Supporting Information

Ammonia-Treated Ordered Mesoporous Carbons as Catalytic Materials for Oxygen Reduction Reaction

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Experimental

Synthesis. Ordered mesoporous carbon (C-ORNL-1) was synthesized following a procedure reported previously by our group.[1] Ammonia heat-treatment was performed by placing 1.0 g of C-ORNL-1 in a quartz tubing under flowing NH_3 (~ 40 ml/min) with a heating ramp rate of 50°C/min to desired temperatures and the temperature was kept for 1 h.

Characterization. N_2 sorption isotherms were recorded on a Micromeritics Tristar analyzer at -196 °C (77 K). Prior to measurement, the sample was purged with flowing N_2 at 150 ºC for 3 h. The specific surface area was calculated using the BET method from the nitrogen adsorption data in the relative range (P/P_0) of 0.05-0.20. Micropore surface area was estimated by the t-plot method using the Harkins and Jura thickness equation. The pore size distribution (PSD) plots were derived from the adsorption branch of the isotherms based on the BJH model. The total pore volume (V_{total}) was determined from the amount of N_2 uptake at P/P0 = 0.95. The micropore volume (V_{micro}) was estimated using the α_s method, where nonporous acetylene carbon black (BET surface area: 80.2 m^2/g) was used as the reference. The mesopore volume was calculated by subtraction of micropore volume from the total pore volume ($V_{meso} = V_{total} - V_{micro}$). STEM images were taken on a Hitachi HD-2000 STEM microscope operating at 200 kV under the SE and TE mode, respectively. XPS experiments were run on a Thermo Fisher Scientific K-Alpha XPS instrument. The instrument is equipped with a micr-focussed, mono-chromatic Al ka x-ray source, Ar-ion sputter gun, and a charge compensation system that uses both low energy electrons and low energy Ar ions to alleviate sample charging. Samples were spread onto well-characterized double sided tape and excess particles were removed with an inert "dusting" spray. Mounted samples were inserted into the XPS instrument through a vacuum load-lock. Survey scan were obtained using a pass energy of 200 eV while high energy resolution scans of specific elements were obtained using a 50 eV pass energy.

Electrochemical measurement. Cyclic voltammetry and linear sweep voltammetry measurements were performed in a three-electrode system. A glassy carbon rotating disk electrode (RDE, Pine Instrument) was used as a working electrode. An Ag/AgCl electrode was used as a reference electrode and Pt wire was used as a counter electrode. The electrocatalyst electrode was prepared by loading a catalyst suspension (1.0 mg/ml in EtOH, 20 μg) onto the surface of the glassy carbon disk (5 mm), followed by drying at room temperature. After air-drying, the electrode was covered with Nafion (0.05 wt %). The electrochemical experiments were performed in oxygen saturated 0.05 M H_2SO_4 (or 0.1 M $HClO_4$ for the measurement of electron transfer number) aqueous solution at room temperature.

Electron transfer numbers were calculated using Koutecky-Levich eq.

$$i^{-1} = i_k^{-1} + i_l^{-1} = 1/(nFk\Gamma C_0) + 1/(0.620nFAD_{O2}^{2/3}\omega^{1/2}\upsilon^{-1/6}\, C_0) = 1/(nFk\Gamma C_0) + 1/(B\omega^{1/2})$$

Where, i is the total current; i_k is the kinetic current; i_l is the diffusion-limited current; n is the number of electrons exchanged per mole of O_2; F is the Faraday constant (96500 C mol^{-1}); Γ is the quantity of catalyst on the surface of the electrode (mol cm^{-2}); k is the rate constant for oxygen reduction; A is electrode area (cm^{-2}); C_0 is bulk concentration of O_2 in 0.1 M $HClO_4$ solution (1.18 x 10^{-6} mol cm^{-3}); D_{O2} is the diffusion

[1] Wang, X. Q.; Liang, C. D.; Dai, S. *Langmuir* **2008**, *24*, 7500.

coefficient of O_2 in 0.1 M $HClO_4$ solution (1.9×10^{-5} cm^2 s^{-1}); ω is the rotation rate (rad s^{-1}) and υ is the kinetic viscosity of the water (0.0107 cm^2 s^{-1})[2]. The slope of the plot of reciprocal current ($1/I$) versus the reciprocal square root of rotation rate ($1/\omega^{1/2}$) gives B values. The value of n can be calculated from B by using the known parameters mentioned above.

CO poison test. Because carbon monoxide (CO) poisoning of most noble-metal electrocatalysts including Pt is a major issue in the current fuel cell technology, we have also tested the possible crossover and poison effects CO on the electrocatalytic activity of N-OMC-1050. To investigate the effect of CO poisoning to N-OMC-1050, we measured the current-time chronoamperometric responses at a potential of 0.2 V (vs. NHE) in oxygen-saturated 0.05 M H_2SO_4 at room temperature. As shown in Figure S3, N-OMC-1050 was almost insensitive to CO poisoning even after adding CO gas in oxygen (ratio = 1:10). This observation is in sharp contrast to the performance of Pt-20 under identical conditions, which showed a quick loss in current with less than 30% remained after 1 h upon exposure to CO. This result clearly indicates that N-OMC-1050 has much higher resistance to CO poisoning than the Pt-based electro-catalysts, due to the characteristic of non-metal active sites[3] for the former.

