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Electronic Supplementary Information for

Nitrogen-doped One-Dimensional (1D) Macroporous Carbonaceous Nanotube Arrays and its Application for Electrocatalytic Oxygen Reduction Reactions

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Experimental Section

Materials synthesis Anodic aluminum oxide (AAO) membranes were purchased from Whatman International Ltd. The average pore size of the membrane was 200 nm and the thickness was 60 mm. Polymer solution syntheses, 0.25 g polyacrylonitrile (PAN) were dissolved in 5 ml N, N-dimethylformamide (DMF). The polymer solution wetting method a drop of solution was placed on a microscope slide and then a piece of AAO membrane was placed on it. The solution entered into the template pores along their inner wall in several seconds. And the solvent also completely evaporated after 2 minutes. Alumina templates were removed by dissolving the templates in a solution of 3 M NaOH. Then washing by distilled water repeatedly, dried at room temperature in vacuum. PAN nanotubes array were obtained. After then, we carbonized the PAN nanotubes array by heating from 25 °C to 1000 °C with a heating rate of 5 °C min and holding the temperature at 1000 °C for 5 h in different atmosphere: ammonia and nitrogen. The resulting materials are denoted as N-PANn, PANn respectively. Besides, we heated the bulk PAN in the same conditions. The resulting materials are denoted as N-PAN, PAN respectively.

Material Characterization The morphology and structure of the above samples were characterized by scanning electron microscopy (SEM, JEOL-JEM-6100F) and transmission electron microscopy (TEM, JEOL-JEM-1200), and X-ray diffraction (XRD, DX2700, X-ray diffractometer with Cu Kα radiation of wavelength $\lambda = 0.1541$ nm at 40 kV and 40 mA). The porous nature of the samples was investigated using physical adsorption of nitrogen at liquid-nitrogen temperature (-196 °C) on an automatic volumetric sorption analyzer (NOVA3200e, Quantachrome,). Prior to the measurement, the sample was degassed at 200 °C for 5 h under vacuum. The specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05-0.2. Their components were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALab-250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150 W Al Kα radiations. Pass energy for the narrow scan is 30 eV and the base pressure was about 6.5×10^{-10} mbar.).

Elemental mapping was conducted using EDAX detector attached on JEM-2010. The Raman spectra of N-PANn-1000, PANn-1000, N-PAN-1000 and PAN-1000 were excited with the 514.5 nm laser and recorded on solid samples in a Lab-RAM HR800 spectrometer.

Electrode preparation and electrochemical characterization All the electrochemical measurements were performed under identical conditions. Cyclic voltammograms, linear sweep voltammograms, rotating disk electrode, and electrode kinetics measurements were carried out using a glassy carbon rotating disk electrode. The data were recorded using a CHI 750E Electrochemical Analyzer/Workstation. The reference electrode was an Ag/AgCl in saturated AgCl-KCl solution and the counter electrode was platinum wire in 0.1 M KOH solution. The reference electrode was a saturated calomel electrode in 0.5 M H_2SO_4 solution.

Taking N-PANn-1000 electrode as an example, 1 mg of the N-PANn-1000 powder was ultrasonically dispersed in a solution containing 25 µL of 5 wt.% Nafion aqueous solution, 0.5 mL of deionized water and 0.5 mL of ethanol. The mixture was ultrasonicated to obtain a homogenous catalyst ink. 5 µL of solution dispersion was coated onto the electrode surface and then dried in the argon atmosphere for 1 h served as a working electrode. The PANn-1000, N-PAN-1000, PAN-1000 and Pt/C (C2-20, 20% Pt on Vulcan XC-72R; E-TEK) electrodes were prepared using the same procedure.

