Electronic Supplementary Material (ESI) for Dalton Transactions.

Hybrid zeolitic imidazolate framework-derived ZnO/$ZnMoO_4$ heterostructure for electrochemical hydrogen production

Experimental Section

Preparation of HZIF-Zn/Mo: HZIF-Zn/Mo was synthesized according to a previously reported method. Specifically, polyvinylpyrrolidone (PVP, 3.3 g) was first dissolved in N, N-dimethylformamide (DMF, 60 mL), followed by adding $Zn(CH_3COO)_2·2H_2O$ (90 mg), 2-methylimidazole (2 mim, 54 mg), and molybdic acid (H_2MoO_4, 22 mg). Thereafter, the mixture was heated at 160 °C in a Teflon-lined stainless-steel autoclave for 48 h. Finally, the obtained light green crystals were collected and washed with water, and then dried in air.

Preparation of ZIF-8: In a typical synthesis, $Zn(NO_3)_2·6H_2O$ (0.3 g) was dissolved in 5 mL of water to form clear solution, and then poured into 2.67 mole per liter 2-methylimidazole water solution (5 mL) with vigorous stirring for 24 h. The resultant white particles were separated by centrifugation at 6000 rpm and washed thoroughly with deionized water for several times and finally dried under vacuum at 60 °C for later reaction.

Preparation of $ZnO@ZnMoO_4$: The dried HZIF-Zn/Mo was grinded to powder and then placed in a porcelain boat. Subsequently, the boat was heated to 500 °C for 3 h with a heating rate of 5 °C/min. After the temperature dropped to room temperature naturally, the final white powder was collected for further measurements. The synthetic process of v-ZnO is in line with $ZnO@ZnMoO_4$ except for using ZIF-8 as precursor.

Preparation of polycrystalline zinc molybdenum oxide (PZMO): Typically, $Zn(NO_3)_2·6H_2O$ (0.6 g) and $Na_2MoO_4·2H_2O$ (0.75 g) were dissolved in a 60 mL mixed solution of ethylene glycol and polyethylene glycol ($V_{\text{ethylene glycol}}:V_{\text{polyethylene glycol}} = 1:20$). Then, the mixture was heated at 140 °C in a Teflon-lined stainless-steel autoclave for 12 h. Finally, the obtained white powder was collected and washed with water, and then dried in air.

Characterizations: The Power X-ray diffraction (XRD) and Raman data were collected on MiniFlex II diffractometer and LabRAM HR instrument, respectively. Field-emission scanning electron microscope (FESEM, JSM6700-F) and transmission electron microscope (TEM, Tecnai F20) were used to characterize the morphologies of different samples. The surface chemical states of all samples were characterized by using X-ray photoelectron spectroscopic (XPS, ESCALAB 250 xi). The porous structures of different samples were determined by N_2 sorption measurement (ASAP, 2010 analyzer).

Electrochemical measurements: All the electrochemical experiments were conducted on the CHI 760E electrochemical workstation with a standard three-electrode setup. The graphite rod and Ag/AgCl electrode are used as counter and reference electrodes, respectively. The working electrode was prepared as follow: 5 mg HER catalysts were dispersed into ethanol/nafion solution (0.5 mL, Vethanol/VNafion ≈ 9:1) to get a uniform suspension by ultrasonication for at least 30 min. Then, the above catalyst ink was dropped on a piece of clear carbon fiber paper and dried naturally to form a homogeneous membrane. The fabricated electrode is firstly activated by performing continuous cyclic voltammetry cycling (from 0.2 to -0.6 V vs. RHE) before a stable cyclic voltammetry curve was obtained. Linear sweep voltammetry is recorded with a sweep rate of 5 mV s^{-1}. All electrode potentials were adjusted to reversible hydrogen electrode (RHE). All linear sweep voltammetry curves were corrected for the *IR* contribution. The electrochemical active surface area (ECSA) was evaluated by performing cyclic voltammetry curves recorded from 0.67 to 0.87 V vs. RHE with various scanning rates.

