



# Platinum nanoparticles supported on nitrobenzene-functionalised graphene nanosheets as electrocatalysts for oxygen reduction reaction in alkaline media



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## ABSTRACT

A systematic study on the electrocatalytic properties of Pt nanoparticles supported on nitrobenzene-modified graphene (Pt-NB/G) as catalyst for oxygen reduction reaction (ORR) in alkaline solution was performed. Graphene nanosheets were spontaneously grafted with nitrophenyl groups using 4-nitrobenzenediazonium salt. The electrocatalytic activity towards the ORR and stability of the prepared catalysts in 0.1 M KOH solution have been studied and compared with that of the commercial Pt/C catalyst. The results obtained show that the NB-modified graphene nanosheets can be good Pt catalyst support with high stability and excellent electrocatalytic properties. The specific activity of Pt-NB/G for O<sub>2</sub> reduction was 0.184 mA cm<sup>-2</sup>, which is very close to that obtained for commercial 20 wt% Pt/C catalyst (0.214 mA cm<sup>-2</sup>) at 0.9 V vs. RHE. The Pt-NB/G hybrid material promotes a four-electron reduction of oxygen and can be used as a promising cathode catalyst in alkaline fuel cells.

## 1. Introduction

Graphene-based nanomaterials are promising electrocatalyst supports for oxygen reduction reaction (ORR) due to the high electrical conductivity, large specific surface area and abundant functional groups present on graphene surface [1–6]. Pt nanoparticles (PtNPs) supported on various graphene materials have shown a high electrocatalytic activity for ORR [7,8]. The functionalisation of catalyst support materials is essential to obtain better electrochemical properties and good stability. It has been demonstrated that heteroatom doping prevents the aggregation and greatly improves the distribution of platinum nanoparticles on graphene support [9,10]. Various heteroatom-doped graphene materials have been used as supports for Pt-based ORR electrocatalysts [9–14]. The electronic interaction between the heteroatom-doped nanocarbon materials and Pt clusters appears to be the main factor for improved electrocatalytic activity towards the ORR [15–17]. Nitrogen-doped graphene supported Pt nanoparticles were employed as a cathode catalyst in polymer electrolyte fuel cells [18].

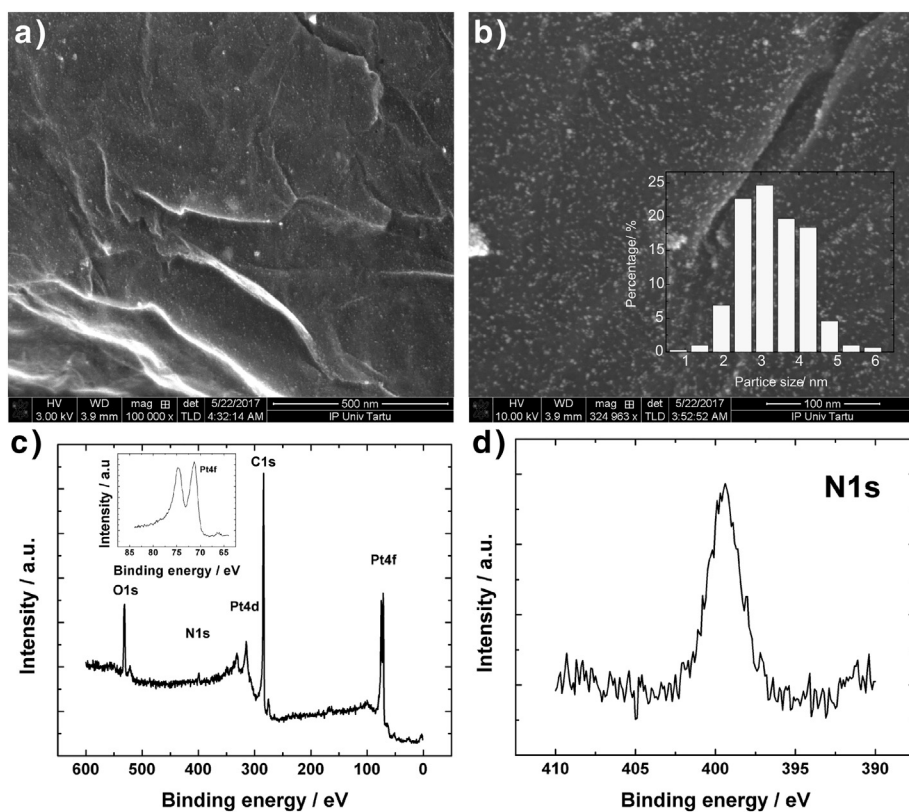
The chemical modification of graphene is a stable alternative that has yet to be thoroughly studied. The utilisation of surface thiol and amine groups to attach PtNPs on carbon supports is a promising

approach to enhance the durability and activity of electrocatalysts [19,20]. An attractive approach is the covalent functionalisation of various carbon materials by diazonium chemistry [21]. The reduction of aryldiazonium salts is a versatile method to obtain a strong covalent bond with carbon support [22]. Commercially available 4-nitrobenzenediazonium salt (NBD) has been frequently utilised for attaching nitrophenyl (NP) groups on different substrate materials by diazonium reduction [23]. NP groups can be further reduced to amino groups to form an important linkage for attachment of metal nanoparticles. NP groups can be covalently bound to carbon surface via electrochemical or spontaneous grafting of NBD. The spontaneous grafting has proven to be very simple and useful method for surface modification of graphene nanosheets [24].

