

Electronic Supplementary Information

Nano Bowl-like Cobalt-Cobalt Molybdenum Carbide Coated by N, P co-doped Carbon as Advanced Bifunctional Oxygen Electrocatalyst for Rechargeable Zn-air battery

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1. Experimental Section

1.1 Synthesis of CoMo-MOF and Co-MOF

The CoMo-MOF was synthesized according to the following procedure: 4 mmol of 2-methylimidazole was dissolved into 40 mL of N, N-dimethylformamide, and 1 mmol of cobalt acetate and 300 mg of phosphomolybdic acid was dissolved into another 40 mL of N, N-dimethylformamide. Then the two solution was mixed and stirred at room temperature for 24 h. Afterword, the precipitate was collected via centrifugation and washed with ethanol for three times. For comparison, Co-MOF was synthesized using the similar procedure without adding phosphomolybdic acid.

1.2 Synthesis of Co-Co₆Mo₆C₂@NPC and Co@NC

Co-Co₆Mo₆C₂@NPC and Co@NC were prepared by directly annealing the CoMo-MOF and Co-MOF in N₂ atmosphere at 800 °C for two hours.

1.3 Structure characterization

The crystal phases of the synthesized materials were examined using X-ray diffraction (XRD) on a Lab XRD-7000s System using a Cu K α radiation ($\lambda=0.1542$ nm). The micro-morphology and element analysis were conducted with a Nova Nano SEM 450 scanning electron microscope (SEM) and transmission electron microscopy (TEM, JEOL-2100F). The chemical composition of catalysts was measured using an X-ray photoelectron spectrometer (XPS) equipped with Al K α radiation.

1.4 Electrochemical measurements

Electrochemical measurements were conducted using a conventional three-electrode electrochemical set-up. Ag/AgCl (saturated) electrode and a graphite rod were used as

reference and counter electrodes, respectively. Catalyst loaded glass carbon electrode is used as the working electrode. The catalyst ink was prepared by dispersing 4 mg of the catalyst into a mixture solution of 960 μL isopropanol and 40 μL Nafion under sonication. Then, 20 μL of the catalyst ink was dipped onto working electrode for measurement.

The Zn-air batteries was fabricated using catalyst loaded carbon paper (1 mg cm^{-2}) as the air cathode and polished Zn foil as anode. The electrolyte is 6.0 M KOH solution containing 0.2 M zinc acetate. The data were collected using a Land-CT2001A testing system.

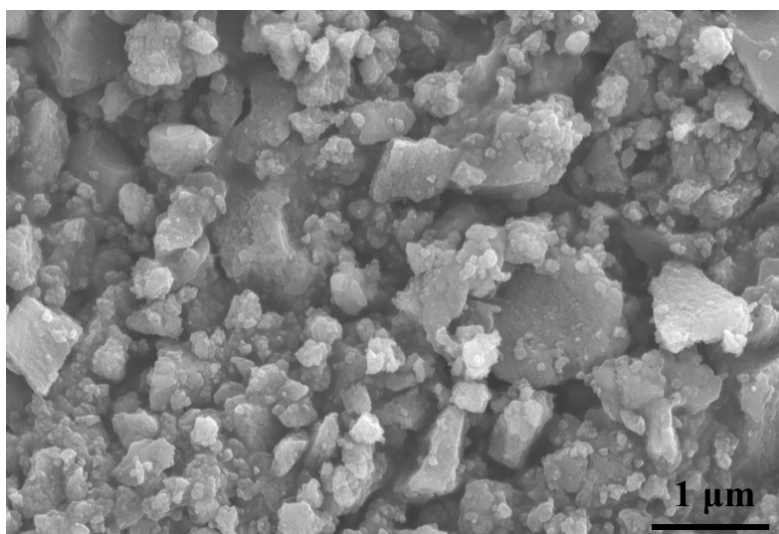


Figure S1 SEM image of Co-MOF.

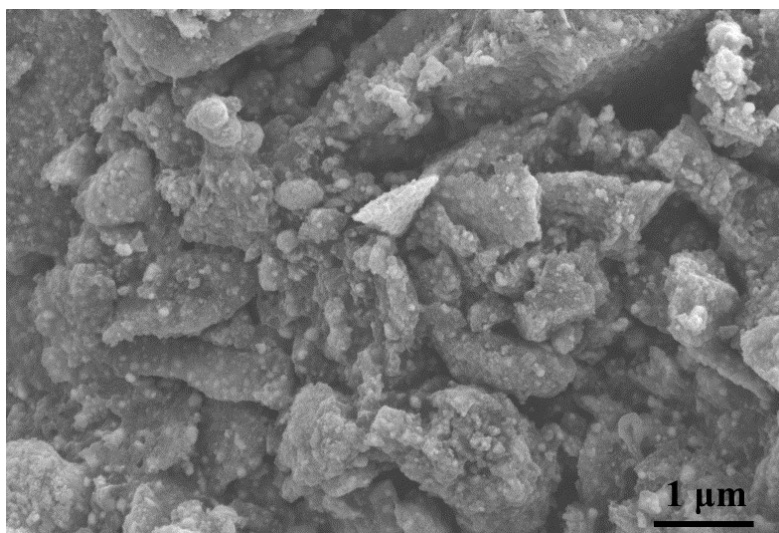


Figure S2 SEM image of Co@NC.

