [11] have reported that Pd and Pd/C catalysts can conquer the CO-poisoning effect and thereby yield high performance

<sup>\*</sup> Corresponding authors. Tel.: +86 773 5846279; fax: +86 773 5832294.

E-mail addresses: [yanchunzhao@aliyun.com](mailto:yanchunzhao@aliyun.com) (Y. Zhao), [birdtjn@sina.com](mailto:birdtjn@sina.com) (J. Tian).  
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in DMFCs; Secondly, Pd is more abundant than Pt (Pd at least fifty times more abundant on Earth than Pt) and has a much lower price. Thus Pd can be substituted for Pt both as anode and cathode materials without worsening fuel cell performance [12].

Recently, more novel catalyst supports have been developed to improve fuel cell performance [12,13]. The catalyst support (i.e., carbon support) used in a fuel cell operation environment requires corrosion resistance and highly electrical conductivity, and desirable water handling capability (hydrophilic character) [14,15]. Among all kinds of carbon supports (such as activated carbon, carbon black, graphitized materials [16] fullerenes and carbon nanotubes etc.), graphene has attracted more attention of researchers in electrochemistry. As a newly reported carbon carrier material with two dimensional nanostructures, graphene has extraordinary electrical, thermal and mechanical properties [17,18]. Besides, it also owns wide potential window, excellent chemical stability in various electrolytes and easy renewable surface [19]. In particular, graphene possesses the high quality of the  $sp^2$  conjugated bond in the carbon lattice, remarkably high electron mobility under ambient conditions with the reported values in excess of  $15,000 \text{ cm}^2/(\text{V s})$  and a very large specific surface area (theoretical value  $2600 \text{ m}^2/\text{g}$ ) [20–22]. These unique properties make graphene a promising supporting component for potential applications in many technological fields, such as, nanocomposites [23], batteries [24] and supercapacitors [25]. It should be mentioned that there are two main difficulties to directly utilize the negative charges of graphene in the nanoparticles deposition process: First, graphene are apt to aggregate due to the very high specific surface area; Second, negative charge of carboxyl, hydroxyl, and epoxy groups etc. on the surface of graphene is too weak to assemble nanoparticles directly. To overcome these obstacles, various polyelectrolyte, including Poly(diallyldimethylammonium chloride) (PDDA) [22,26], such as branch poly (ethylenimine) [27], polyacrylic acid [28] have been used as inter-linkers for depositing metal nanoparticles on graphene. The modification proves to be an effective strategy to enhance the functionality of materials and the deposition of nanoparticles on graphene. Recently, Shi et al. [26], fabricated PdPt nanocomposites with sonoelectrochemical technique on PDDA modified RGO as electrocatalyst for DAFCs, which displayed electrocatalytic activity and stability for the electro-oxidation of ethanol. Zhang et al. [29], reported the synthesis of high Pt-loadings on the surface of functionalized graphene, and proposed that PDDA plays a crucial role in the highly dispersion and stabilization of Pt nanoparticles on graphene and PDDA-RGO could be an alternative support for Pt immobilization in DMFCs.

In this paper, PDDA is used as the functional macromolecule to produce the stable building block dispersion of the cationic polyelectrolyte-functionalized graphene as a supporting material. In the as-prepared Pd-PDDA/RGO nanocomposites, PDDA can alter the electrostatic charges of graphene, create net positive charge in the carbon plane via intermolecular charge transfer, and so favor the loading of the Pd nanoparticles [30]. The use of PDDA modifier not only changes the electrostatic charges of graphene, but also provides a convenient approach for the hybridization of graphene

[22]. To prove whether the graphene has been modified with PDDA successfully, we studied the shift of the UV–vis absorption peak of the 20% PDDA, PDDA/RGO and Pd-PDDA/RGO samples. Furthermore, the morphologies and structures of the as-prepared Pd-PDDA/RGO nanocomposites were extensively investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The composition was evaluated by energy dispersive X-ray spectrometry (EDS). Moreover, Raman spectra revealed the surface properties of graphene and its interaction with metallic nanoparticles. Cyclic voltammetric (CV) and chronoamperometry experiments exhibited their catalytic activity and stability for the electro-oxidation of ethanol in alkaline media.

## Experimental method

### Materials and instruments

Chemicals used in the experiment were of analytical grade. Graphite powder, NaCl,  $\text{H}_2\text{SO}_4$ , 30%  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ ,  $\text{NaBH}_4$ , ethanol, NaOH, N, N-dimethylformamide (DMF) and PDDA were procured commercially and used without further purification. The XC-72 carbon black was purchased from Cabot Corporation and MWCNTs were purchased from Shenzhen Nanotechnologies Port Co. Ltd (Shenzhen, China) with the diameter of 40–60 nm, length of 5–15  $\mu\text{m}$ , and purity of 98%. Main characterization instrument are scanning electron microscope (SEM) (FEI Quanta 200 FEG Holland), TEM (Hitachi H-800 Japan), high-resolution transmission electron microscopy (HRTEM) (JEM-2100F, Japan), XRD (Rigaku D/max 2500v/pc X Japan), Raman spectroscopy (Invia, Renishaw UK) and UV–vis absorption (TU-1901 China).

### Preparation of reduced graphene oxide

The preparation of RGO is briefly described as follows [31]: 1 g graphite powder and 20 g NaCl were mixed and ground for 30 min, then the mixture was leached to remove the NaCl. The dried graphite was transferred to a 250 mL beaker and 23 mL  $\text{H}_2\text{SO}_4$  ( $18 \text{ mol L}^{-1}$ ) was added with constant stirring at  $25^\circ\text{C}$  for 24 h. Then 0.12 g of  $\text{KNO}_3$  was added at  $40^\circ\text{C}$  and followed by slowly adding 0.5 g of  $\text{KMnO}_4$ , keep stirring for 30 min. Afterwards, 186 mL of water was added to the beaker slowly and 10 mL of 30%  $\text{H}_2\text{O}_2$  were added to end the reaction. The product was centrifuged and washed with 5% HCl solution and distilled water, respectively. Finally, the sample was dried in a vacuum oven at  $60^\circ\text{C}$  and then roasted in a tubular resistance furnace at  $900^\circ\text{C}$ , marked with RGO.

### Preparation of Pd-PDDA/RGO

The PDDA functionalized RGO used as supports for the formation of Pd-PDDA/RGO catalyst were prepared by two steps: firstly, preparation of PDDA/RGO. 30 mg RGO and 1.5 mL 20 wt % PDDA were mixed in 30 mL ethanol-water solution (1:1, v/v ratio) and ultrasonic treatment at  $25^\circ\text{C}$ , pH of the solution was adjust to 9–10 with 0.5 M NaOH solution [26,32]. Then the mixture was centrifuged and washed to remove redundant PDDA, dried at  $60^\circ\text{C}$  for 24 h in a vacuum oven. Secondly,

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