

Cobalt-based ZIF-68 and ZIF-69 as precursors for non-platinum electrocatalysts for oxygen reduction

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1. Electron microscopy

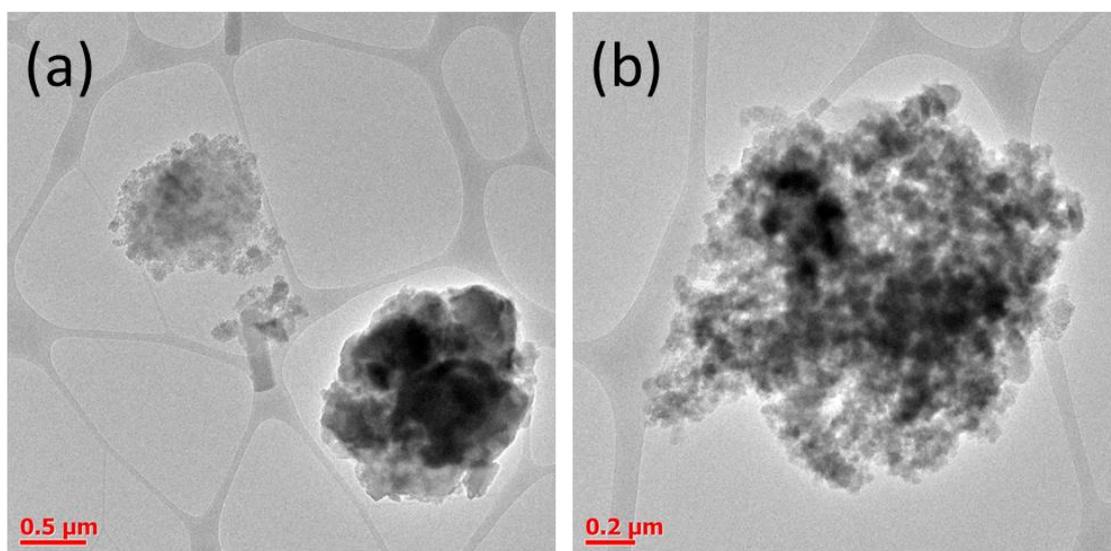


Figure S1. TEM images of CoZ-68 at different magnifications.

