Electronic Supporting Information

Iron (II) Phthalocyanine Coated on Single-walled Carbon Nanotubes Composite for Oxygen Reduction Reaction in Alkaline Media

Guofa Dong, Meihua Huang, and Lunhui Guan*

**State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, P. R. China. (350002)*

E-mail: guanlh@fjirsm.ac.cn; Fax: (+86) 591 83792835

1. Synthesis and characterization of FePc/SWCNTs

FePc and SWCNTs were purchased from Alfa Aesar (Tianjin, China) and Chengdu Organic Chemicals Co. Ltd. (Chengdu, China), respectively, and used as received. $CHCl_3$ was analytical grade and from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used without further purification. To prepare SWCNTs supported FePc composite, 30 mg SWCNTs and 15 mg FePc were dispersed into $CHCl_3$ under ultrasonication for 10 hours, then the black suspension was stirred for 4 hours, and kept still for 8 hours at room temperature. The final solution was filtered with 0.45 μm micropore membranes and dried under vacuum at 80 ℃ overnight. The result complex was denoted as FePc/SWCNTs and characterized by transmission electron microscopy (TEM), Raman spectrum, thermogravimetric analysis (TGA), and electrochemical potential cycling.

TEM was carried out on a JEOL 2010 microscope with an accelerating voltage of 200 kV. Samples were attached to the TEM grid in two steps: first, dispersing the samples into ethanol in an ultrasonic bath, and then depositing a droplet of the suspension onto the copper micro-grid coated with holey carbon and drying.

Raman spectra were recorded at room temperature using a Renishaw in Via Plus Raman microscope equipped with a CCD camera and a Leica microscope. An excitation source of 785 nm laser (Renishaw Model HPNIR 785; maximum output 300 mW) was used. Measurements were taken with 10 seconds of exposure time at varying number of accumulations. The data was collected and analyzed with Renishaw Wire and Origin software.

The thermogravimetric analysis was conducted on a Netzsch-STA449C instrument in an inert atmosphere of nitrogen. The heating rate was 10 ºC min^{-1}, and the flow rate of N_2 was 30 ml min^{-1}, the weight changes were recorded as a function of temperature.

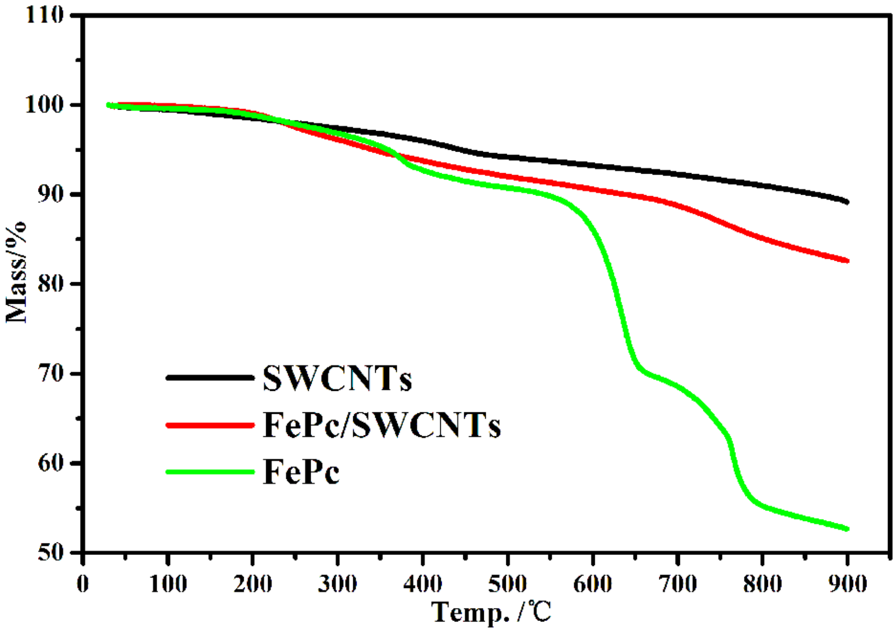

Fig. S1 TGA curves of FePc, SWCNTs, and SWCNTs/FePc.