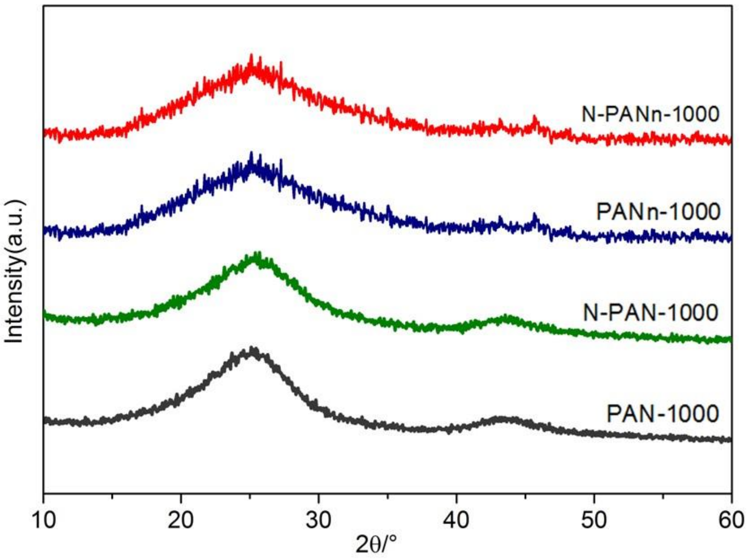

Fig. S1 XRD patterns of N-PANn-1000, N-PAN-1000, PANn-1000 and PAN-1000.

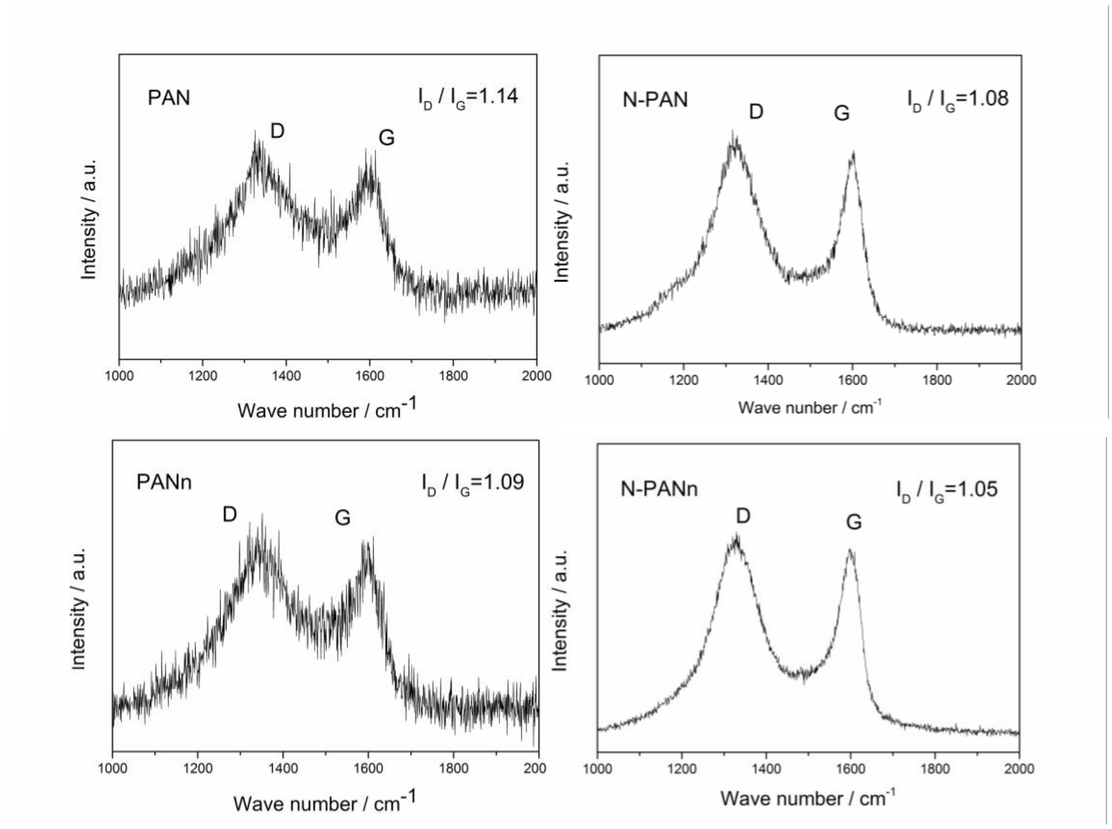

Fig. S2 Raman spectra for N-PANn-1000, PANn-1000, N-PAN-1000 and PAN-1000.

