



# The effect of oxygen content of carbon nanotubes on the catalytic activity of carbon-based iron phthalocyanine for oxygen reduction reaction

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## ARTICLE INFO

### Article history:

Received 1 March 2018

Received in revised form

27 April 2018

Accepted 28 May 2018

Available online 2 June 2018

### Keywords:

Iron phthalocyanine

Carbon nanotubes

Oxygen content

Physical mixing method

Oxygen reduction reaction

## ABSTRACT

The development of cost-effective non-precious metal catalysts has attracted much research attention because of their high oxygen reduction reaction (ORR) performance. Herein, based on three kinds of carbon nanotubes (CNTs) with different oxygen content, we prepare three CNTs-based iron phthalocyanine (FePc) composites via only a simple physical method. In surprise, the FePc-CNTs composites with the most oxygen content exhibit the highest ORR catalytic activity in comparison with commercial Pt/C in alkaline media, especially its half-wave potential ( $E_{1/2}$ ) and durability as well as methanol tolerance. A large amount of experimental measurements show that these superb catalytic activities can be mainly attributed to the possible formation of novel interactions between FePc and oxidized CNTs. It not only provides more active sites, but also is in favor of stabilizing active centers and removing intermediates in catalytic process. This work displays the effects of oxygen content and roughness of CNTs on the interactions between FePc and CNTs and their important role in ORR catalysis, providing a new insight into simple application of carbons materials.

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## 1. Introduction

Because of the sluggish kinetics reaction, ORR is the critical process in limiting the performance of various renewable and sustainable energy conversion and storage devices, such as fuel cells and metal-air batteries [1–5]. The commercialization of these devices thus prominently depends on the development of efficient ORR catalysts. Platinum-based catalysts (Pt/Pd core-shell [6], PtNi alloy [7] and Pt/Co layer [8] present the most efficient activity in both acidic and alkaline environment. However, the large-scale application of Pt-based catalysts in fuel cells is restricted owing to the high cost, depletable resource and the poor stability. In addition, Pt-based catalysts are obviously deactivated in the presence of CO and methanol. Therefore, great efforts have been devoted to

developing the advanced non-precious metal catalysts (NPMCs) with low cost, high stability and excellent catalytic activity to rival the Pt-based catalysts towards ORR [1–5,9–30].

Among various NPMCs, metal N-doped carbon-based nano-materials (M-N/C) have been widely considered to be one of the most promising candidates. The N-doped carbon matrix such as graphene [13–16], CNTs [17–19] and carbon nanofibers [5,20,21], have effective resistance to methanol poisoning and admirable catalytic activity toward ORR. Particularly, FePc-based catalysts are typical M-N/C electrocatalysts, attracting increasing attention because of the low over-potential to ORR and the nitrogen ligand structure [22–29]. Unfortunately, these catalysts are still inferior to commercial Pt/C due to the poor electrochemical stability, poor electron conductivity and easy aggregation of FePc molecules. So far, the previous methods to solve the above problems are mainly divided into high-temperature pyrolysis [22–25], chemical synthesis [26] and physical mixing treatments [27–30]. High temperature pyrolysis treatments were mostly used to solve the above problems, but the original planar structure and active sites might

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be completely destroyed. Carbon-based FePc composites synthesized through complicated chemical reaction can also obviously promote the catalytic activity of FePc. After the axial coordination with CNTs, the composites exhibit high stability and catalysis for ORR as a result of the synergetic effects of FePc and carbon materials [26]. At present, many simple physical methods are usually used to prepare the FePc-based catalysts, such as physical mixing [27–29] method and ball-milling process [30]. It is worth noting that CNTs are widely utilized as electrocatalytic substrates via simple physical mixing owing to their excellent physical and chemical properties. Several reports have been done to investigate the influence of oxidized CNTs on the ORR catalysis [31,32]. However, few articles have discussed the effect of oxygen content of oxidized CNTs on catalytic performance of carbon-based FePc nanocomposites and provide exact evidence to unveil the reasons why their ORR performance can be significantly improved.

In general, metal phthalocyanine can be easily oxidized since the central metal atoms are willing to absorb the water and oxygen at room temperature [28]. In fact, carbon materials usually contain a large number of oxygen-functional groups on the surface, including carboxyl (–COOH), hydroxyl (–OH) and ether linkage (C–O–C), etc. Theoretically, FePc and carbon materials is easy to link together because partial oxygen-functional groups can be broken lightly, especially C–O–C (326 kJ mol<sup>-1</sup>). However, the systematic studies of the interactions between FePc and carbon materials based on plentiful oxygen content have rarely been reported. Here, CNTs with different oxygen content are used as carbon substrate to prepare three carbon-based FePc composites via simple physical ultrasonic treatment in N, N-dimethyl formamide (DMF) solution. The resultant FePc-HCNTs with highest oxygen content possesses the higher ORR activity, stability and methanol tolerance than commercial Pt/C in alkaline media. This work opens up a simple way for the design and development of advanced non-precious metal catalysts.

## 2. Experimental section

### 2.1. Chemicals and materials

MWCNTs (Multi-walled carbon nanotubes, >95%, Chengdu Organic Chemicals Co., China), FePc (95% J&K Chemicals Co., China), potassium permanganate (KMnO<sub>4</sub>, 99.5%, Sinopharm Chemical Reagent Co., China), sodium nitrate (NaNO<sub>3</sub>, 99%, Xilong Scientific Co., China), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, >30%, Sinopharm Chemical Reagent Co., China), hydrochloric acid (HCl, 36–38%, Sinopharm Chemical Reagent Co., China), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95–98%, Xilong Scientific Co., China), nitric acid (HNO<sub>3</sub>, 100%, Merck Chemicals Co., Germany), N, N-dimethyl formamide (DMF, 99.5%, Sinopharm Chemical Reagent Co., China) were used in this report. All chemical reagents were used as received without any further purification. Milli-Q ultrapure water was obtained using a Water Purifier apparatus (WP-UP-IV-20) with a resistivity of 18.25 MΩ cm<sup>-1</sup>.