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[2] *J. Electrochem. Soc*. **1997**, *144*, 2973; *J. Power Sources* **2009**, *193*, 495.

[3] Gong, K. P.; Du, F.; Xia, Z. H.; Durstock, M.; Dai, L. M. *Science* **2009**, *323*, 760.

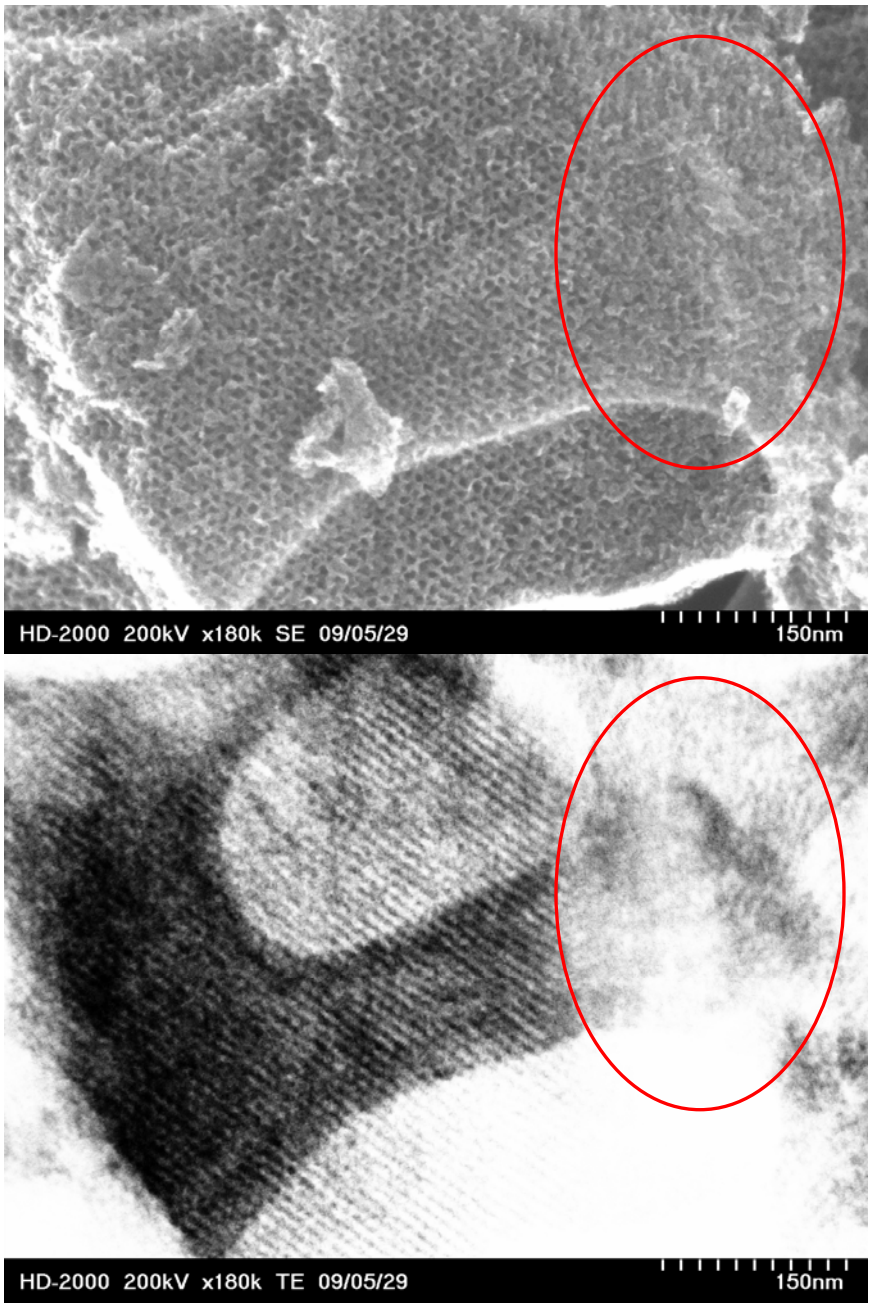

Figure S1. STEM images of N-OMC-1050 at the same area under the SE (top) and TE (bottom) mode, respectively, showed that mesoporous structure was retained after ammonia heat treatment at 1050 ^{o}C although a structural degradation was observed (indicated by red circles).