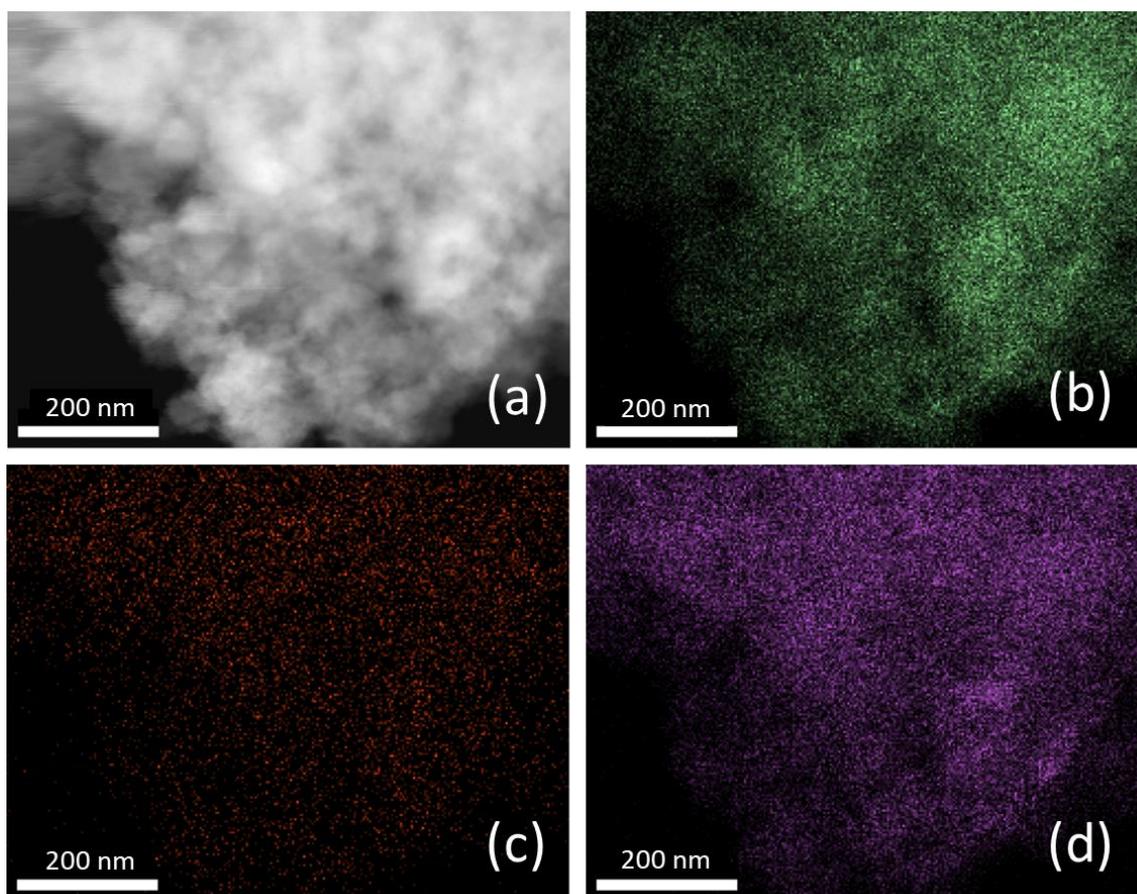


Figure S2. STEM-EDX mapping of CoZ-68: (a) TEM micrograph, (b) N *K*-edge, (c) Fe *K*-edge and (d) Co *K*-edge.

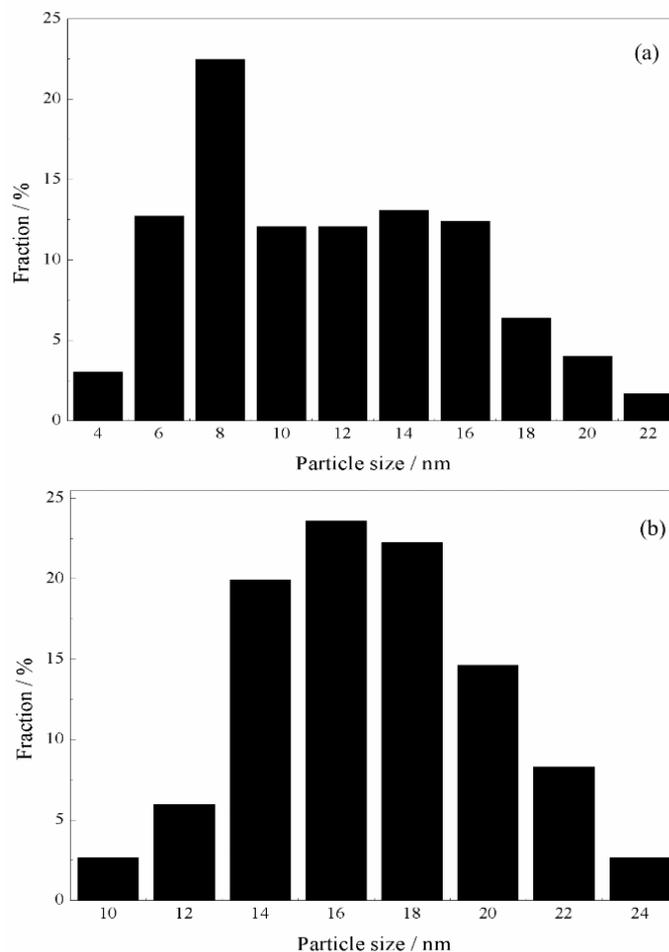


Figure S3. Particle size distributions for (a) CoZ-68-C and (b) CoZ-69-C.

2. Diffractometry

Experimental. Rigaku SmartLab diffractometer with CuK α radiation (wavelength $\lambda = 1.5406 \text{ \AA}$) and a Ni filter was used. It was operating in the Bragg–Brentano focusing geometry at standard 40 kV voltage and 30 mA current. ZIFs were measured between the $5\text{--}80^\circ 2\theta$ with a step of 0.02° , while carbons were recorded between the $20\text{--}120^\circ 2\theta$ with a step of 0.01° .

