

Supporting Information

Chelate resin self-assembled quaternary Co-N-P-C catalyst for oxygen reduction reaction

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Preparation of Co-N-P-C samples

Chelating resins are known as specific exchangers or chelating sorbents and usually perceive as a subgroup of ion exchange resins. The chelating resins are solids with organic mainframes containing active groups, which are able to interact with metal ions forming coordinative bonds to obtain stable structures being similar as small molecule chelates.

The resin was pretreated before use as follows. The purchased resin was firstly washed with deionized water and then dried at 60 °C. The dried resin was then smashed into powders. In a typical preparation, pretreated aminophosphonic acid chelate resin (10 g, Sunresin New Materials Co. Ltd., China) in 100 mL of 0.4 mol L⁻¹ CoCl₂·6H₂O solution at 50 °C for 8 h. The resulting resin was then washed with deionized water and dried at 80 °C for 24 h. Heat treatment of the dried resin was performed in a tube furnace at 1200 °C for 1 h at a heating rate of 5 °C min⁻¹ in N₂ atmosphere. After cooling down to room temperature, the resulting product was ground into powders and treated with dilute hydrochloric acid to remove unstable species and impurities from the catalysts. The Co-N-C and metal-free N-P-C prepared by heat treatment of poly(vinylpyridine) resin coordinating with Co²⁺ ions and aminophosphonic acid chelate resin under the same condition, respectively.

Physical characterizations

The X-Ray powder diffraction (XRD) patterns were measured on a D/Max-III (Rigaku Co., Japan) with Cu K α radiation source (30 kV and 30 mA), recorded at a scan rate of 10° (2 θ) min⁻¹. The X-ray photoelectron spectroscopy (XPS) measurements were performed in an ESCALAB 250 spectrometer under vacuum (about 2×10⁻⁹ mbar). Monochromatic Al K α (150 W, 1486.6 eV) was used as the excitation source. All the binding energies were calibrated with respect to C1s peak at 284.8 eV. The Raman spectroscopic measurements were carried out on a Raman spectrometer (Renishaw Corp., UK) using a He-Ne laser with a wavelength of 514.5 nm. Thermogravimetry coupled with Fourier transform infrared spectrometry was carried out on TG-209 / Vector-22. The aminophosphonic acid chelate resin was heated from 20 to 800 °C at a rate of 20 °C min⁻¹ in N₂ atmosphere. The morphology characterizations were performed on a scan electron microscopy (SEM) (Quanta 400 FEG, FEI Company). The transmission electron microscopy (TEM) and EELS investigations were carried out on a JEOL JEM-2010 (JEOL Ltd.) operating at 200 kV and FEI Tecnai G2 F30. The pore structure of the Co-N-P-C sample was characterized by the analysis of nitrogen adsorption-desorption isotherms, performed at 77K with Micromeritics ASAP 2420 in a relative pressure (P/P₀) range from 10⁻⁶ to 1 after degassing the samples at 150 °C for 5 h.

Electrochemical measurements

The performance of the electrocatalysts for ORR was measured on a rotating ring-disk electrode (RRDE) with a biopotentiostat (Pine Instrument Co., USA) in a three-electrode cell by using a reversible hydrogen electrode (RHE) as the reference electrode, and a graphite electrode as the counter electrode. The working electrode was a rotating ring/disk electrode with a glassy carbon disk (5.61 mm in diameter). The electrocatalyst (10.0 mg) was added into 1.9 mL ethanol and 0.1 mL Nafion solution (5 wt%, DuPont, USA) and ultrasonicated for 30 min to form a well-dispersed ink. The ink (120 μ L) was transferred onto the surface of the glass carbon electrode and then dried under infrared lamp for 5 min to obtain a catalyst thin film. The ORR tests were performed with a scan rate of 5 mV s⁻¹ in an O₂-saturated 0.1 mol L⁻¹ HClO₄ solution at 25 °C and the rotating speed was controlled at 1600 rpm. In RRDE tests, the ring potential was set to 1.2 V.

Additional data:

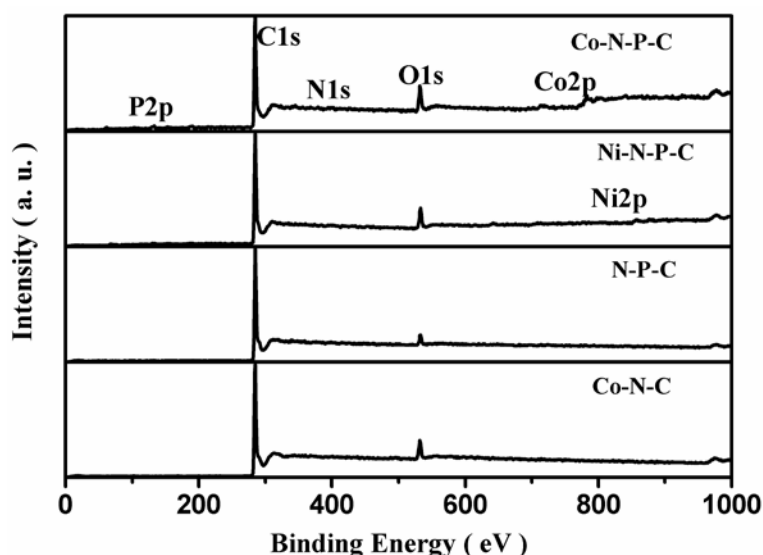


Figure S1. XPS spectra of Co-N-P-C, Ni-N-P-C, N-P-C and Co-N-C.