The TGA curves were shown in Fig S1, and the weight percent of FePc in FePc/SWCNTs was calculated to be about 20 wt % from Fig S1.

2. Electrochemical experiments

Instruments and methods Electrochemical measurements were conducted on an electrochemical workstation (CHI 660C, CH Instruments, Inc., Shanghai, China) coupled with a rotating disk electrode (RDE) system. A standard three-electrode electrochemical system equipped with gas flow systems was employed. A glassy carbon disk electrode (GCE) with a diameter of 5 mm was used as the working electrode, an Ag/AgCl electrode (saturated KCl-filled) as the reference electrode, and a platinum wire as the counter electrode. Pt/C (20 wt % Pt on Vulcan XC-72) was purchased from Alfa Aesar (Tianjin, China).

NaOH and other regents were analytical grade and from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used without further purification. The water used was doubly deionized water. The ORR performance of the catalysts was studied by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in an aqueous solution of 0.1 M NaOH. CVs were measured at a scan rate of 100 mV/s. LSVs were measured at a scan rate of 10 mV/s under different disk rotation rates of 900, 1600, 2500, and 3600 rpm. The NaOH solution was bubbled with pure nitrogen (99.999%) or pure oxygen (99.999%) at least 30 minutes before and during the electrochemical measurements. ORR activity was determined based on steady-state polarization curves, which were recorded after 20 sweeps. All the potentials in this study were with respect to the Ag/AgCl reference electrode. All the Electrochemical experiments were conducted at room temperature (25 ± 1°C).

Electrode preparation Before every measurement, the electrode surface was polished with the slurry of α-Al_2O_3 powder with different particle sizes (500nm, 100nm, and 50 nm) and rinsed with DI water. The electrode was then ultrasonicated with DI water, ethanol, and DI water accordingly for 5 minutes and dried in hot air. In order to modify the GCE with the thin film catalyst layer, 2.0 mg FePc/SWCNT, 1.0 mL isopropanol and 50.0 μL Nafion (Du Pont Corp., 5 wt %) were mixed and ultrasonically blended in a weighing bottle to obtain a homogeneous ink.

Then, 30 μL of the ink was coated on a clean GCE surface with a catalyst loading of 0.29 mg cm^{-2}. For comparison, the GC electrodes coated with FePc, SWCNT or Pt/C (20 wt % Pt on Vulcan XC-72) were also fabricated with the same procedure.

In order to evaluate the stability of the interaction between FePc and SWNTs, we did a potential cycling of 500 cycles from 0.2 V to -1.2 V in 0.1 M NaOH solution saturated with O_2. As shown in Fig. S2, after the potential cycling there were no new peaks arising in the CV curve and only a slight drop in the ORR peak, which assured the stability of structure of FePc/SWNTs.

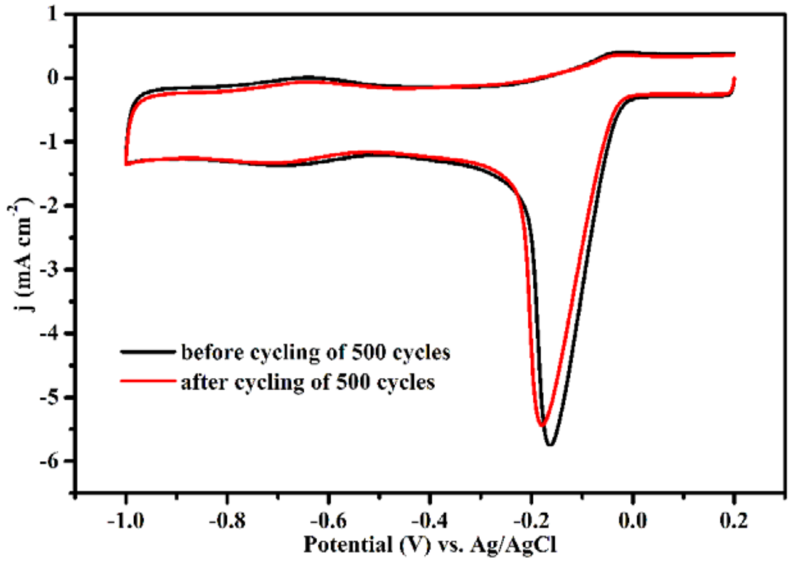

Fig. S2 CVs of FePc/SWCNTs before and after potential cycling of 500 cycles at a scan rate of 100 mV s^{-1} in 0.1 M NaOH solution saturated with O_2.

