Comparative Study of Bimetallic Cu/Co MOF Synthesis Strategies and Their Electrochemical Features

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1.1 Characterization

The crystal structure of the all-active materials was analyzed by X-ray diffraction (XRD) using a (PANalytical X'pert Pro MRD) with Cu Kα radiation (1.5406 Å). The microstructure of the active material observed using field-emission scanning electron microscopy (FE-SEM) images was obtained at an accelerating voltage of 10 kV with FE-SEM-4800. Element composition and surface properties were investigated by X-ray photoelectron spectroscopy (XPS) (ThermoFisher). For transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements, all samples were sonicated using a C_2H_5OH solution and suspended on a copper grid (400-mesh, with 3.5-mm diameter) with a high-resolution transmission electron microscope (H-7600; Hitachi Inc., Japan) accelerating 120 kV microscope.

1.2 Electrochemical test

All the electrochemical measurements were carried out on a Biologic Sp-200 electrochemical workstation with a standard three-electrode setup. As-synthesized CC-1-3 samples were used as the support for the working electrode. The Hg/HgO electrode and Platinum mesh served as the reference electrode and the counter electrode, respectively. CV, galvanostatic charge-discharge (GCD), and EIS were used to assess the electrochemical activity of the electrodes. The CV tests were performed at several scan rates, ranging from 2 to 150 mV s-1 at a potential of 0 to 0.6 V. The GCD tests were executed in a 1 M KOH electrolyte within the range of 0 to 0.55 V versus Hg/HgO at various current densities. The EIS measurements were conducted over a frequency range of 1 MHz to 100 Hz at an open circuit potential. All the electrochemical experiments were performed on a Biologic SP-200 electrochemical workstation in a 1 M KOH solution.

1.4 Preparation of gel electrolyte (PVA/KOH)

To prepare the alkaline PVA/KOH gel electrolyte, 3 g of polyvinylalcohol was dissolved in 24 mL of pure deionized water at 90 °C with continuous and vigorous stirring to obtain a clear solution. After 1 h, we obtained a clear viscous solution. KOH (3 g) was liquefied in 6 mL deionized water and then dropped into the cleared PVA solution with continuous stirring until complete dissolution and the formation of a gel-like solution. Finally, the PVA/KOH gel electrolyte was cooled to room temperature for further use.

1.3 Asymmetric and Symmetric Device Fabrication

For an aqueous symmetric supercapacitor, the CC-1 sample was used as both positive and negative electrodes, whereas, for the asymmetric device, CC-1 was positive and AC was a negative electrode. The wide potential window of 0-1.4 V was applied for the two-electrode system and gel electrolyte was used as the electrolyte. The electrode (7 mg of active material (80%), 2 mg of carbon black (10%), and 1 mg of PVDF (10%)) paste was coated on 12 mm diameter of Ni foam. The paste was then coated on the respective electrodes, and heated at 80°C for 12 h.

Specific capacitance (C_s) of CC-1-3 electrodes were evaluated from GCDs with the help of succeeding equivalence:

$$C_s = \frac{I.\Delta t}{m.\,\Delta V} \text{ F/g} \qquad \text{(E1)}$$

I is constant current, I_d is current density, Δt is discharging time, m is the mass of active material, V is potential, and ΔV is potential change.

The energy density (ED) in Wh/kg associated with a power density (PD) in W/kg of asymmetric supercapacitor were calculated from the GCD curves by using the following equations:

$$ED = \frac{0.5 C_s V^2}{3.6} \text{ Wh/Kg} \qquad \text{(E2)}$$

$$PD = \frac{3600\ ED}{\Delta t} \text{ W/kg} \qquad \text{(E3)}$$

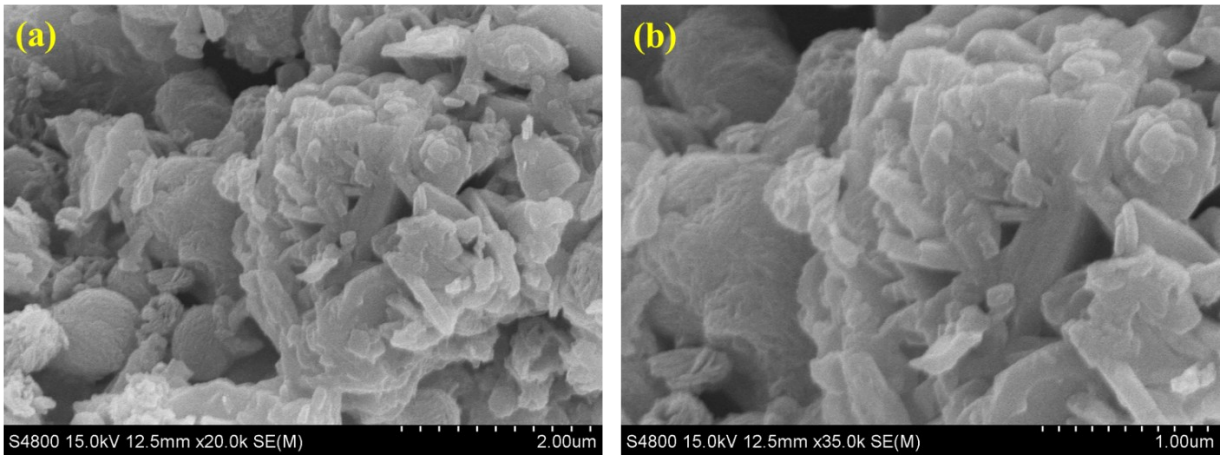

Fig. S1 FESEM image of CC-1 after the stability test.

Table: S1 Comparison of electrochemical activity of CC-1-3 electrodes and other popular MOF-based electrodes in previous reports.

Materials	**Electrolyte**	**Scan rate or Current density (A/g)**	**Specific Capacitance (F/g)**	**References**
Cu-MOF/rGO	1 M Na_2SO_4	0.8	462	[1]
Co-Ni-MOF	6 M KOH	1	650	[2]
CuMOF	6 M KOH	0.5	1148	[3]
Ni-Co-MOF	3 M KOH	1	236.1 mAh/g	[4]
Co-MOF/rGO	6 M KOH	1	430	[93]
Ni@CoNi-MOF	6 M KOH	1 A/cm^2	772 C/cm^2	[5]
Ni-MOF-5/rGO	1 M KOH	1 mV s^{-1}	758	[6]
Cu MOF/rGO	PVA−Na_2SO_4	1	385	[7]
UIO-66/rGO	6 M KOH	0.15	302	[8]

PANI-ZIF-67-CC	3 M KCl	10 mV/s	21.46 mF/cm^2	[9]
Zn-Ni MOF	6 M KOH	0.25	1620	[10]
CC-1	1 M KOH	1	438	[This work]
CC-2	1 M KOH	1	383	[This work]
CC-3	1 M KOH	1	289	[This work]

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