Table S1. XPS N 1s regions analysis (relative atomic ratios of N species) for the catalysts

Sample	N-I	N-II	N-III	N-IV
Co-N-P-C	16.21%	44.58%	33.73%	5.48%
Ni-N-P-C	26.96%	30.05%	25.32%	17.67%
N-P-C	16.0%	22.4%	40.53%	21.07%
Co-N-C	33.84%	32.16%	17.56%	16.44%

The SEM images of Co-N-P-C (Figure S2a and b) display a morphology of 3D porous framework. It indicates that the carbon frameworks have uniformly distributed pores with different sizes. The high-magnified SEM microgram of Co-N-P-C (Figure S2b) clearly shows that the macropores are at or less than 200 nm. The formation of macropores is most probably due to the gas evaporation and part phosphorus volatilization during the thermolysis of the resin. The SEM images of Ni-N-P-C (Figure S2c) and N-P-C (Figure S2d) showed similar porous framework morphology as that of Co-N-P-C.

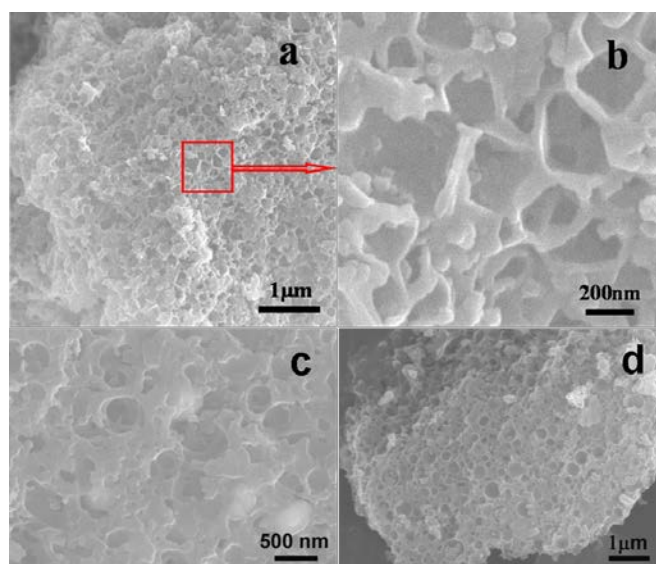


Figure S2. (a, b) SEM micrograms of Co-N-P-C, (c) SEM microgram of Ni-N-P-C and (d) SEM microgram of N-P-C.

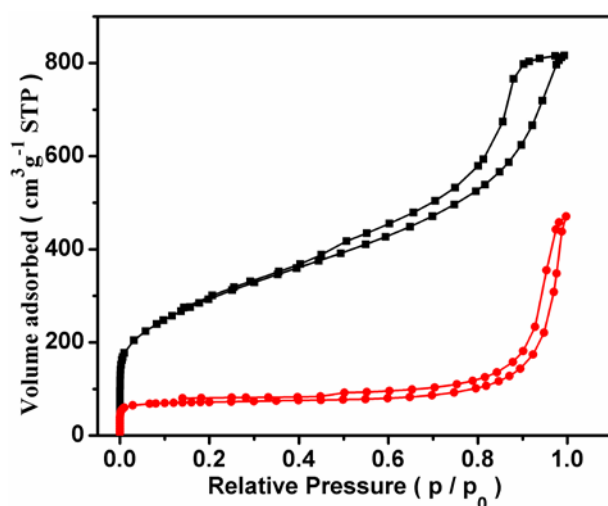


Figure S3. The nitrogen adsorption/desorption isotherms at 77 K of the Co-N-P-C and Co-N-C.

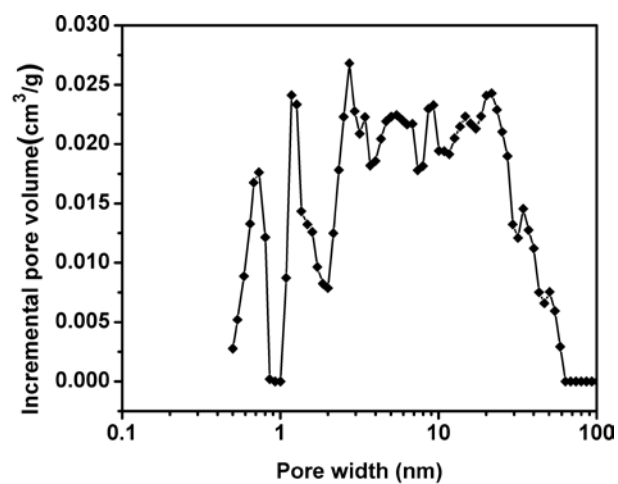


Figure S4. Pore size distribution curve of the Co-N-P-C.

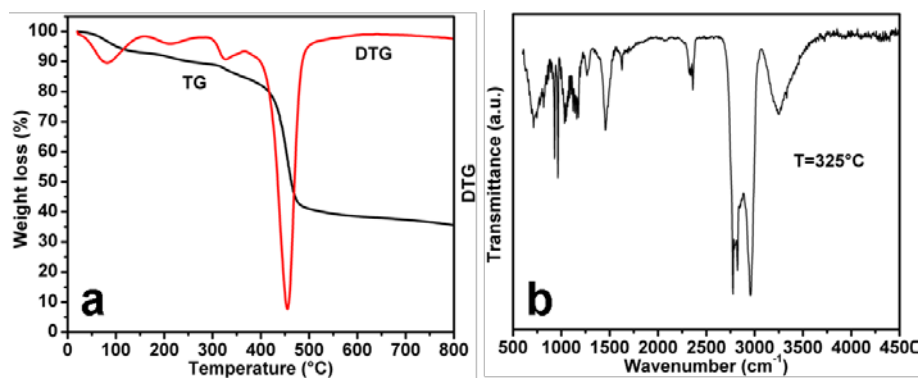


Figure S5. TG-DTG of the aminophosphonic acid resin and FTIR spectrum of corresponding pyrolysis products at 325 °C.