



## Functionalization of multiwall carbon nanotubes with nitrogen containing polyelectrolyte by a simple method

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### ABSTRACT

Commercially available multiwall carbon nanotubes (MWCNTs) have been functionalized with poly (diallyl dimethylammonium) chloride (PDDA), a nitrogen containing polyelectrolyte by a simple on-off ultrasonication method. The results obtained from Raman and X-ray photoelectron spectroscopy (XPS) studies confirm the functionalization of MWCNTs with PDDA. An up- shift in the positions of C1s XPS peak and a down-shift in the positions of the N1s XPS peak, has been observed along with an up-shift in the G-peak position in the Raman spectra, which suggest the occurrence of inter-molecular charge transfer from carbon atoms in MWCNTs to N<sup>+</sup> centres in PDDA. The preliminary linear sweep voltammetry (LSV) results show good electrocatalytic activity of MWCNTs functionalized with nitrogen containing polyelectrolyte, which is comparable to the results with platinum based electrodes. Thus, MWCNTs non-covalently functionalized with a nitrogen containing polyelectrolyte (PDDA) by a simple on-off ultrasonication method could be advantageous for developing efficient metal-free electrocatalysts for the oxygen reduction reaction (ORR).

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## 1. Introduction

The activity of cathode in the oxygen reduction reaction (ORR) is very important for the commercialization of fuel cells. The lower activity of this reaction at the cathode necessitates the use of costly noble metals (such as platinum) as electrocatalysts, which make them commercially unviable. Platinum is generally used to reduce oxygen from air at the cathode. ORR is a multi-electron reaction which occurs either by a four-electron pathway or, by a two-electron pathway, with hydrogen peroxide as an intermediate product. The platinum based electrocatalysts being used at present are not viable due to their high cost along with the problem of carbon monoxide (CO) poisoning, and methanol crossover [1]. The efforts made by several research groups to understand the ORR

activity and to develop efficient electrocatalysts are still based on platinum [2–4]. Although they are highly efficient, yet their aforementioned problems limit their commercial use. Non-noble metal electrocatalysts have also been reported but the limitations like poor durability, high cost and undesirable side products limit their usefulness [5].

With the advent of nanotechnology, there have been reports on the development of metal-free electrocatalysts based on carbon nanomaterials (carbon nanotubes, graphene, nanofibers etc.) [6–12]. The electrochemical properties of these metal-free electrocatalysts have been reported to be comparable to the commercial platinum based electrocatalysts. As the carbon nanomaterials are generally corrosion resistant so they can be suitable candidates for use as metal-free electrocatalysts over the conventional metal based electrocatalysts. Recently, multiwall carbon nanotubes (MWCNTs) functionalized with a polyelectrolyte have been reported to facilitate the ORR catalytic activity [13,14]. The spectroscopic analysis by XPS and photoacoustic Fourier transform infrared spectroscopy (PA-FTIR) studies revealed the presence of  $\pi$ - $\pi$  stacking interactions between PDDA and MWCNTs [15]. The

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enhancement in ORR activity in nitrogen-doped carbon nanomaterials is generally explained to be due to electronegativity difference between nitrogen (3.04) and carbon (2.55) atoms in the graphitic-carbon network and it results in polarization of neighbouring carbon atoms. The presence of a strong electron-withdrawing group ( $N^+$ ) in PDDA creates net positive charge on the carbon atoms in the MWCNTs plane due to the inter-molecular charge transfer process. The positively charged carbon atoms can then readily attract electrons from the anode of fuel cell, and enhance the ORR activity. Carbon nanomaterials functionalized with nitrogen containing groups or doped with nitrogen hetero-atoms have been reported to be very efficient for the ORR activity [16–24]. As the ORR catalytic activity also depends upon the nature of nitrogen species as well as on the nitrogen content so an optimum amount of nitrogen is required for high ORR activity. A comparison of the structural, textural and compositional features of the nitrogen doped carbon nanofibers has already been reported [25]. It has been observed that incorporating nitrogen atoms into carbon nanofibers could lead to an easier  $O_2$  adsorption and higher activity for the  $H_2O_2$  decomposition. The high surface area mesoporous nitrogen doped carbons made from ionic liquids and nucleobases have also been reported to show efficient ORR [26]. Besides nitrogen, in-situ doping or functionalization of carbon nanomaterials with various other hetero-atoms such as P, S, I, B and Se has also been reported to show higher electrocatalytic activity and long term stability in fuel cells [27–34].

Recently, electrocatalysts based on vertically aligned nitrogen doped CNTs (VA-NCNTs) have been reported to exhibit a four-electron ORR process with higher electrocatalytic activity, lower overpotential, smaller crossover effect and an enhanced stability as compared to the commercial platinum based electrodes [13,17]. The electrocatalytic activity of the VA-NCNTs based electrodes has been found to be insensitive to the CO poisoning, even up to 10 wt% CO in hydrogen whereas conventional platinum based electrodes were rapidly poisoned under identical conditions. The vertically aligned MWCNTs were used in that study [13,17], whereas commercial CNTs are generally available in the non-aligned form. For the commercial use of these electrocatalysts there is a strong reason to develop a simpler approach for the synthesis of electrocatalysts based on pristine carbon nanomaterials with no need for any post treatment.