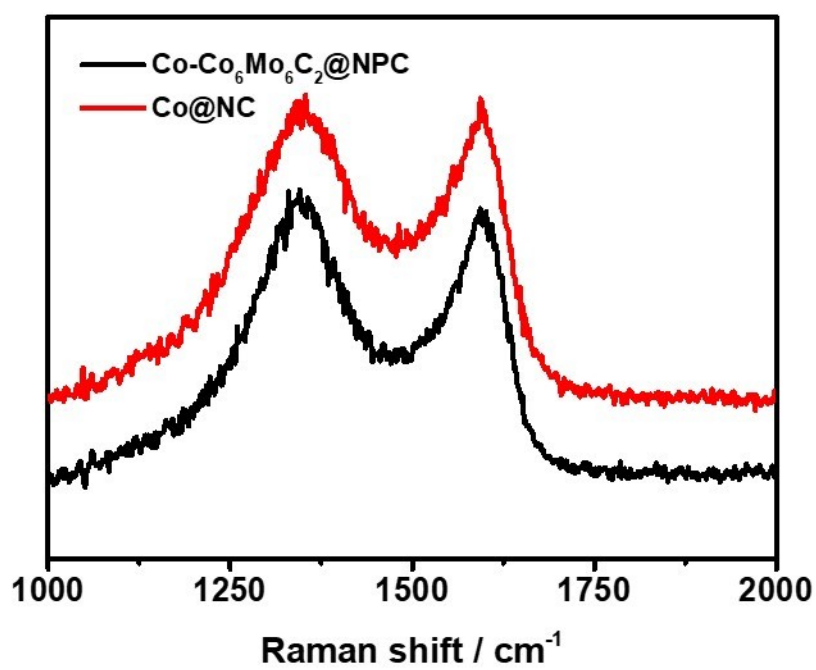


Figure S3 Raman spectra of Co-Co₆Mo₆C₂@NPC and Co@NC.

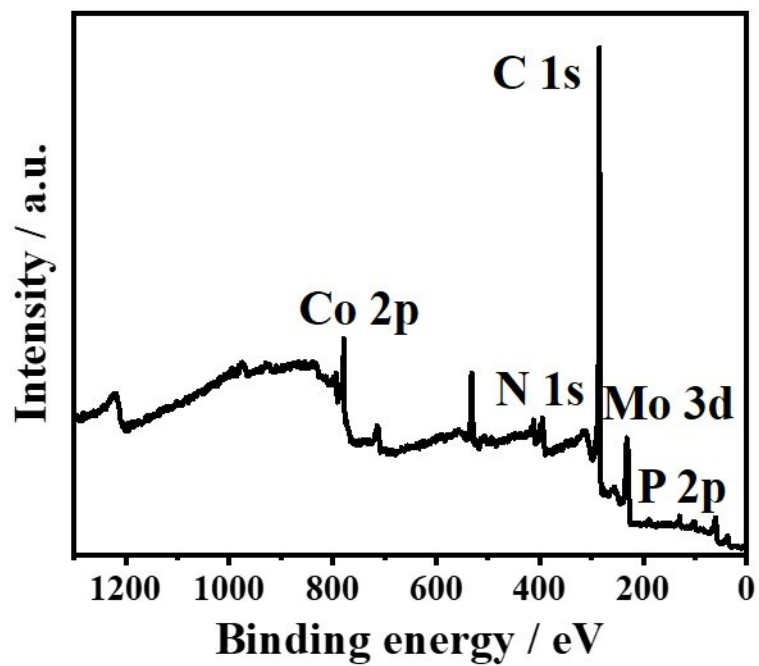


Figure S4 XPS survey spectra of Co-Co₆Mo₆C₂@NPC.

