



# Palladium nanoparticle catalysts synthesis on graphene in sodium dodecyl sulfate for oxygen reduction reaction



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## ABSTRACT

We prepare large areas of graphene on carbon paper from graphite powder and anionic surfactant, assisted electrochemical exfoliation as previous work. Using a four-point probe technique, we found the conductivity of graphene on carbon paper to be  $66 \text{ mS cm}^{-1}$ , which is approximately 1.2 and 1.65 times better than that of graphite coated carbon paper and carbon paper. Then palladium is electro-reduced onto the carbon paper based electrodes (with or without graphene) in absence or presence of different concentrations of sodium dodecyl sulfate (SDS), that are used in oxygen reduction reaction (ORR) for direct methanol fuel cells. The electrochemically reduced Pd is carefully characterized by scanning electron microscopy (SEM). Their electrochemical properties are investigated with cyclic voltammetry, linear sweep voltammetry, and electrochemical impedance spectroscopy. Particularly, SEM images show that the size of the nanoparticles decreases from 1000 to 70 nm as SDS concentration increases from 0 to 14 mM. The catalytic activities of graphene-supported Pd nanoparticles and Pd-carbon paper electro-catalysts for ORR are 112 and  $2 \text{ Ag}^{-1} \text{ Pd}$ , which can reveal the particular properties of the exfoliated graphene supports and SDS media.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) hope to be the future energy technology for transportation and portable devices [1,2]. In fuel cells, one of the challenging areas is to find non-platinum catalysts for oxygen reduction reaction (ORR) that allow high efficiency and durability [3]. Direct methanol fuel cell (DMFC) cathodes have the problem of requiring high cost catalysts and their degradation because of methanol crossover [4]. Thus, Pd and Pd-based alloy nanoparticles (NPs) might be promising candidates for the ORR in DMFC cathode, not only because of lower costs and more abundance but also because of the high tolerance observed for the Pd toward methanol oxidation [5]. Nano-structured materials have a large surface area and usually exhibit high surface concentrations of edges, corners, defect sites, and other uncommon structural characteristics, and much attention has thus been given to the fabrication and characterization of metal NPs for applications in catalysis [6]. Currently, Pt NP and Vulcan XC-72 carbon black (C) are the state-of-the-art catalyst and catalyst support materials respectively; but the durability of Pt/C electrocatalyst, during

extended operation and repeated cycling (e.g., automotive applications), needs significant improvement [7].

A great deal of attention was paid to the use of graphene as supporting matrixes for the immobilization of catalytically active noble metal NPs. Graphene is a two-dimensional single-layer sheet of graphite with p-electrons fully delocalized on the graphitic plane. It is highly conductive and mechanically strong and has been found for molecular electronic device, energy storage, fuel cell and catalytic applications [8]. In catalytic studies, graphene is often used as a support, and its close contact with catalysts is believed to play an important role in increasing the catalytic activity. In recent years, some researchers have attempted to investigate the hybrid material based on graphene for ORR and methanol oxidation. It has been shown in the Pt (or Pd)-based NP catalysts grown on graphene for electro-catalytic reactions [9] and in the activation of FePt and Palladium NPs by graphene for ORR in  $\text{HClO}_4$  media [10] and highly active ORR in an alkaline solution [11]. Shao and co-workers report graphene nanoplatelets (GNPs), which exhibit the advantages of both single-layer graphene and highly graphitic carbon, as a durable alternative support material for Pt NPs for ORR in fuel cells [12]. Zhuang et al. [13] investigated a novel one-step method for biocathode fabrication in microbial fuel cell (MFC), which graphene/biofilm composites could enhance the electro-catalytic activity toward ORR and facilitate the electron transfer between bacteria and electrode. Zhang et al. [14] studied the catalytic

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activity of manganese oxide (MnOx)–graphene for ORR in KOH solution. In a similar work [15] MnO<sub>2</sub>/reduced graphene oxide (RGO) composites were synthesized by an easy and effective polymer-assisted chemical reduction method. Nam et al. [16] prepared hexadecyl trimethyl ammonium bromide (CTAB)-functionalized graphene as a carbon support for Pt or PtCo NPs catalysts for fuel cell cathodes.

Different methods have been carried out to obtain graphene sheets such as, epitaxial growth by ultra high vacuum graphitization [17], chemical vapor deposition [18], chemical oxidation of graphite, further reduction [19], and solvothermal synthesis with pyrolysis [20]. Electrochemical techniques are alternatively used to produce graphene flakes because they are simple, economic, undestructive, environment friendly, operate at ambient temperature and pressure, and provide thickness control by adjusting the electrode potential. In recent years, some researchers have attempted to produce graphene sheets by using electrochemical methods [21–23].

