



# Electroreduction of oxygen on palladium nanoparticles supported on nitrogen-doped graphene nanosheets



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## ARTICLE INFO

### Article history:

Received 2 May 2014

Received in revised form 31 May 2014

Accepted 4 June 2014

Available online 10 June 2014

### Keywords:

Oxygen reduction

Pd-based catalysts

Pd nanoparticles

Nitrogen-doped graphene

## ABSTRACT

The electrochemical reduction of oxygen on Pd nanoparticle-decorated nitrogen-doped graphene (Pd/NG) catalyst has been investigated in acid and alkaline solutions using the rotating disk electrode (RDE) method. The Pd/NG nanocomposites were prepared by NaBH<sub>4</sub> reduction. The surface characterisation of Pd/NG composites was performed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The TEM images showed the uniform distribution of Pd nanoparticles over the N-doped graphene nanosheets. The RDE results indicated that Pd/NG catalysts possess a high electrocatalytic activity towards the oxygen reduction reaction (ORR). The prepared materials catalyse a 4-electron reduction of oxygen. The Tafel behaviour of O<sub>2</sub> reduction on Pd/NG catalysts was similar to that of bare Pd. The Pd/NG composite showed excellent ORR performance in alkaline media and is a promising material to be used as a cathode catalyst for alkaline membrane fuel cells.

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## 1. Introduction

Due to its large surface area and the high electrical conductivity graphene is being used more frequently for electrochemical applications [1,2]. In the area of electrocatalysis, graphene-based two-dimensional nanostructures have a great potential as support materials for catalysts and a great number of graphene supported noble metal nanoparticles have been developed for various electrocatalysis purposes [3,4], including oxygen reduction [5,6].

Graphene exhibits several advantages over carbon nanotubes, such as lower cost, larger surface area and more simple preparation. Very important advantage is that graphene synthesised from graphite powder does not contain metallic impurities, which can alter electrochemical properties of carbon nanotubes [7,8]. Number of theoretical and experimental investigations has shown that doping graphene with nitrogen, sulphur, boron or other heteroatoms can modify the physical and chemical properties of graphene and open its new potential applications in scientific

and technological fields [9–11]. Doping of graphene with nitrogen atoms is known to result in tunable chemical and physical properties [12] due to conjugation between the nitrogen lone-pair electrons and the graphene  $\pi$ -system. In electrocatalysis, N-doping improves electrical conductivity of materials, as chemically synthesised graphene usually has comparatively low electrical conductivity [13]. Furthermore, N-doping accelerates the growth of nanoparticles on graphene substrate and enhances the catalytic activity of composite materials [14]. Different techniques have been employed for the synthesis of nitrogen-doped graphene sheets. N-doped graphene is traditionally synthesised by chemical vapour deposition [10], annealing of graphite oxide with nitrogen-containing compounds [15] and NH<sub>3</sub> [16] and by nitrogen plasma treatment of graphene [17,18]. Zhou et al. demonstrated that growing Pt and Pt alloy nanoparticles on N-doped graphene has more advantages, such as formation of uniform dispersion, different morphology and smaller size nanoparticles [19]. Doping carbon supports with nitrogen also leads to increased stability of catalyst materials, since it results in a better adhesion between support and metal nanoparticle that prevents the removal of catalyst from the support surface and its subsequent agglomeration [20]. It has been reported that N-doping introduces disorders in the graphene stacking and these disordered and defect structures act as good

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anchoring sites for deposition of Pt particles [21]. The higher the amount of N atoms and the closer they are to the C atom which bonds directly to the Pt metal, the stronger the binding energy [22].

Palladium is a promising alternative to the costly Pt for fuel cell applications [23,24]. Since Pd is considerably cheaper than rare platinum and its electrocatalytic activity and stability is much higher than that of other 3d transition metals (for example Ni, Co and Fe), the incorporation of Pd nanoparticles into high surface area carbon support matrix can result a promising fuel cell cathode catalyst material. Recently, an attempt has been made to attach Pd nanoparticles onto the surface of N-doped graphene [25]. It was found that single Pd atoms embedded into divacancies of graphene are promising candidates for use in fuel cell cathodes for oxygen reduction reaction (ORR) [26]. Vinayan et al. succeeded to develop a facile synthesis method for electroactive and relatively stable in acid solution triangular Pd nanoparticles anchored onto N-doped graphene with controlled growth [27].

In the present work N-doped graphene was synthesised by pyrolysis of graphite oxide in the presence of dicyandiamide as nitrogen precursor. Nitrogen-doped graphene nanosheets were further modified with Pd nanoparticles prepared by borohydride reduction. Transmission electron microscopy and X-ray photoelectron spectroscopy were utilised to study the size and distribution of Pd nanoparticles on substrate surface and the type of nitrogen groups present in the N-doped graphene (NG) sheets. The electrocatalytic activity of Pd/NG catalysts for ORR in acid and alkaline solutions was investigated using the rotating disk electrode technique.

## 2. Experimental

### 2.1. Synthesis of N-doped graphene and Pd/NG catalysts

Graphene oxide (GO) used in this work was synthesised from graphite powder (Graphite Trading Company) by a modified Hummers' method as described elsewhere [28]. Dicyandiamide (DCDA) was purchased from Aldrich and used as a precursor for nitrogen doping. Briefly, GO was dispersed in deionised water and ethanol (3:1) solution with the aid of ultrasonic agitation. Nitrogen precursor was added to form GO/DCDA mixture with ratio of 1/20. Small amount of polyvinyl pyrrolidone was added to reaction media and mixture was sonicated for 2 h. The resulting mixture was dried at 75 °C in vacuum. Subsequent pyrolysis of the prepared material was performed in flowing argon at 800 °C for 2 h.

