Supporting Information

A Novel CoN Electro catalyst with Excellent Activity and Stability toward Oxygen Reduction Reaction

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Experiment section

Synthesis of the supported CoN precursor

The supported CoN precursor was synthesized by reduction of Co(acac) 2 in o-xylene solution in a reflux system. Typically, 0.2 mmol Co(acac) 2 and 47 mg Vulcan XC-72 carbon were dissolved in a three-neck flask with 150 mL o-xylene solution, which acted as the solvent. Then, the mixture was treated in an ultrasound bath for 3 hours till the solution got uniformly dispersed and refluxed in an oil bath at 140 °C for 4.5 h without adding any reductant. Finally, the mixture was filtered, washed with absolute ethyl alcohol several times and dried at 80 °C for 10 h in a vacuum oven.

Synthesis of the supported CoN NPs

The precursor materials were put in tube furnace and treated under the reducing atmosphere NH 3 at 550 °C for 3 hours. The obtained sample particles were characterized by various techniques after it had cooled down. In order to check the effect of heated temperature on the phase transformation, the different annealed temperature (450-650 °C) samples were also synthesized (The results were summarized in Fig. S1).

Materials Characterization

The X-ray Diffraction (XRD) patterns for the crystal structure of the electro catalysts were performed on a Bruker D8 Advance X-ray diffractometer using filtered Cu Kα (λ = 1.5405 Å) radiation source (40 kV, 40 mA). The measurements of transmission electron microspectroscopy
TEM, high resolution transmission electron microspectroscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were carried out with TECNAI-F20 microscope and JEM-ARM200F, FEI operating at 200 kV, respectively, with a nominal resolution deposited onto copper microgrid coated with carbon. The information on the bulk composition of the prepared catalysts was obtained with inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PROFILE SPEC, Leeman) after dissolution of the samples in aqua regia. The amount of CoN was also determined by TG analysis (EXSTAR TG/DTA7300) for comparison. Surface status was determined by using XPS (AXIS-Ultra instrument from Kratos Analytical, Al Kα radiation, hν = 1486.6 eV). The BET surface areas were calculated from the adsorption data. The pore volumes were determined from the adsorbed amount at the relative pressure of 0.995. Pore size distributions were fitted by the Quenched Solid Density Functional Theory (QSDFT) using the desorption branch. XAFS data at the Co K-edge were carried out at beamline B14W1 of Shanghai Synchrotron Radiation Facility (SSRF) of China. The storage ring of SSRF was operated at 3.5 Gev with an average current of 300 mA. The fixed-exit Si(111) double crystals were used as monochromator. The XAFS spectra were collected in transmission mode with ionization chambers filled with Ar/N2 at room temperature. The soft XAS data were collected at beamline 4B7B station of Beijing Synchrotron Radiation Facility (BSRF) with a maximum current of 300 mA operating at 2.5 Gev. The measurements were done in the total electron yield (TEY) mode for the Co L_{II,III} edges.

Electrochemical mesurements

The electrochemical measurements were carried out in a conventional three electrode cell using a BioLogic SP 240 electrochemical workstation. The glassy carbon rotating disk electrode (GC-RDE) with electrocatalyst was used as the working electrode (geometric area 0.1257 cm²). The counter electrode and the reference electrode were GC film and Hg/HgO (0.1 M KOH), respectively. All the potentials in this study were referred to reversible hydrogen electrode (RHE). The Hg/HgO (0.1 M KOH) reference electrode is 0.164 V versus NHE. Before using the GC electrode as substrates for the catalysts, it was polished with 0.5 μm and 50 nm alumina to a mirror-finish. For the fabrication of working electrode, 2.7 mg of the electrocatalysts was suspended in 1 mL of isopropyl alcohol and one drop 2% Nafion solution in an ultrasonic bath during 30 min to form the homogeneous catalyst ink. The suspension (20 μL) was pipetted onto
the surface of the GC electrode. The catalyst-coated electrode surface was then dried in an air overnight.

Cyclic voltammetry (CV) experiments and Polarization tests were conducted in a N₂ and O₂-saturate 0.1 mol L⁻¹ KOH in the potential range of 0.2~1.2 V (vs RHE), with a scan rate of 50 mV s⁻¹, 10 mV s⁻¹, respectively. Chronoamperometry and methanol-tolerant tests were conducted at 0.75 V in O₂ saturated 0.1 M KOH solution. All the electrochemical data were obtained at room temperature, i.e., 25 °C. The accelerated durability tests (ADT) were performed by potential cycling between 0.6 and 1.1 V (vs. RHE) for 10,000 cycles in O₂-saturated 0.1 M KOH, with scan rate of 200 mV s⁻¹. The kinetics of the ORR for CoN/XC-72 and Commercial Pt/C catalysts were studied by the RDE method. The Koutecky-Levich equation was used to determine the electron transfer number of the catalyzed ORR¹³.

\[
\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}
\]

\[
B = 0.62nFC_0(D_0)^{2/3}V^{-1/6}
\]

\[
J_K = nFkC_0
\]

where \(J\) is the measured current density, \(J_K\) and \(J_L\) are the kinetic- and diffusion limiting current densities, \(\omega\) is the angular velocity, \(n\) is transferred electron number, \(F\) is the Faraday constant, \(C_0\) is the bulk concentration of O₂, \(V\) is the kinematic viscosity of the electrolyte, and \(k\) is the electron-transfer rate constant. For the Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by:

\[
J_K = \frac{J \times J_L}{J_L - J}
\]

All the catalyst electrodes were cleaned before data collection with a steady-state CV scanned for several cycles in the range of 0.2~1.2 V at a sweep of 50 mV s⁻¹. Commercial 20 wt% Pt/C (Pt/C’s loading 20 µg cm⁻²) was also used to compare their catalytic activities.
Figure S1. Powder XRD patterns of supported CoN compound (JCPDS NO. 16-0116) annealed at different temperature under NH$_3$ atmosphere.

Figure S2. TG/DTG curves of CoN/C composite measured from 20 to 700 °C at a heating rate of 5 °C/min in air.
Figure S3. (a) XANES of Co K-edge for CoN, CoO, Co$_3$O$_4$; (b) Co 2p XPS spectra of CoN/XC-72 composite
Figure S4. a) CV curves of Commercial Pt catalyst at a scan rate of 50 mV s⁻¹ in N₂-(black line) or O₂-(red line)-saturated 0.1 M KOH solutions. (b) RDE voltammetric response for the ORR in O₂-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹ at different rotation rates.
Figure S5. (a) RDE polarization curves of the CoN/C NPs catalyst before and after 10,000 cycles in O₂-saturated 0.1 M KOH. Potential cycling was carried out between 0.6 and 1.0 V versus RHE at 200 mV s⁻¹. (b) Chronoamperometric responses of commercial Pt/C catalysts at 0.75 V in O₂-saturated 0.1 M KOH, which are normalized to the initial current responses. b) Chronoamperometric responses to injection of 1 M methanol into O₂-saturated 0.1 M KOH solution at 0.75 V commercial Pt/C catalyst modified electrodes.
Figure S6. Nitrogen adsorption/desorption isotherms of CoN/C NPs and (inset) its corresponding pore size distributions based on the QSDFT model.

Figure S7. Co 2p XPS spectra of CoN/XC-72 composite after stability test.