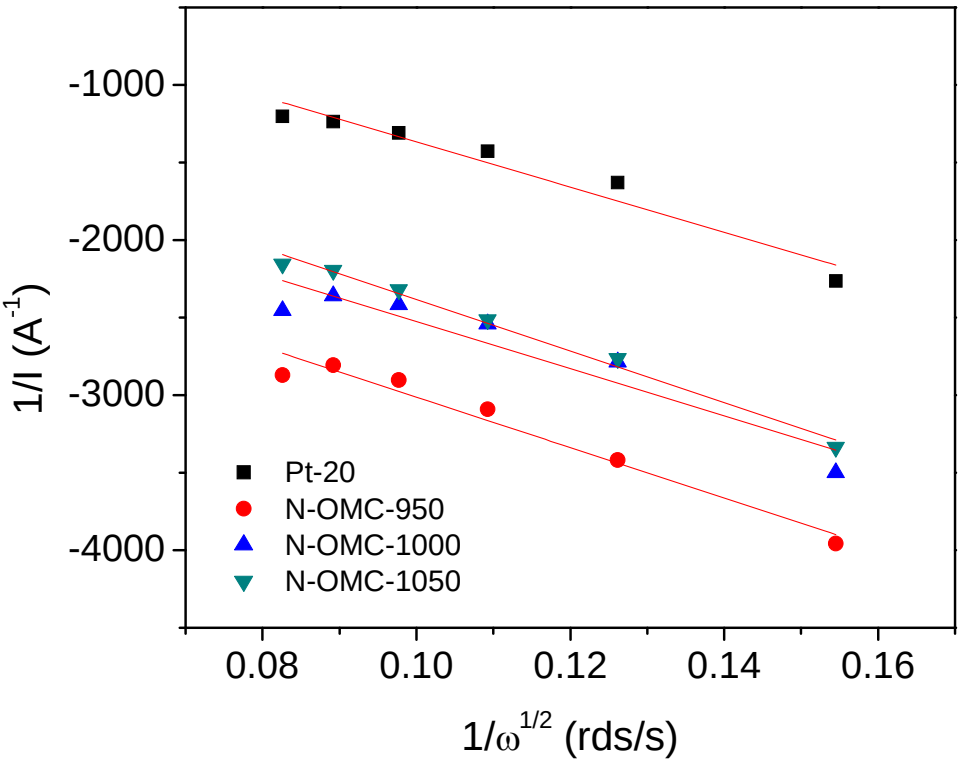

Figure S2. The relationship between 1/I and $1/\omega^{1/2}$ for electrocatalysts in oxygen saturated 0.1 M $HClO_4$ solution.

Table S1. Calculated electron transfer number *n* using the slopes in **Figure S2**.

	slope	*n*
Pt-20	-14586	3.88
N-OMC-950	-16255	3.48
N-OMC-1000	-15196	3.72
N-OMC-1050	-16621	3.41

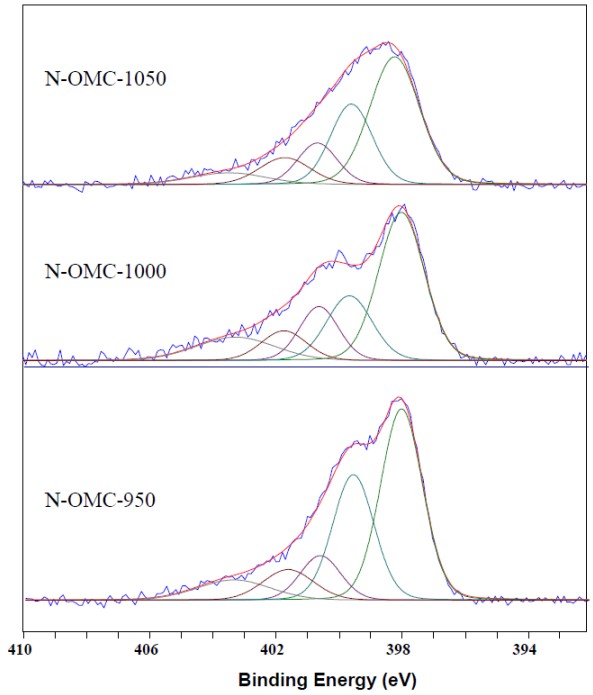

Figure S3. XPS N 1s narrow-scan spectra of N-OMC-*x*.

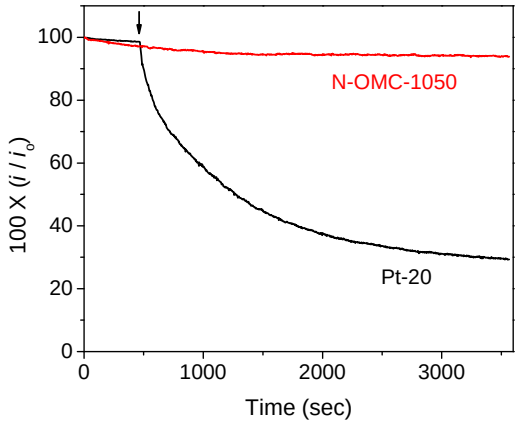

Figure S3. CO-poison effect on the *i-t* chromoamperometiric response for the Pt-20 and N-OMC-1050. The arrow indicates the addition of CO gas; flow rate: CO = 10 mL min^{-1} and O_2 = 100 mL min^{-1}. i_0 represents the initial current.