Anchoring of Pd nanoparticles (PdNPs) to N-doped graphene (NG) nanosheets was performed using the following procedure. First 0.1 g of PdCl<sub>2</sub> (Aldrich) with 0.1 mL of concentrated HCl was added to 60 mg of NG dispersed in 60 mL of deionised water. The suspension was sonicated for 15 min and then 0.021 g of NaBH<sub>4</sub> was added during agitation. The suspension was sonicated for additional 15 min, filtered and washed with ethanol solution. The resulting powder was dried at 60 °C for 2 h. Pd nanoparticles were distributed over N-doped graphene nanosheets and the prepared catalyst materials were designated as Pd/NG.

### 2.2. Surface and electrochemical characterisation of Pd/NG catalysts

Surface morphology and composition studies of the prepared electrodes were performed using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). TEM measurements were performed on a Tecnai 12 instrument operated at a 120 kV accelerating voltage. The samples were prepared by depositing diluted ethanol solution of the catalyst material on holey carbon grids (Agar Scientific, 300 mesh Cu). The XPS

measurements were carried out with a SCIENTA SES-100 spectrometer using nonmonochromatised Al K $\alpha$  X-ray radiation (1486.6 eV), a take-off angle of 90° and a source power of 400 W. The pressure in the analysis chamber was less than 10<sup>-9</sup> Torr. For collecting the survey scan, the following parameters were used: energy range 600–0 eV, pass energy 200 eV, and step size 0.5 eV. In specific regions, high-resolution scans were performed with the pass energy of 200 eV and the 0.1 eV steps.

The rotating disk electrode (RDE) method was employed for O<sub>2</sub> reduction measurements at various electrode rotation rates ( $\omega$ ). The RDE setup has CTV101 speed control unit and EDI101 rotator (Radiometer). Electrochemical measurements were carried out in 0.1 M KOH (p.a. quality, Merck) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (Suprapur, Merck) solutions. Electrolytes were saturated with O<sub>2</sub> (99.999%, AGA) or Ar (99.999%, AGA). A counter electrode was Pt wire and all the potentials are referred to reversible hydrogen electrode (RHE). The potential was applied by Autolab potentiostat PGSTAT30 (EcoChemie B.V., The Netherlands) and General Purpose Electrochemical System (GPES) software was used to control the experiments.

Glassy carbon (GC) disks with geometric area (*A*) of 0.126 cm<sup>2</sup> in a Teflon holder were polished to a mirror finish with 1 and 0.3  $\mu$ m alumina slurries (Buehler) and were sonicated in 2-propanol and Milli-Q water for 5 min in each solvent. The GC disk electrodes were modified by drop-casting of 8  $\mu$ L Pd/NG suspension in 2-propanol (1 mg mL<sup>-1</sup>) and catalyst ink was dried in air. Afterwards 5  $\mu$ L of 0.5% Nafion solution in ethanol was pipetted onto the modified electrode surface. The Pd loading was 32  $\mu$ g cm<sup>-2</sup> per geometric GC area. For comparison the reduction of O<sub>2</sub> was also studied on NG catalyst deposited on GC and bulk Pd electrode. Bulk Pd electrodes (*A* = 0.196 cm<sup>2</sup>) were prepared by mounting Pd (99.95%, Alfa Aesar) disks into Teflon holders. The Pd disk electrode was polished with 1.0, 0.3 and 0.05  $\mu$ m alumina slurry. After alumina polishing, the electrodes were sonicated in Milli-Q water for 5 min.

## 3. Results and discussion

### 3.1. Surface characterisation of Pd/NG samples

Graphene-based materials are interesting supports for electrocatalysis because of their high surface area and high conductivity. However, graphene is susceptible for stacking induced by  $\pi$ - $\pi$  interactions between the nanosheets and this reduces surface area and may even prevent mass transfer of reactants to the active sites on the catalyst surface. TEM measurements were performed in order to obtain information about the surface morphology of the prepared Pd/NG catalysts. Transparent corrugated flake-shaped sheets characteristic for few-layered graphene are observed revealing a high exfoliation degree. No evidence of agglomeration of NG flakes is observed. Pd nanoparticles deposited on the micron-sized NG support are visible in Fig. 1a. The TEM images show a good dispersion of Pd nanoparticles on the support surface and the average size of the PdNPs is 2.6  $\pm$  0.7 nm (Fig. 1b) indicating successful synthesis. To determine the particle size, 250 isolated particles were measured.

X-ray photoelectron spectroscopy was used to identify chemical state of nitrogen species. The XPS survey spectrum showed O1s, N1s, C1s and Pd3d peaks for Pd/NG sample (Fig. 1c). Fig. 1c shows the main peak of C1s at 284.5 eV, which corresponds to sp<sup>2</sup> carbon. As suggested in previous studies, the smaller peaks formed at 285.6 eV and 287.2 eV correspond to the formation of N-sp<sup>2</sup> C and N-sp<sup>3</sup> C bonds [10] or be due to the formation of C-OH and C=O bonds [28]. Four different types of nitrogen species can be seen in inset N1s spectra. Namely, pyridinic-N at binding energy of 397.8 eV prevails on the surface, peak shoulder between 399 and 400 eV corresponds

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