

Electronic Supplementary Information

Water Oxidation Electrocatalysis by a Zeolitic Imidazolate Framework

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Experimental section

Chemicals

Chemical reagents used for the synthesis of Co-ZIF-9 catalyst and water oxidation reactions were all purchased from Alfa Aesar without further purification, including $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, benzimidazole (H-PhIM), N,N-dimethylformamide (DMF), dichloromethane, KH_2PO_4 , K_2HPO_4 and Nafion D520 dispersion (5% w/w in water and 1-propanol). All the solutions were prepared with Mill-Q ultrapure water (> 18) unless stated otherwise.

Instruments

X-ray diffraction (XRD) patterns was obtained on a Bruker D8 Advance instrument (Cu $K\alpha 1$ irradiation, $\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 KV and 40 mA, respectively. Data were collected at a scanning rate of $0.02^\circ 2\theta/\text{s}$ in the 2θ region of $5\text{-}50^\circ$. Fourier transformed infrared (FTIR) measurement was conducted on a Nicolet Magna 670 FTIR spectrometer in KBr at a concentration of ca. 1 %wt. Morphology of Co-ZIF-9 was characterized by Hitachi New Generation SU8010 field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) image and energy dispersive X-ray spectrum (EDX) were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV with the sample supported on a copper grid. Thermal gravimetric analysis was performed on a Netzsch STA 449 F3 Thermoanalyzer with a heating rate of $10^\circ\text{C}/\text{min}$ from 20°C to 1000°C under a helium atmosphere. X-ray photoelectron spectroscopy (XPS) measurement was

carried out on a PHI Quantum 2000 XPS system with a monochromatic Al K α source and a charge neutralizer. Elemental analysis was conducted on an Elementar Vario EL CUBE elemental analyzer (Hanau, Germany). A QxySense* System (OxySense Gen III 300 Series, Texas) was employed to test the oxygen gas produced quantitatively.

Synthesis of Co-ZIF-9

In the synthesis,¹ Co(NO₃)₂·H₂O (0.210 g) and benzimidazole (0.060 g) were dissolved in 18 ml DMF and capped in a 20 ml glass vial after stirred for 30 min. The vial was placed in a programmed oven, heated to 130 °C from the room temperature with a heating rate of 5 °C/min and held at this temperature for 48 h. Then the vial was cooled to the room temperature at 0.4 °C/min. The purple cubic crystal were separated from the mother liquor, washed thrice with DMF and dichloromethane, and allowed to dry under vacuum at 200 °C. The yield for the synthesis of Co-ZIF-9 was *ca.* 30% (based on the ligand benzimidazole), which is consistent with the results of the literature.¹

Elemental analysis of Co-ZIF-9 (C₁₇H₁₉N₅O₂Co = Co(PhIM)₂·(DMF)(H₂O)).

Calcd.: C, 53.13; H, 4.98; N, 18.22.

Found: C, 54.07; H, 4.97; N, 18.76.

DFT calculation

Theoretical calculations were carried out using DFT as implemented in Gaussian 09. Tao-Perdew-Staroverov-Scuseria (TPSS) functional was used with LanL2DZ basis set for Co atom and all-electron 6-31G (d, p) basis set for H, C, N, O atoms. The geometric configurations of all species were optimized at their gas phase states. Harmonic vibrational frequency analysis confirmed that the initial state and final state had no imaginary frequency and transition state structure had only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations also confirmed that the latter connected reactants and products. The

gas-phase free energies, G , were obtained at $T = 298.15$ K at optimized structures. The effect of solvent was taken into account by single point calculations on gas-phase optimized structures using integral equation formalism polarizable continuum model (IEFPCM) for water ($\epsilon = 78.3553$). The energies mentioned in the text are free energies with solvent corrections.

Electrochemical measurements

The working electrode was prepared on a fluorine-doped tin oxide transparent conductive film glass. Co-ZIF-9 powder (3 mg) and Nafion solution (40 μ L) were mixed with 1 mL ethanol under sonication for 30 min to get slurry. The slurry was spread onto FTO glass whose side part was previously covered by Scotch tape, and the electrode was dried in air for 24 h. The side part of the FTO glass was connected with a copper wire using conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. Electrochemical measurements were performed in a typical three electrode cell, using a graphite rod and an Ag/AgCl electrode as counter electrode and reference electrode, respectively. The electrochemical experiments were taken on a ZAHNER Zennium workstation. The sweep rate for CVs was 10 mV/s unless otherwise stated. The electrolyte was a 0.1 M potassium phosphate buffer (pH = 7.0) aqueous solution without additive and was purged with argon gas for 30 min prior to the measurements. For pH dependent experiments, the potassium phosphate buffers were adjusted by KOH or H_3PO_4 to obtain the electrolytes with required pH values. During the experiments, the solution was not stirred unless otherwise stated. The reaction temperature was controlled at 20 °C by cooling water.

