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Defect-induced Catalysis toward the Oxygen Reduction Reaction in Single-walled Carbon Nanotube: Nitrogen doped and Non-nitrogen doped

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) are post-treated by argon (Ar) or ammonia (NH_3) plasma irradiation to introduce defects that are potentially related to catalysis towards the oxygen reduction reaction (ORR). Electrochemical characterization in alkali medium suggests that the plasma irradiated SWNTs demonstrate enhanced catalytic activity toward the ORR with a positively shifted threshold potential. Moreover the enhanced desired four-electron pathway catalytic activity, which exhibited as the positive shifted threshold potential, is independent of the nitrogen dopant. The nature of the defects is probed with Raman and X-ray photoelectron spectroscopy. The results indicate that the non-nitrogen doped defects of SWNTs contribute to the actual active site for the ORR.

1. Introduction

The oxygen reduction reaction (ORR) plays a key role in fuel cells and metal/air batteries and has thus become an important research topic in catalysis [1–4]. In the past few decades, alternatives to precious metal catalysts such as platinum (Pt) were intensively explored for cost reduction and longevity of the fuel cells. Recently, heteroatom doped carbon nanotubes (HDCNT) [5], especially nitrogen doped carbon nanotubes (NCNTs) [2,5–10], have drawn tremendous attention because they provide comparable [11] or superior [2] catalytic performance compared to Pt-based catalysts towards the ORR. In addition to their low cost, NCNTs also exhibit outstanding stability, selectivity, and resistance to carbon monoxide poisoning, from which Pt-based catalysts suffer [1,11].

However, fundamental issues, such as uncertainty regarding the actual active site of the metal-free catalysts, are still being debated. Transition metal and nitrogen containing macrocycles were believed to act as the active site of Fe/N/C catalysts based on earlier works [12], and are applied in developing ORR catalysts with nanomaterials [1,13]. However, D. Yu et al. prepared NCNT via metal-free growth processes to clarify that the transition metals in the macrocycles are not essential to the ORR catalytic activity [14]. Furthermore, according to the recent experimental results and theoretical calculations, non-heteroatom doped defects contributed to the ORR activity. For instance, topological defects in the form of pentagon–heptagon defect pairs may enhance the activation behavior of ORR [15–17].

Unlike the heteroatom defects in HDCNTs, the tuning and characterization of the defects in non-heteroatom doped CNTs, especially in SWNTs, is difficult, as the oxygen functionalities are difficult to exclude [18,19]. In this work, various defects are introduced to SWNTs by mild plasma irradiation as a post-treatment. The resulting SWNTs show different catalytic activities depending on the different plasma post-treatments. Our results indicate that the non-heteroatom defects are highly important in ORR performance. The result shed new light on carbon-only catalysis [20] in the sense that topological defects should be paid more attention in catalysis toward ORR.

2. Experimental

2.1. Chemicals and catalyst preparations

2.1.1. Chemicals

The SWNT samples are purchased from J&K Scientific Ltd. The product specifications indicate that it contains >90 wt% single-walled nanotubes. The nanotubes are also specified to be 1–2 nm in

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diameter with lengths of 5–30 microns. The 5% Nafion solution is purchased from Sigma-Aldrich.

2.1.2. Plasma treatment

A plasma cleaner (PDC-32G provided by Harrick Plasma) is reconfigured (see Fig. 1.) for the plasma irradiation process. The plasma is ignited by the radio frequency (RF) power introduced by the coil. A customized sample stage with a copper mesh electrode coated with PMMA is connected to an outside electrode through a feed-through flange. There is another flange sealed with a quartz window for the observation of the emission spectrum of the plasma. A typical process of plasma irradiation is described as follows: approximately 7–8 mg of the SWNT samples are loaded onto the sample stage. The chamber is first evacuated and then a gas flow of argon (Ar) or ammonia (NH_3) is introduced to the chamber to reach 4.5 Pa for the plasma ignition. A radio frequency power of 10.5 W is applied for a desired period of time with no extra DC bias. The samples treated with different plasma irradiation are named N-SWNT-1, N-SWNT-2, P-SWNT-1 and P-SWNT-2 are listed in Table 1. A raw SWNT sample without plasma treatment is used as the control sample in structural and electrochemical characterizations.

2.1.3. Ink preparation

Approximately 2–3 mg samples of SWNTs (treated and not treated by plasma) are dispersed into the N-methyl-2-pyrrolidone (NMP) and sonicated for 30 min to form an ink with concentration of 1 mg/mL. Then, 0.95 mL of ink is mixed with 0.05 mL of 5% Nafion solution and sonicated for 15 min to form a "paste-ink" for the electrochemical measurement. For the Raman and XPS characterization, the nanotube ink is made by dispersing SWNT into either NMP or isopropanol.