Also, electrochemical depositional techniques are often reported as the simple and low-cost methods of choice for nanostructuring and nanopatterning of electrode surfaces. Started the process of metal deposition on metal electrodes through atomic layer-by-layer, with monolayers under-potentially deposited occurs [6]. In fact, metal NPs can be electrochemically deposited on to carbon supports by applying short potential pulses to initiate the creation of metal nucleation centers, the size of which can be controlled by adjusting the length, number, and amplitude of the potential pulses [24]. The enhancement of surface catalytic activity by the metal-support interaction as well as the large surface area achieved with low-loading levels makes such a system attractive for electrochemical application. The objective of our work is to use the electro-deposition method to disperse small palladium particles on graphene sheets, which were previously electrosynthesized on a carbon paper electrode from an aqueous acid solution. This kind of modification typically concerns the insertion of small Pd particles into the graphene film after the production process. Thus, the graphene film is expected to have a highly porous structure for ORR in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH. To reach this goal, we prepared the graphene nanosheets in the presence of surfactant (sodium dodecyl sulfate) and graphite powder with cyclic voltammetry (CV) [25]. Surfactants in solution spontaneously aggregate at solid–liquid interfaces due to surface forces (i.e., electrostatic interaction between the surfactant headgroup and the surface charge). After being Pd synthesis at various concentration of surfactant, the Pd NPs are characterized by scanning electron microscopy (SEM), CV, electrochemical polarization measurement, and electrochemical impedance spectroscopy (EIS).

## 2. Experimental

### 2.1. Preparation of graphene

Electrochemical reduction of graphene was performed on carbon paper by CV technique in a potential range from 0.22 to –1.38 V vs, RHE (reference hydrogen electrode) at 50 mV s<sup>–1</sup> for 100 cycles in mixture containing graphite (Merck) (5 mg/ml), sodium dodecyl sulfate (SDS) (14 mM) (Fluka), and water with magnetic stirring. Experiment was carried out at 50 °C and saturated with N<sub>2</sub> [25]. The SEM has been published and described in the earlier article [25].

### 2.2. Synthesis of Pd–graphene and Pd–carbon paper electrodes

Pd particles were electrodeposited on the surface of Carbon paper (a) or graphene coated on carbon paper (b, c, d and e) electrodes from 6 mM PdCl<sub>2</sub> and different concentration of SDS (0, 4,

8.1, and 14 mM) solution with chronoamperometry at –0.25 V relative to Ag|AgCl for 400 s. Thus, to study the effects of SDS concentration, 5 electrodes were studied in the present work. The experimental conditions of these electrodes are reported in Table 1. The palladium loadings on Pd–Graphenes and Pd–Carbon paper were estimated from the charge consumed during the sweep provided (assuming a 100% current efficiency) [26].

### 2.3. Electrochemical characterization

The electrochemical measurements were performed using a potentiostat–galvanostat. A three-electrode cell was employed in all experiments with a Pt counter electrode, Ag|AgCl, KCl, 3 M as reference electrode, and carbon paper or glassy carbon with the Pd nanostructure as working electrode. The CV was carried out in a potential window between –0.2 and 1.1 V vs. Ag|AgCl and glassy carbon modified with graphene and Pd nanostructure as working electrode (geometric area 0.031415 cm<sup>2</sup>) in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH at a scan rate of 50 mV s<sup>–1</sup> in N<sub>2</sub> saturated for 15 min.

The ORR was investigated at the gas diffusion electrode (GDE) with geometric exposed area of 1 cm<sup>2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH. All measurements were performed at 25 °C with flowing oxygen in a conventional three-electrode cell [27–29]. The temperature of the cell is controlled by flowing heated/cooled water through the jacket of the electrochemical cell by a circular water bath. The GDEs were mounted onto a Teflon holder containing a high pyrolytic graphite disk as a current collector and oxygen feed from the back of the electrode. An Ag|AgCl reference electrode was placed close to the working electrode surface. However, all potentials were calculated with respect to the measured reversible hydrogen potential and a Pt wire was used as counter electrode. The electrochemical cell was connected to a potentiostat–galvanostat for *I*–*V* polarization measurements, and to a frequency response. The linear sweep voltammogram (LSV) measurement was recorded at 1 mV s<sup>–1</sup>. Prior to LSV and EIS experiments, oxygen purged solutions at the back of the electrode at a rate of 30 ml min<sup>–1</sup>. EIS measurement was carried out at 0.5 V relative to RHE.

### 2.4. Comparison with the previous works

Hsieh and coworkers [30] dispersed nanostructured palladium on graphene nanosheets using a pulse microwave-assisted polyol (MP) synthesis approach at different pH values of 7, 9, and 11. Kim et al. [31] studied the graphene supported palladium or platinum in alkaline media for ORR. These authors [30,31] deposited the palladium particles in different ways and prepared graphene by a different method. Other words, graphene nanosheets have been synthesized by Hummer method and so the synthesis process cannot be scaled up to large area.

In present paper, graphene was prepared on carbon paper by CV technique in mixture containing graphite, sodium dodecyl sulfate (SDS) and water with magnetic stirring. Experiment was carried out at 50 °C and saturated with N<sub>2</sub> as published in earlier work [25],

**Table 1**

The experimental conditions of electrodes, consuming charges, particle size and Pd loadings.

Electrodes	SDS conc./mM	Graphene	Q/mC consumption	Pd particle size/nm	Pd loading/μg cm <sup>–2</sup>
a	0	–	8.1	900–1000	142.3
b	0	+	5.95	500–700	104.52
c	4	+	4.58	196–500	80.46
d	8.1	+	3.95	96–126	69.5
e	14	+	3.41	73–75	59.9

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