With this aim, we used a very simple and easily available on-off ultrasonication method for the non-covalent functionalization of commercial (as available) MWCNTs (non-aligned) with PDDA. The same samples were also prepared by magnetic stirring method for the comparison purposes. The functionalization of MWCNTs with PDDA has been studied by XPS and Raman studies. The electrochemical properties have been studied by LSV using a rotating disc electrode (RDE).

## 2. Materials and Methods

### 2.1. Materials

MWCNTs (CNT M95, Carbon Nano-material Technology Co. Ltd., South Korea) with average diameter of the order of 5–15 nm, length 10  $\mu m$  with > 95% purity, and PDDA (Sigma Aldrich) have been used as received in the present study.

#### 2.1.1. Non-covalent functionalization of MWCNTs with PDDA

MWCNTs have been non-covalently functionalized by using two different methods. One set of samples has been prepared by an on-off ultra-sonication method (S1) and the second set by magnetic stirring method (R1). For both the samples, chemical precursors have been taken in the same ratio and the same

procedure was followed except that they were prepared using different methodologies. Pristine MWCNTs (P) sample has also been studied for comparison purposes.

**2.1.1.1. Preparation of S1.** Sample S1 was prepared by taking 40 mg of MWCNTs and 0.5 mL of PDDA in a conical flask. To this mixture, 20 mL of deionized (DI) water was added. It was ultrasonicated for 30 min (5 min on-off basis) at room temperature for its homogeneous mixing. The mixture was then given multiple washings (5 times) by centrifuging it at 5000 rpm for 10 min and was finally retrieved by drying it overnight in an oven at 60 °C.

**2.1.1.2. Preparation of R1.** Sample R1 was prepared by taking 40 mg of MWCNTs and 0.5 mL of PDDA in a conical flask. 20 mL of DI water was added to this mixture. The solution was then stirred using a magnetic stirrer for 30 min at room temperature. It was then given multiple washings (5 times) by centrifuging it at 5000 rpm for 10 min each. The sample was finally retrieved by drying it overnight in an oven at 60°C.

### 2.2. Methods

#### 2.2.1. Measurements of Raman and XPS

Raman spectroscopy studies were carried out at room temperature using a FRA 106/S (BRUKER OPTIK GMBH, Ettlingen, Germany) Raman spectrometer, with a 1006 nm Nd-YAG laser and a 4  $cm^{-1}$  resolution. XPS measurements were performed on a VG Microtech ESCALAB 201 using a monochromatic Al X-ray source (Mg (1253.6 eV)/Al (1486.6 eV), 0.5 eV).

#### 2.2.2. Electrochemical measurements

Electrochemical measurements were performed using a computer-controlled potentiostat (Bio-Logic SP-150, France) with a typical three-electrode cell. A platinum wire was used as counter electrode and Ag/AgCl/3.0 M NaCl (RE-1B, ALS Co., Ltd., Japan) as reference electrode. All the experiments were conducted at room temperature ( $25 \pm 1^\circ C$ ). The electrodes for electrochemical measurements in the three-electrode system were prepared by introducing a predetermined amount of various samples (P, R1, S1, Pt/C) in ethanol (1 mg  $mL^{-1}$ ), loading 10  $\mu L$  of the MWCNTs/ethanol solution on to the surface of a pre-polished glassy carbon electrode (GCE) and dropping 5  $\mu L$  of nafion dispersion (Dupont, USA) in isopropanol (0.5 wt%) as binder. LSV curves of ORR on GCE in  $O_2^-$  saturated 0.1 M KOH solutions were recorded at a scan rate of 10  $mV s^{-1}$ . All potentials in the text are represented based on Ag/AgCl/sat' KCl. The commercially available 60 wt% Pt/C (HiSPEC 6000), which is used as a reference in the present study was purchased from Johnson Matthey.

## 3. Results and discussion

The pristine MWCNTs (P), and MWCNTs functionalized with PDDA by using on-off ultra-sonication (S1) and magnetic stirring (R1) methods have been studied. The functionalization has been characterised by XPS and Raman studies.

XPS spectra have been recorded in the full binding energy (B.E.) range but as the B.E. values for C and N are widely different, so the spectrum for each atom has been plotted in the relevant narrow B.E. range. The XPS spectra in the narrow B.E. range for C1s peak are shown in Fig. 1 for the samples P, S1 and R1, and the peak B.E. values for these samples are 284.45, 284.5 and 284.5 eV, respectively. As most of the XPS peaks are not symmetrical so curve fitting (not done in the present case) may help to determine the peak positions more accurately. The relatively higher intensity of C1s peak for sample P is due to the absence of any functional

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