Faradaic efficiency tests

Electrolysis was performed in a gas-tight electrochemical cell using high surface Pt mesh and Hg/HgSO₄ (saturated) as the counter electrode and the reference electrode, respectively. Before the measurements, the solution was purged with argon gas for long time to completely remove the oxygen gas in the system. The

produced O₂ was detected by a QxySense* System with a sensor placed in the headspace of the reaction cell. The experiments were conducted at room temperature and stirred during the reaction.

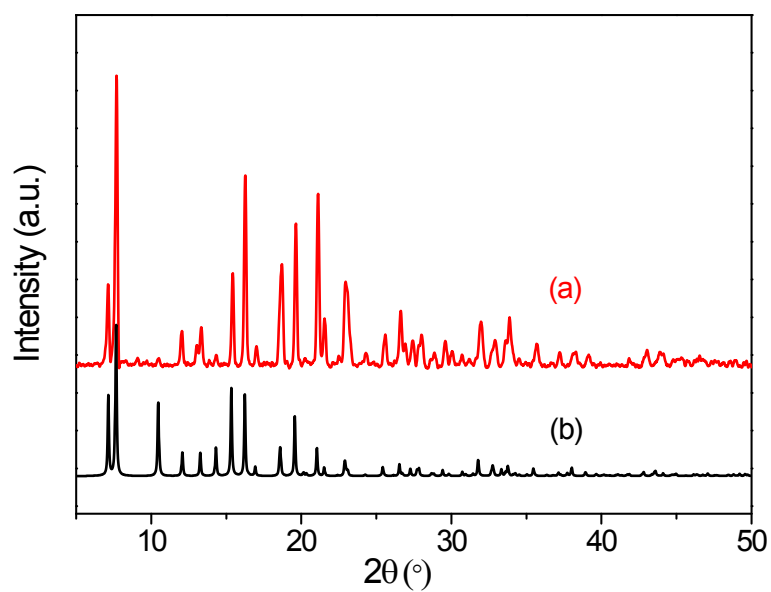


Figure S1. XRD patterns of Co-ZIF-9: (a) as-prepared; (b) simulated. The accurate match of the XRD patterns firmly validates the successful synthesis of the Co-ZIF-9 catalyst.

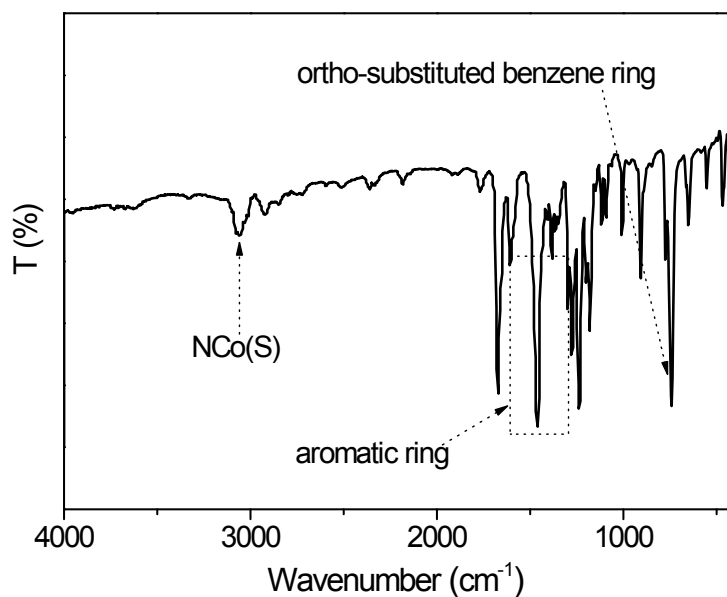


Figure S2. FTIR spectra of the Co-ZIF-9 catalyst and the benzimidazole ligand. The absence of the strong and broad peak (3400-2200 cm⁻¹) of N-H...N hydrogen bond, and the medium bend vibration peaks (1650-1580 cm⁻¹) of N-H group indicated the complete deprotonation of the benzimidazole linkers during solvothermal crystallization, which provides a proof of the well development of Co-ZIF-9 structure.¹



Figure S3. FESEM image of the Co-ZIF-9 catalyst.