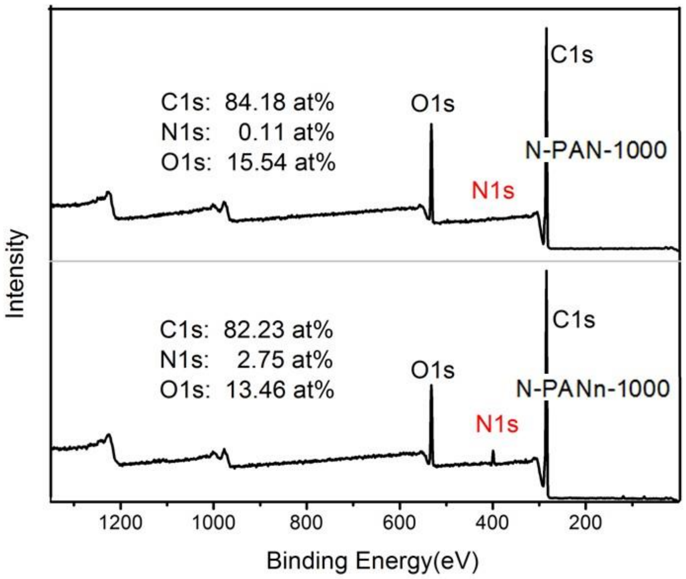

Fig. S3 XPS survey spectra for N-PANn-1000 and N-PAN-1000.

