A "MOFs plus ZIFs" Strategy towards Ultrafine Co Nanodots Confined into Superficial N-doped Carbon Nanowires for Efficient Oxygen Reduction

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EXPERIMENTAL SECTION

Material Synthesis

Synthesis of MOF-74 nanowires: MOF-74 nanowires were prepared by the reported hydrothermal method. 1.0 g of cobalt acetate tetrahydrate was dissolved in 50 mL of methanol and 0.3 g of 2, 5-dihydroxyparaxic acid was dissolved in another 50 mL of methanol under stirring. Both solutions were stirred for 10 min for completely dissolution. The ligand solution was slowly added to cobalt nitrate solution by drop to produce the orange suspension and stirred for another 1 h. The suspension was collected by centrifugation and washed twice with deionized water. Then the precipitation was dispersed in 80 mL of deionized water and transferred into a 100 mL Teflon autoclave. After heated at 180 °C for 12 h and cooled, the MOF-74 nanowires were collected and washed several times with deionized water by centrifugation. These nanowires were dried at 80 °C for 24 h under low pressure (~100 Pa) to remove the water and methanol molecules in the channel.

Synthesis of MOF-74@ZIF-67 nanowires: 0.5 g of activated MOF-74 nanowires was uniformly placed in the porcelain boat. Then 4 g of 2-methylimidazole was placed on a petri dish around the porcelain boat. The petri dish with samples was transferred into a vacuum oven to react at 120 °C for 6 h under low pressure (~100 Pa). After cooled to room temperature, the MOF-74@ZIF-67 nanowires in the porcelain boat were obtained. Pure ZIF-67 was also synthesized by the previous report to compare the structure of MOF-74@ZIF-67.

Synthesis of Co@C@NC nanowires: the core-shell Co@C@NC nanowires were obtained by pyrolyzing MOF-74@ZIF-67 nanowires at 600 °C for 2 h with a rate of 5 °C min⁻¹ in flowing

 Ar/H_2 (5 wt% of H₂). The Co@C was synthesized by directly heating MOF-74 nanowires with calcination condition unchanged.

Material Characterization

XRD analysis of the crystal structure was measured on a smart lab diffractometer (Rigaku, Japan) working at 30 kV and 10 mA with a Co K α radiation source ($\lambda = 1.79$ Å). The SEM images of the morphology of samples were collected using a scanning electron JSM-7100F microscope (JEOL, Japan) at an accelerating voltage of 15 kV. TEM images were collected by a JEM-2100F/Titan G2 60-300 microscope (JEOL, Japan). HRTEM and HAADF-STEM were performed on a JEOL JEM-2010F microscope. EDS analysis was conducted on an Oxford IE250 (Oxford Instruments, UK) system. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was accomplished using a Thermo ICAP6300 equipment (Thermo Fisher Scientific Co., USA). XPS analysis was carried out on an ESCALAB 250 Xi spectrometer (VG Scientific Co., UK) with an Al Ka X-ray radiation (1486.6 eV). BET surface area and pore size distribution were measured by a TriStar-3020 gas adsorption analyzer (Micromeritics Instrument Co., USA) at 77 K. Raman spectra were recorded on a Renishaw InVia Reflex Raman microscope with an excitation laser of 633 nm. FTIR spectra were recorded using a Nicolet 6700 IR spectrometer (Thermo Fisher Scientific Co., USA). TG and DSC was performed by using a STA449F3 integrated thermal analysis instrument (Netzsch, Germany) under an argon environment at a rate of 10 °C min⁻¹

Electrochemical Measurements

All ORR measurements were performed on an electrochemical workstation CHI 760E. The test utilized a typical three-electrode system. The Hg/HgO electrode, graphite electrode, and glass

carbon electrode (GCE) were used as the reference electrode, counter electrode, and working electrode, respectively. To investigate the electrochemical ORR performance, the prepared catalyst was formulated into ink that could be used for examination. The mixed powder of asprepared Co@C@NC (8 mg) and Vulcan-XC72R (1 mg) was dissolved in the solution containing 750 μ L of isopropanol and 200 μ L of deionized water. The suspension was sonicated for 1 h for full dispersion. Then 50 μ L of nafion solution was added to the suspension and continue sonicated for another 1 h to obtain the ink. The ink was cast onto the polished GCE surface until the catalyst loading was 0.40 mg cm⁻² and dried at room temperature. In all ORR measurements, the O₂-saturated KOH (0.1 mol L⁻¹) solution was used as the electrolyte and protected by continuously O₂. LSV measurements used a RDE to perform at different rotation rates of 400, 625, 900, 1225, and 1600 rpm with a scan rate of 5 mV s⁻¹. The ORR kinetics analysis could be estimated from the slope of the K-L diagram according to the following equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_D}$$
(1)