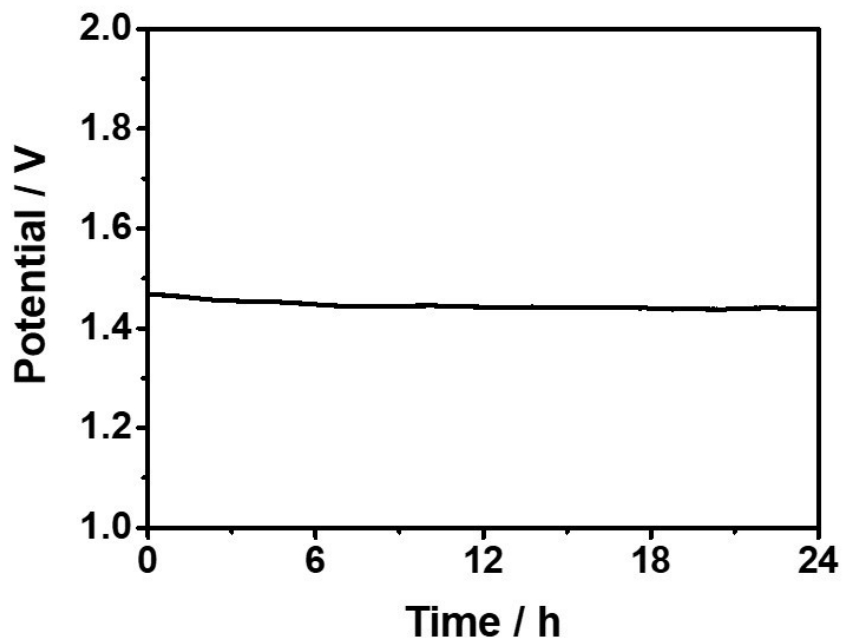


Figure S5 Stability of Co-Co₆Mo₆C₂@NPC for OER.

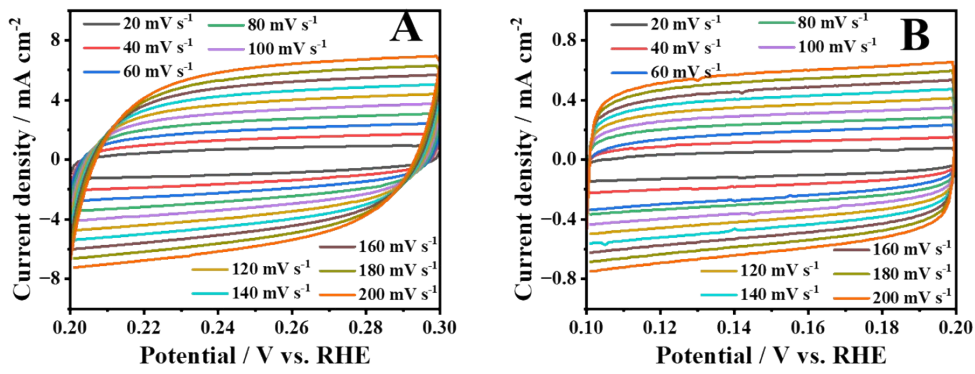


Figure S6 CV curves of Co-Co₆Mo₆C₂@NPC (A) and Co@NC (B).

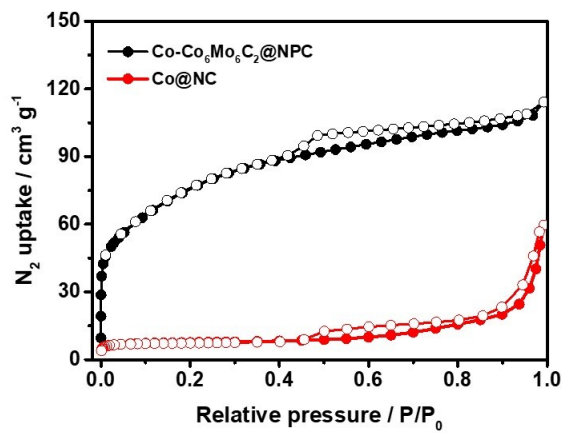


Figure S7 N₂ adsorption-desorption curves of Co-Co₆Mo₆C₂@NPC and Co@NC.

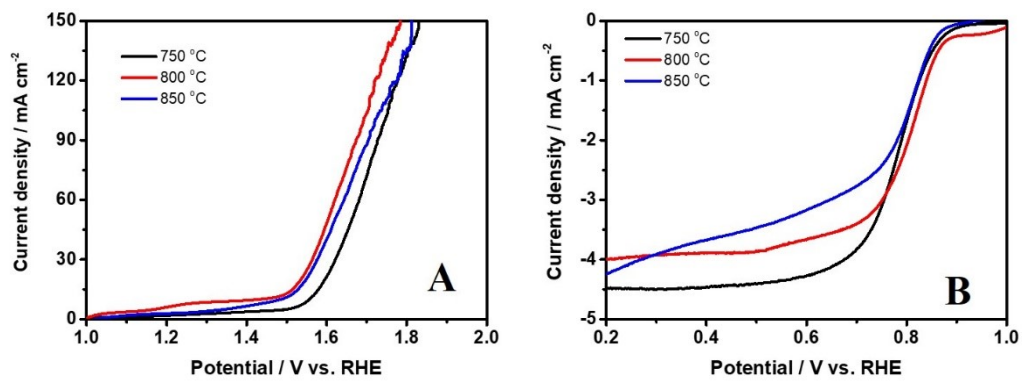


Figure S8 LSV curves of Co-Co₆Mo₆C₂@NPC for OER (A) and ORR (B) obtained at different temperatures.