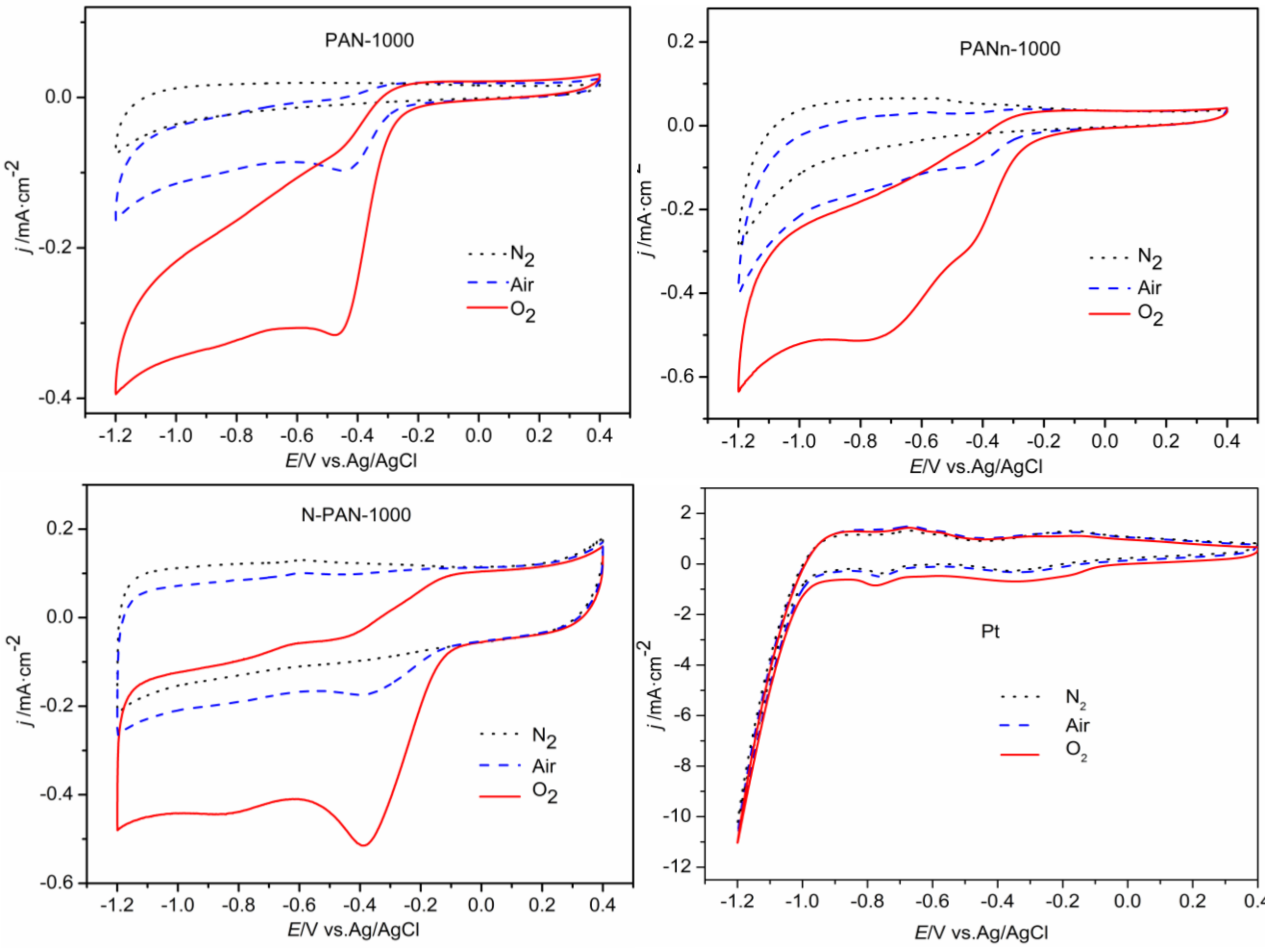

Fig. S4 CV curves of N-PAN-1000, PANn-1000, PAN-1000 and Pt/C electrodes in O_2, N_2 or air-saturated 0.1 M solution of KOH.