where J, J_K , and J_D represent the measured, kinetic, and diffusion limiting currents, respectively. The yield of the obtained the peroxide species (HO_2^-) and electron reduction number (*n*) are calculated as follows:

$$HO_{2}^{-} = 200 \frac{\frac{l_{R}}{N}}{l_{D} + \frac{l_{R}}{N}}$$
(2)

$$n = 4 \frac{I_D}{I_D + \frac{I_R}{N}} \tag{3}$$

where I_D and I_R represent disk current and ring current; N represents the current collection efficiency (0.37) of the RRDE. Reversible hydrogen electrodes are calibrated from measured potentials according to the Nernst equation:

$$E(RHE) = E(Hg/HgO) + 0.0591pH + 0.098V$$
(4)

The durability and methanol tolerance were examined at 0.7 V at a speed of 1225 rpm. The stable current at 10 s is recorded as 100% activity in these examinations. The methanol tolerance measurement was adding 0.3 mL of methanol to 200 mL of the electrolyte at 150 s.



Figure S1. (a) SEM and (b) TEM images of MOF-74 nanowires.



Figure S2. (a) SEM and (b) TEM images of Co@C.



Figure S3. High magnification HAADF-STEM image and corresponding EDS element mapping of C, N, and Co at the tip of a Co@C@NC nanowire.



Figure S4. HAADF-STEM image and distribution of N and all element mapping along radial direction of Co@C@NC.



Figure S5. TG-DSC curves of MOF-74, ZIF-67, and MOF-74@ZIF-67 from 35 °C to 700 °C.



Figure S6. High-resolution Co 2p XPS spectra for Co@C@NC and Co@C.



Figure S7. (a) XRD pattern and (b) TEM image of C@NC obtained by leaching Co@N@NC with 25 wt% H_2SO_4 .



Figure S8. (a) CV curves at different scan rates and (b) C_{dl} values of Co@C@NC.



Figure S9. TEM images of Co@C@NC after durability examination.



Figure S10. XRD patterns and XPS survey spectra of Co@C@NC before and after durability examination.



Figure S11. Spin polarized DOS with (a) spin down and (b) spin up states of Co@pyri-NC, Co@pyrr-NC, Co@grap-NC, and Co@C systems near the Fermi level (0 eV).

| Table S1. A summary of various similar electrocatalysts reported received | ntly for ORR | |
|---|--------------|--|
|---|--------------|--|

| Electrocatalysts | Half-wave potential (V) | n | References |
|------------------|-------------------------|-----------|------------|
| Co@C@NC | 0.83 | 3.99-4.00 | Our work |

| BCNT/Co | 0.803 | 3.89-3.98 | ACS Appl. Mater. Interfaces 2020 , 12 (4), 4463-4472. |
|-------------------|-----------|-----------|---|
| PCA-CoCN | 0.79-0.82 | 3.79-3.81 | Appl. Catal. B 2020, 270, 118869. |
| FeCo/SWCNT | 0.80 | 3.6-3.8 | <i>Chem. Commun.</i> 2020 , DOI: 10.1039/D0CC00229A. |
| CoNC/NCNTs@CNF | 0.78 | 4.00-4.07 | Compos. B. Eng. 2020, 193, 108058. |
| Co/N-C | 0.826 | 3.87 | J. Power Sources 2020, 451, 227747. |
| CoNMC | 0.81 | 3.78-3.72 | Nanoscale 2020, 12 (10), 6089-6095. |
| MnO/Co/PGC | 0.78 | 4 | Adv. Mater. 2019, 31 (39), 1902339. |
| Co,N-PCLs | 0.831 | 3.97 | Appl. Catal. B 2019, 246, 322-329. |
| CuCo@N-C | 0.81 | 3.89 | J. Mater. Chem. A 2019, 7 (20), 12851-12858. |
| Co@N-CNTF | 0.81 | 3.96 | J. Mater. Chem. A 2019, 7 (8), 3664-3672. |
| GCN-Co@CoO | 0.76 | 3.92 | ACS Sustain. Chem. Eng. 2019, 7 (6), 6335- 6344. |
| CoN-GH-h | 0.78 | 3.96 | J. Colloid Interface Sci. 2020, 559, 143-151. |
| FeCo/FeCoNi@NCNTs | 0.81-0.82 | 3.98-4.00 | Appl. Catal. B 2019, 254, 26-36. |