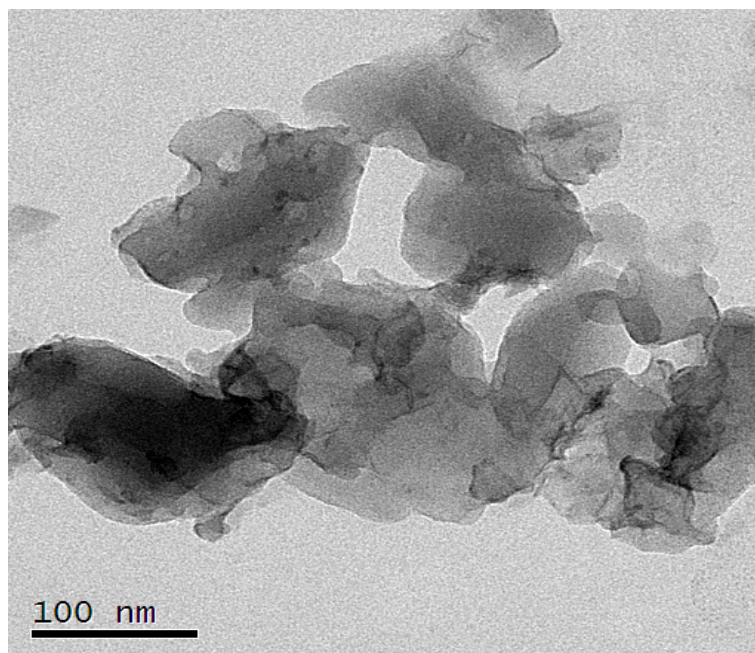


Figure S4. TEM image of the Co-ZIF-9 catalyst.

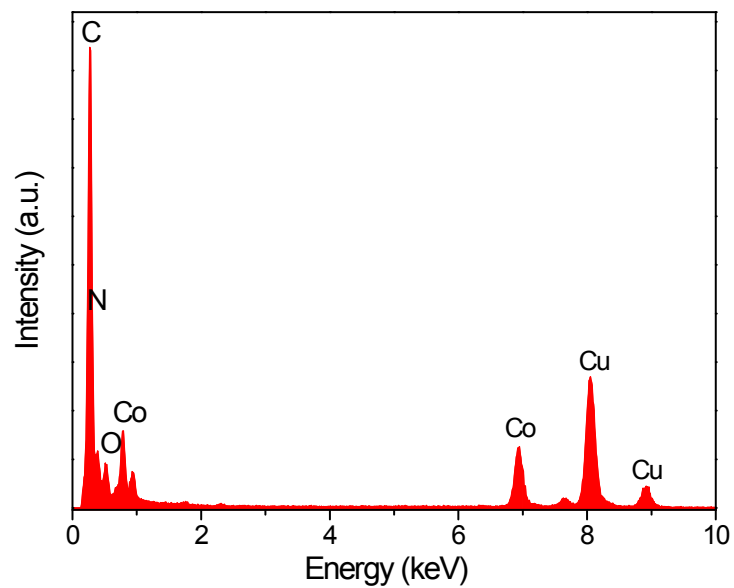


Figure S5. EDX spectrum of the Co-ZIF-9 catalyst. The presences of Cu peaks were originated from the sample supporter of copper grid.