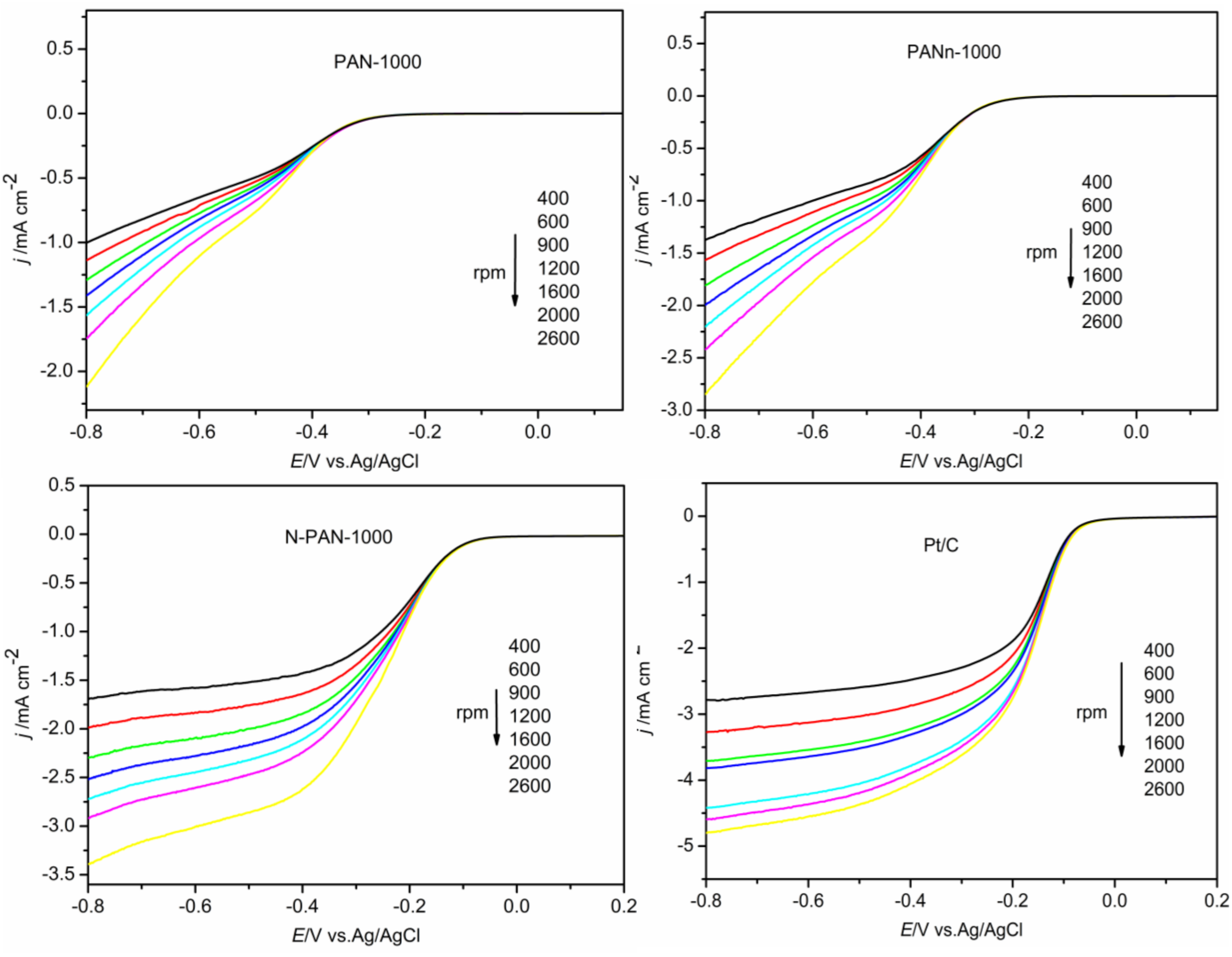

Fig. S5 LSV curves for the N-PAN-1000, PANn-1000, PAN-1000 and Pt/C electrodes in O_2-saturated 0.1 M solution of KOH at various rotating speeds.

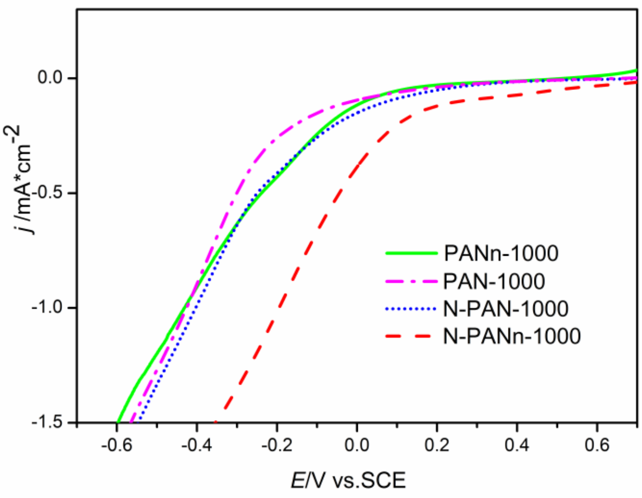

Fig. S6 LSV curves for various materials at a rotation rate of 1600 rpm in 0.5 M H_2SO_4 solution.

S1. Rotating-disk voltammetry measurements

To further study the ORR electrochemical procedures of N-PANn-1000, we performed rotating-disk electrode (RDE). The RDE current-potential curves at various rotating speeds are shown in Fig. 3c and Fig. S5. The limited diffusion currents are dependent on the rotating rates. The transferred electron numbers (n) per oxygen molecule in the ORR process at the N-PANn/GCE can be calculated from the Koutecky-Levich (K-L) equation:

$$J^{-1} = J_K^{-1} + B^{-1}\omega^{-1/2} \qquad (1)$$

$$B = 0.62 n F C_0 D_0^{2/3} \nu^{-1/6} \qquad (2)$$

Where J is the measured current density, J_K is the kinetic current density, ω is the angular velocity of the disk (ω=2pN, N is the linear rotation speed). n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F =96485 C·mol^{-1}), C_0 is the bulk concentration of O_2, (C_0 =1.2×10^{-6} mol·cm^{-1}), ν is the kinematic viscosity of the electrolyte (ν=0.01 cm^{2}·s^{-1}). D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9 × 10^{-5} cm^{2}·s^{-1}). According to Equations (1) and (2), the number of electrons transferred n and J_K can be obtained from the slope and intercept of the plots, respectively.

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