### 2.2. Preparations of oxidized CNTs

MWCNTs (3 g) were put into tube furnace and heated under argon atmosphere for 1 h at 500 °C and the heating rate was 5 °C min<sup>-1</sup>. The collected solid powder was labeled as PCNTs.

NCNTs were prepared as follows: PCNTs (1 g) and pure HNO<sub>3</sub> (30 mL) were transferred to a 100 mL round-bottom flask. The flask was stirred for 30 min and then refluxed for 6 h in an ice bath with ultrasonic treatment. Subsequently, the mixture was filtered and washed with large amounts of deionized water until the pH reached to neutral and dried in vacuum for 12 h.

HCNTs were prepared as follows: PCNTs (1 g), H<sub>2</sub>SO<sub>4</sub> (100 mL)

and NaNO<sub>3</sub> (0.4 g) were added into a 1 L beaker under vigorous stirring for 3 h and ultrasonicated for another 30 min at room temperature. Afterwards, KMnO<sub>4</sub> (2.5 g) was slowly added in an ice bath and stirred for 30 min. The reaction beaker was heated to 40 °C in an oil bath for 1 h. Therewith, H<sub>2</sub>O (200 mL) and H<sub>2</sub>O<sub>2</sub> (20 mL) were successively added to terminate the reaction. The precipitate was filtered and washed with large amounts of deionized water until the pH reached to neutral. The collected solid powder was finally dried at 60 °C under vacuum condition for 12 h.

### 2.3. Synthesis of catalysts

FePc (20 mg) and PCNTs (100 mg) were respectively dispersed in 25 mL DMF with ultrasonic treatment for 1 h. Subsequently, the FePc solution was poured into PCNTs suspension and the mixture was stirred for another 6 h at room temperature. Then, the mixture was filtered, successively washed with ethanol and deionized water and dried at 80 °C under vacuum condition for 12 h. Finally, the obtained solid powder was marked as FePc-PCNTs. In comparison, FePc-NCNTs and FePc-HCNTs were also prepared under the same conditions.

### 2.4. Physical characterizations

The morphology of all samples was investigated by transmission electron microscope (TEM, F20) and high-resolution field emission scanning electron microscope (SEM, Hitachi SU8010). Fourier transform infrared spectra (FTIR) were measured using a Vertex 70 analyzer. Raman spectra were acquired by a 532 nm laser on a LabRAM HR spectrometer (HORIBA Jobin-yvon). The X-ray diffraction (XRD) patterns were obtained by MiniFlex 600 with a Cu K1 ceramic X-ray tube ( $\lambda = 1.54 \text{ \AA}$ , Rigaku). The diffraction angle ( $2\theta$ ) was varied from 5 to 60° at a scan rate of 5° min<sup>-1</sup>. X-ray photoelectron spectra (XPS) were conducted on an ESCALAB 250Xi instrument (East Grinstead).

### 2.5. Electrochemical experiments

Electrochemical experiments were conducted on a CHI760E electrochemical workstation with a standard three-electrode cell at room temperature, using a Pt net as the counter electrode and Ag/AgCl electrode (saturated KCl solution) as the reference electrode, respectively. The rotating disk electrode (RDE,  $S = 0.1963 \text{ cm}^2$ ) and the rotating ring-disk electrode (RRDE,  $S_{\text{disk}} = 0.2375 \text{ cm}^2$ ,  $S_{\text{ring}} = 0.2355 \text{ cm}^2$ ) were acted as the working electrode. To prepare the working electrode, 5 mg catalysts were dispersed in the solution of isopropanol (900  $\mu\text{L}$ ) and Nafion (100  $\mu\text{L}$ , 5 wt%) and sonicated for 30 min, after which the catalyst ink (4  $\mu\text{L}$ ) was added onto the glassy carbon surface and dried at room temperature. The mass loading of catalysts and commercial Pt/C (20 wt%, Heson, China) was 0.1 mg cm<sup>-2</sup>. Cyclic voltammetry (CV) was measured in N<sub>2</sub> or O<sub>2</sub>-saturated 0.1 M KOH solution at the scan rate of 100 mV s<sup>-1</sup>. Linear sweep voltammetry (LSV) were performed in O<sub>2</sub>-saturated 0.1 M KOH solution at the scan rate of 10 mV s<sup>-1</sup> and the various rotating speeds of 625, 900, 1225, 1600, 2025 and 2500 rpm. The accelerated degradation testing was measured by the running 5000 cycles in a potential range of 0.6 and 1 V (vs. RHE) at a scan rate of 50 mV s<sup>-1</sup>. The chronoamperometry was carried out at a constant potential of 0.264 V (RHE). Electrochemical impedance spectroscopy (EIS) measurements were characterized by using an alternating current voltage in a frequency scope from 0.1 to 100000 Hz at open circuit potential in 1 M KOH solution. The electrochemical double-layer capacitances ( $C_{\text{dl}}$ ) of catalysts were calculated from the CV curves according to the equation of  $C_{\text{dl}} = I_c/\nu$ , where  $I_c$  is the charging current density and  $\nu$  is the scan rate. All

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