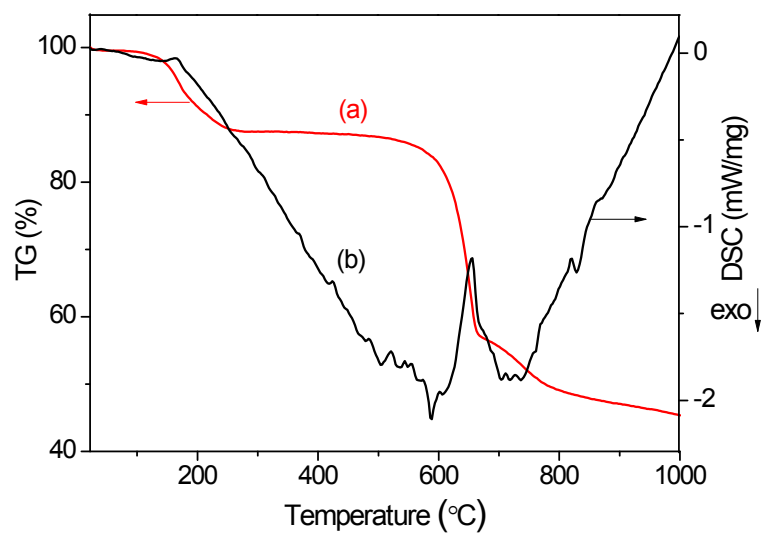


Figure S6. STA of Co-ZIF-9: (a) TG; (b) DSC. Note that the first weight loss at 50-210 °C in TG is attributed to desorption of water and organic solvents trapped in the pores.

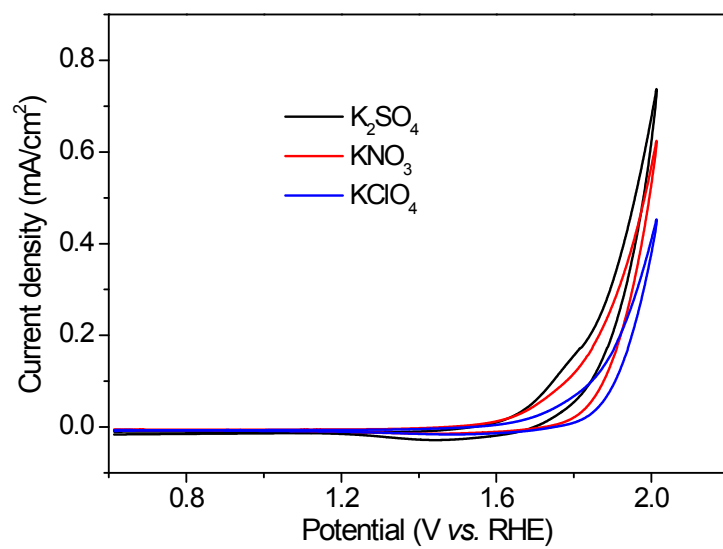


Figure S7. CVs of Co-ZIF-9/FTO electrode obtained in K₂SO₄ (0.1 M, pH = 7.0, black line), KNO₃ (0.1 M, pH = 7.0, red line) and KClO₄ (0.1 M, pH = 7.0, blue line) solution.

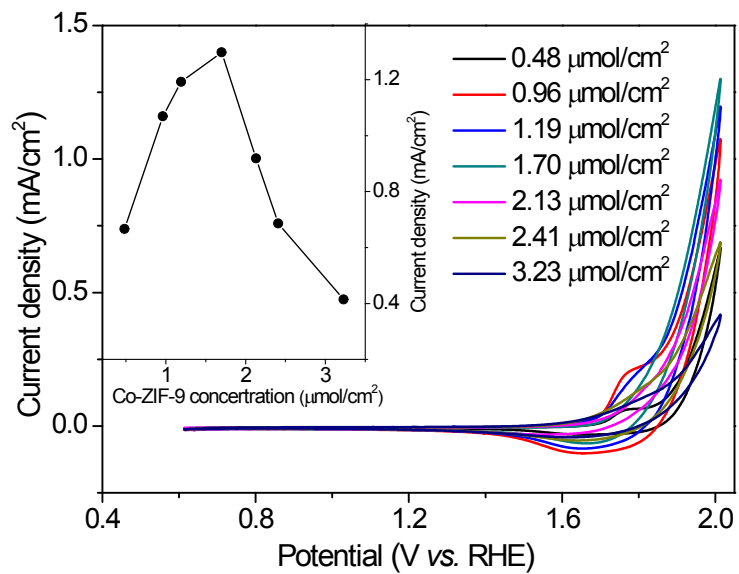


Figure S8. CVs of Co-ZIF-9/FTO electrodes with different concentration of Co-ZIF-9 in 0.1M potassium phosphate buffer (pH = 7.0). Insert: Plot of catalytic current density at 1.9 V (vs. RHE) versus the concentration of Co-ZIF-9.