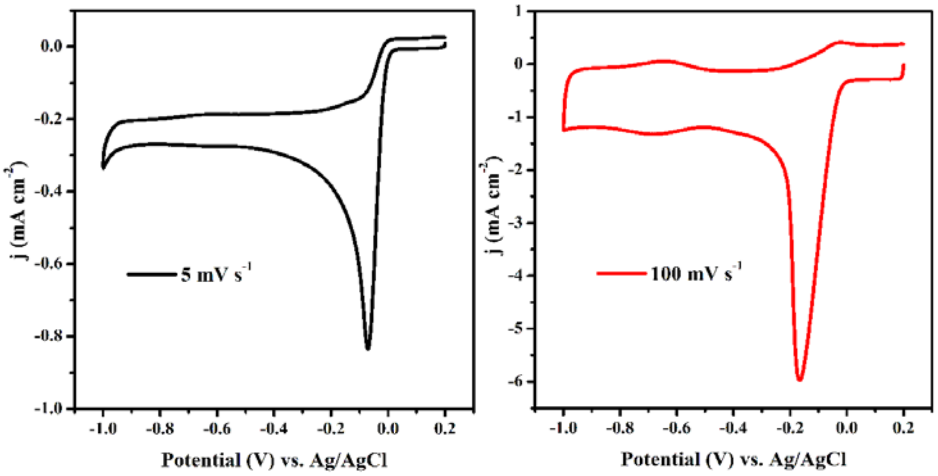

Fig. S3 CVs of FePc/SWCNTs at a scan rate of 5 mVs^{-1} (left) or 100 mVs^{-1} (right) in 0.1 M NaOH solution saturated with O_2.

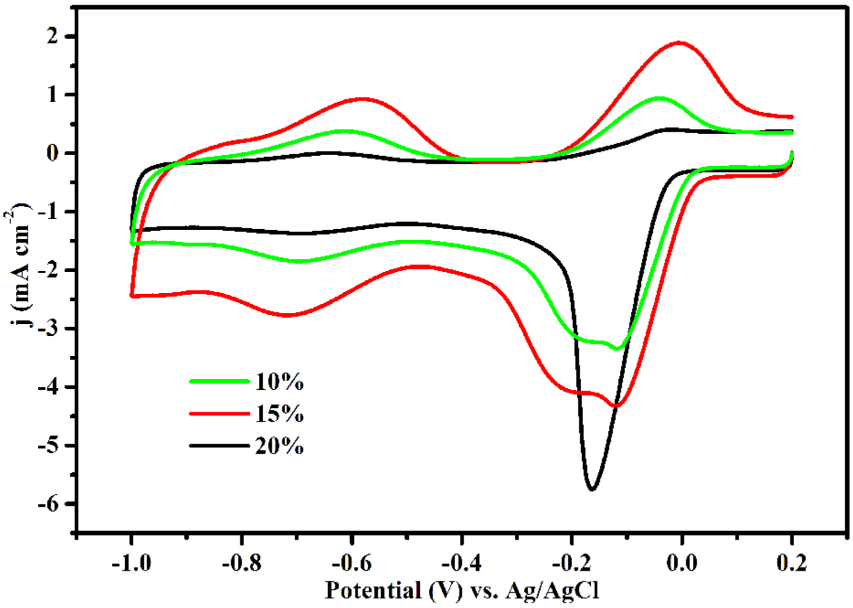

Fig. S4 CVs of FePc/SWCNTs with different loading percentage of FePc at a scan rate of 100 mVs^{-1} in 0.1 M NaOH solution saturated with O_2.