Diffraction peaks for **CoZ-68** are located at $2\theta = 6.1^\circ, 6.6^\circ, 7.6^\circ, 9.0^\circ, 9.5^\circ, 10.2^\circ, 11.2^\circ, 11.6^\circ, 12.5^\circ, 13.3^\circ, 14.4^\circ, 14.7^\circ, 16.1^\circ, 16.8^\circ, 17.6^\circ$.

Diffraction peaks for **CoZ-69** are located at $2\theta = 6.3^\circ, 7.0^\circ, 8.1^\circ, 9.3^\circ, 10.7^\circ, 11.6^\circ, 12.9^\circ, 13.9^\circ, 14.4^\circ, 15.2^\circ, 16.0^\circ, 16.7^\circ, 17.4^\circ, 18.4^\circ$.

3. Porosimetry

Measured N₂ adsorption-desorption isotherms (Figure 2) are of Type I (IUPAC) with a slight hysteresis loop. The surface areas for CoZ-68 and CoZ-69 were found to be 581 m²/g and 690 m²/g according to BET theory, 703 m²/g and 834 m²/g according to Langmuir theory. The larger surface area of CoZ-69 may cause higher uptake of the iron(II) complex with 1,10-phenanthroline in the impregnation process leading to the bigger nanoparticles in CoZ-69-C.

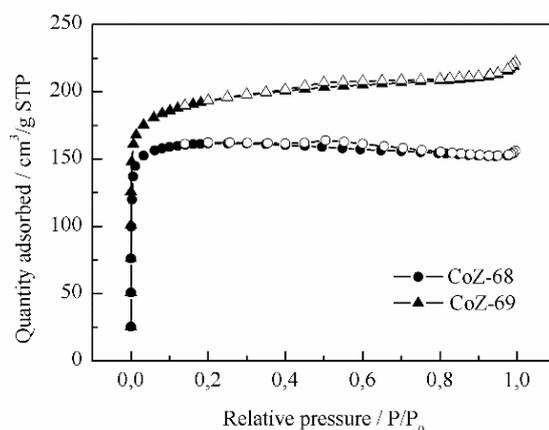


Figure S4. N₂ adsorption-desorption isotherms for the ZIF samples.

4. Raman spectroscopy

Experimental. The Raman spectra were recorded using a LabRam HR Evolution Raman Spectrometer (Jobin-Yvon Horiba Scientific) with the excitation line of $\lambda = 532$ nm and the laser power of 350 μ W. Detection was achieved with a confocal microscope equipped with an air-cooled CCD detector and a grating 600 grooves/mm. The confocal aperture was adjusted to 150 μ m and a 50 \times objective of 0.75 numerical aperture was used. After changing the excitation wavelength and before recording the spectrum of a new sample, the calibration of the spectrometer is checked by using the line at 521 cm^{-1} of the silicon sample.

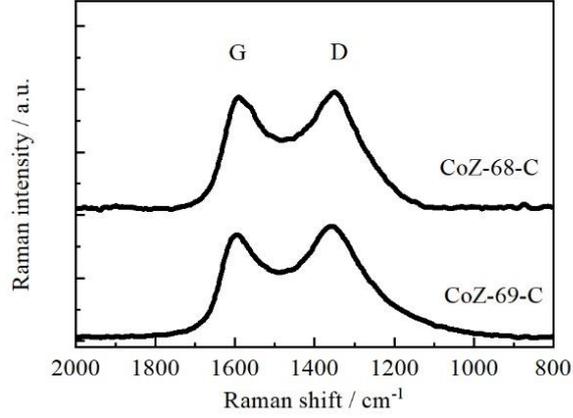


Figure S5 Raman spectra of pyrolyzed carbons.

5. The Koutecky-Levich equation

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{0.62nFD^{2/3}\nu^{-1/6}C_0\omega^{1/2}},$$

where j is the measured current density, j_k is the kinetic current density, j_d is the diffusion-limiting current density, n is the electron transfer number, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the saturated concentration of O_2 in the electrolyte ($C_0 = 1,26 \times 10^{-6} \text{ mol cm}^{-3}$), D is the diffusion coefficient of O_2 in the electrolyte ($D = 1,93 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity of the electrolyte ($\nu = 1,009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), and ω is the angular rotation rate of the electrode ($\omega = 2\pi N \text{ rad s}^{-1}$, N is the linear rotation rate).