Recently we have explored O<sub>2</sub> reduction on Pt catalysts deposited on N-doped graphene [25]. This paper reports a systematic study on the electrocatalytic properties of Pt nanoparticles supported on nitrobenzene-modified graphene sheets as catalyst for ORR in alkaline media. The catalyst support was modified by spontaneous grafting of 4-nitrobenzenediazonium salt. The electrocatalytic activity towards the ORR and stability of the prepared catalysts in 0.1 M KOH solution have been studied and compared with that of the commercial Pt/C catalyst.

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**Fig. 1.** SEM images of Pt-NB/G modified GC electrodes (a and b); Inset of 1b: Pt particle size distribution in Pt-NB/G catalyst; (c) XPS survey spectra for Pt-NB/G sample; Inset of 1c shows Pt4f spectra; (d) The XPS core-level spectrum in the N1s region.

## 2. Experimental

Graphene nanoplatelets ( $S_{\text{BET}} = 750 \text{ m}^2 \text{ g}^{-1}$ , oxygen content of < 2 wt% and carbon content of > 98 wt%) purchased from Strem Chemicals were stirred in 10 mM 4-nitrobenzenediazonium tetrafluoroborate (Sigma-Aldrich) aqueous solution for 30 min, filtered and dried in air. Further decoration of nitrobenzene (NB)-modified graphene nanosheets by Pt nanoparticles was performed using a simple ethylene glycol method described elsewhere [26], yielding a 20 wt% Pt catalyst supported on NB-graphene (Pt-NB/G). For comparison, Pt electrocatalyst on NB-modified Vulcan carbon XC-72R (Cabot Corp.) was also prepared (Pt-NB/C).

For preparation of catalyst ink 10 mg of Pt-NB/G was suspended in 2 mL of 0.5 wt% Nafion (Aldrich) solution in ethanol by sonication for 15 min. 4  $\mu\text{L}$  of the suspension was transferred to the polished glassy carbon electrode surface by pipetting and dried for 5 min at 60 °C.

Cyclic voltammetry (CV) and rotating disk electrode (RDE) tests were carried out in a three-electrode glass cell using an Autolab potentiostat/galvanostat PGSTAT30 (Metrohm-Autolab, The Netherlands). Reversible hydrogen electrode (RHE) was used as a reference electrode and Pt foil as a counter electrode. The glassy carbon (GC) disk electrode coated with catalyst ink served as working electrode. GC disks (GC-20SS, Tokai Carbon) with geometric area ( $A$ ) of 0.196  $\text{cm}^2$  were pressed into a Teflon holder and were polished to a mirror finish with 1 and 0.3  $\mu\text{m}$  alumina slurries (Buehler), followed by sonication in Milli-Q water for 5 min.

Electrochemical experiments were performed in 0.1 M KOH (p.a., Merck) solution saturated with Ar (99.999%, AGA) or  $\text{O}_2$  gas (99.999%, AGA). The RDE measurements were carried out at various electrode rotation rates ( $\omega$ ) using RDE setup with CTV101 speed control unit and EDI101 rotator (Radiometer). The RDE results of  $\text{O}_2$  reduction were compared with those obtained with commercial 20 wt% Pt/C (E-TEK) and bulk Pt electrodes (99.95%, Alfa Aesar). The Pt disk electrode ( $A = 0.196 \text{ cm}^2$ ) was finally polished with 0.05  $\mu\text{m}$  alumina slurry. The scan rate ( $\nu$ ) used for the oxygen reduction measurements was

10  $\text{mV s}^{-1}$ . For durability testing 2000 potential cycles were applied at 50  $\text{mV s}^{-1}$  between 0.05 and 1.1 V vs RHE.

Surface morphology and composition of the Pt-NB/G catalyst material was studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM imaging was performed on Helios™ NanoLab 600 (FEI) instrument. The XPS measurements were carried out with a SCIENTA SES-100 spectrometer using non-monochromatised Al K $\alpha$  X-ray source (1486.6 eV), a take-off angle of 90° and a source power of 400 W. The pressure in the analysis chamber was <  $10^{-9}$  Torr. For collecting the survey spectra, 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.

## 3. Results and discussion

### 3.1. Surface characterisation

SEM images of Pt-NB/G samples are shown in Fig. 1a and b. Inset to Fig. 1b presents a size distribution for 300 Pt particles analysed and calculated. Pt nanoparticles of  $3.6 \pm 0.8 \text{ nm}$  are observed and they are uniformly dispersed over NB-modified graphene support. The catalyst surface composition was examined by XPS. Fig. 1c displays the XPS survey spectra for Pt-NB/G catalyst sample, showing the peaks of Pt, C, N and O. Platinum is in the zero-valent state (see inset to Fig. 1c) and the binding energy of N1s corresponds to amino functionality (399.7 eV), which is formed by the reduction of nitro groups. The XPS core-level spectrum in the N1s region is shown in Fig. 1d and only a single type of N is present.

### 3.2. Electrochemical characterisation

Fig. 2a shows typical CVs recorded for all the electrodes studied. Cyclic voltammograms of the prepared catalyst look similar to the CVs of bulk Pt electrodes. The charge integrated under the hydrogen

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