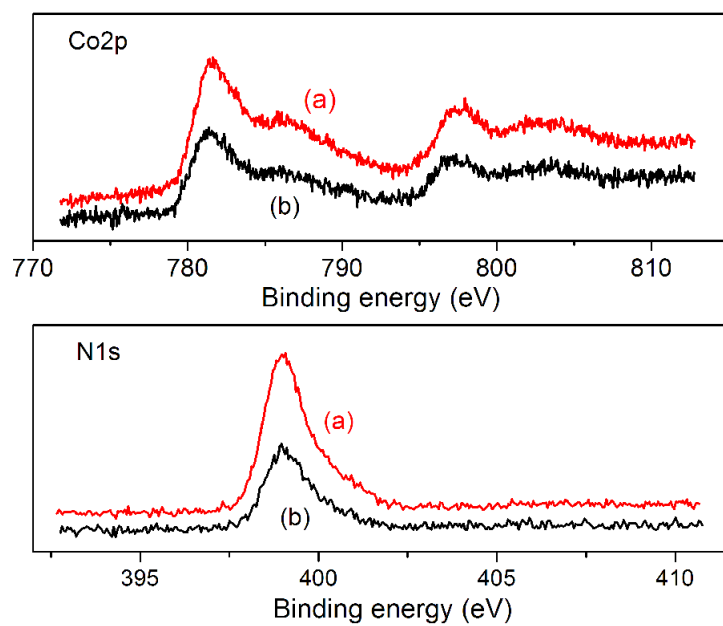


Figure S9. Co2p and N1s XPS spectrum of the catalyst Co-ZIF-9 before (a) and after (b) CV scans.

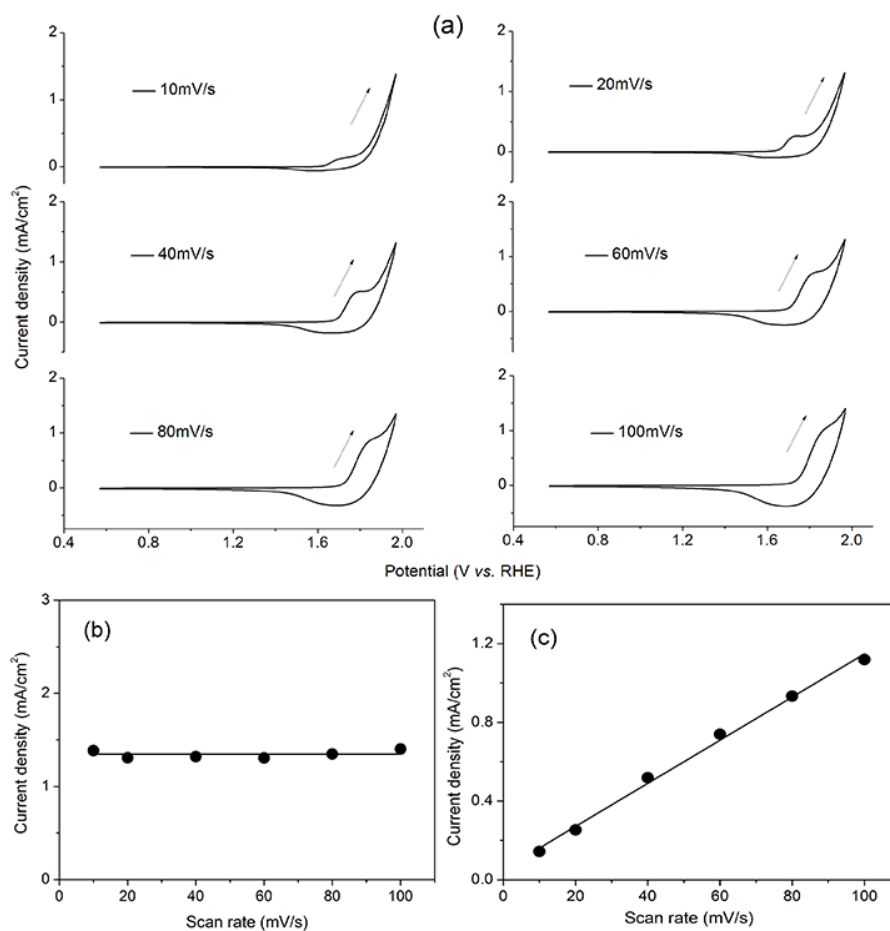


Figure S10. (a) CVs of Co-ZIF-9/FTO electrode in 0.1M potassium phosphate buffer (pH = 7.0) at different scan rates. The arrows indicate the forward potential scan direction. (b) Plot of catalytic current density at 1.9 V (vs. RHE) versus scan rate. (c) Plot of the anodic wave current density versus scan rate.

Reference

1. K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* 2006, **103**, 10186.