2.2. Electrochemical Characterization

2.2.1. Electrochemical measurements

The electrochemical characterization for ORR was carried out in a conventional electrode arrangement using a potentiostat (Autolab PGSTAT302N), with Ag/AgCl (4 M KCl) as the reference electrode. For the investigations on the kinetics, rotating ring-disk electrode (RRDE, AFE7R9GCPT, Pine Instrument Co.) voltammetry experiments were performed on a MSR electrode rotator (Pine Instrument Co.).

For the electrochemical characterization, a glassy carbon electrode is polished with an alumina slurry on a micro cloth and then washed with 18.2 MΩ cm distilled water prior to use. 12 μL of the "paste-ink" is deposited to the electrode by drop-casting. Finally, the electrode with the samples is carefully baked

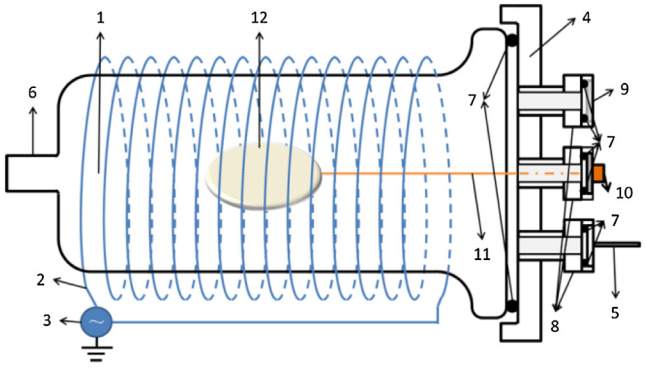

Fig. 1. 1, chamber (quartz glass); 2, RF coil; 3, RF power source; 4, front plate (stainless steel); 5, gas inlet; 6, gas outlet; 7, seal O-ring; 8, flange; 9, quartz window; 10, electrode; 11, lead-wire; 12, sample stage with PMMA coated mesh-electrode.

Table 1
Comparison of Samples with different plasma treatment.

Samples	Plasma Treatment	Threshold 1	Threshold 2	I_G/I_D
SWNT	N/A	0.60	0.28	15.45
N-SWNT-1	NH_3 3 min	0.68	0.17	13.44
N-SWNT-2	Ar 1 min and NH_3 10 min	0.72	0.40	18.09
P-SWNT-1	Ar 1 min	0.74	0.42	9.30
P-SWNT-2	Ar 3 min	0.73	0.17	8.25

under an infrared lamp. The cyclic and linear sweep voltammetry (CV and LSV) of the RRDE method are performed on the AutoLab electrochemistry workstation. Different revolutions (0 ~ 1600 rpm) are applied in 0.1 M KOH with a Pt counter electrode and an Ag/AgCl reference electrode in 25 °C maintained by a thermostatic water bath to assess the ORR activity of the SWNT samples with scan rate of 5 mV/s. All potentials in this study refer to that of reversible hydrogen electrode (RHE) [21]. For the N_2 and O_2 saturation, the N_2/O_2 gas is introduced to the electrolyte and purged for more than 30 min with the gas outlet kept over the electrolyte to ensure the presence of a desirable atmosphere without disturbing the electrolyte.

2.2.2. Data analysis

The Koutecký-Levich equation and threshold potential [22]

The current collected by the disk electrode of the RRDE method could be described by the Koutecký-Levich equation as:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,c}} \tag{1}$$

where i_K is the kinetic limited current, while $i_{l,c}$ is limiting cathodic current.

The threshold potential

As the overlapped two-wave features are revealed in the voltammograms of the SWNT samples, either the half-wave potential or the onset potential (in traditional definition) is inappropriate for the comparison to the ORR kinetics.

The half-wave potential could be estimated by determining the maxima of the derivatives of the reduction current, similar method is applied and the value is noted as *the threshold potential* [23]. As described in the supplementary material, the peak position in the differential plot represents *the threshold potential* when the i_K=$i_{l,c}$, from which the kinetic current contributes more than the limiting cathodic current in the total current with the increasing over-potential. Therefore, in this work, *the threshold potential* is chosen for the comparison instead.

The HO_2^- yield

The HO_2^- yield is calculated from the following equation:

$$HO_2^-(\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D} \tag{2}$$

Here, I_D and I_R are the disk and ring currents, respectively, and $N = 0.365$ is the ring collection efficiency (provided by vendor of electrode and calibrated by reduction of $K_3Fe[CN]_6$).

The number of electrons transferred

The Levich equation tells us that:

$$i_{l,c} = 0.62 \cdot n \cdot F \cdot A \cdot D_O^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot C_O^* \tag{3}$$

where n is the number of electrons transferred in the redox reaction, F is the Faraday constant, A is the area of the electrode, D_O is the diffusion coefficient of the oxidized form of the species, ω is the angular frequency of rotation, ν is the kinematic viscosity and C_O^* is the concentration of the oxidized form in the redox reaction. This equation applies ***to the totally mass-transfer-limited condition*** at the RDE and predicts that $i_{l,c}$ is proportional to