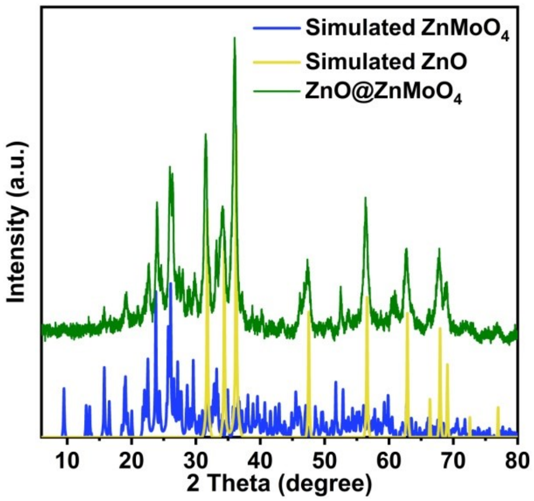


Figure S1. XRD pattern of ZnO@ZnMoO$_4$.

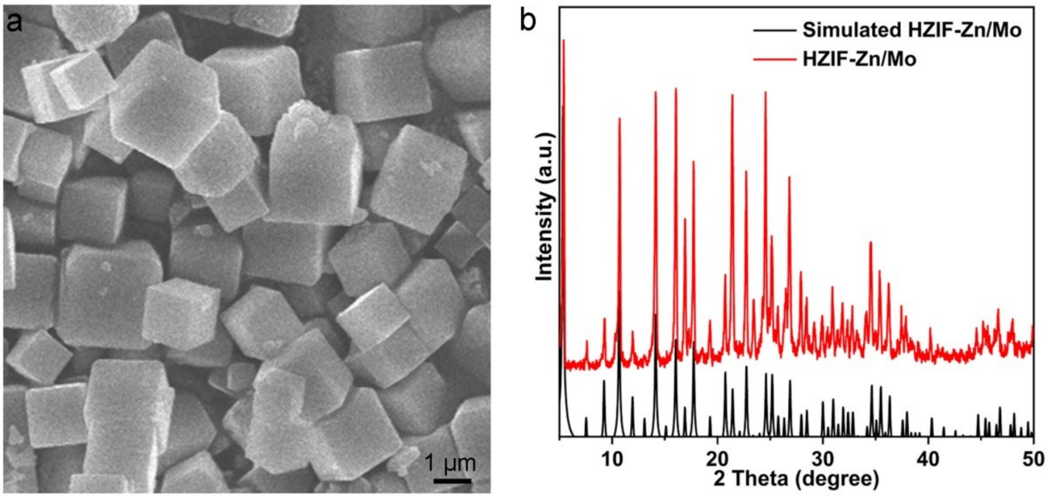


Figure S2. (a) SEM image and (b) XRD pattern of HZIF-Zn/Mo.

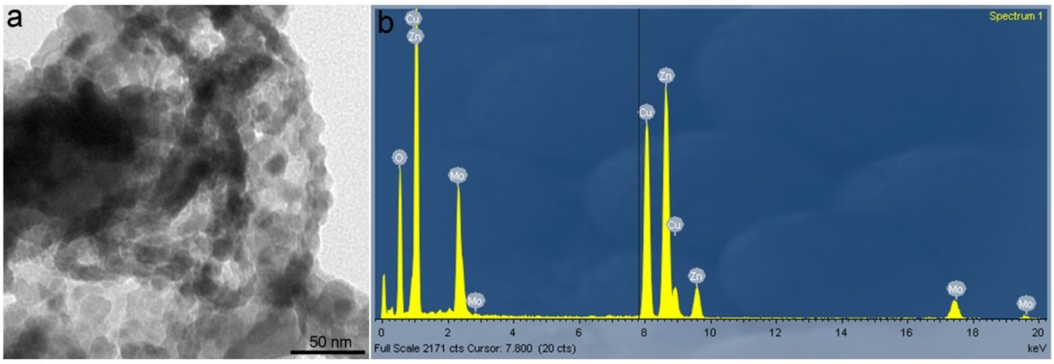


Figure S3. (a) TEM image and (b) EDS of ZnO@ZnMoO_4.

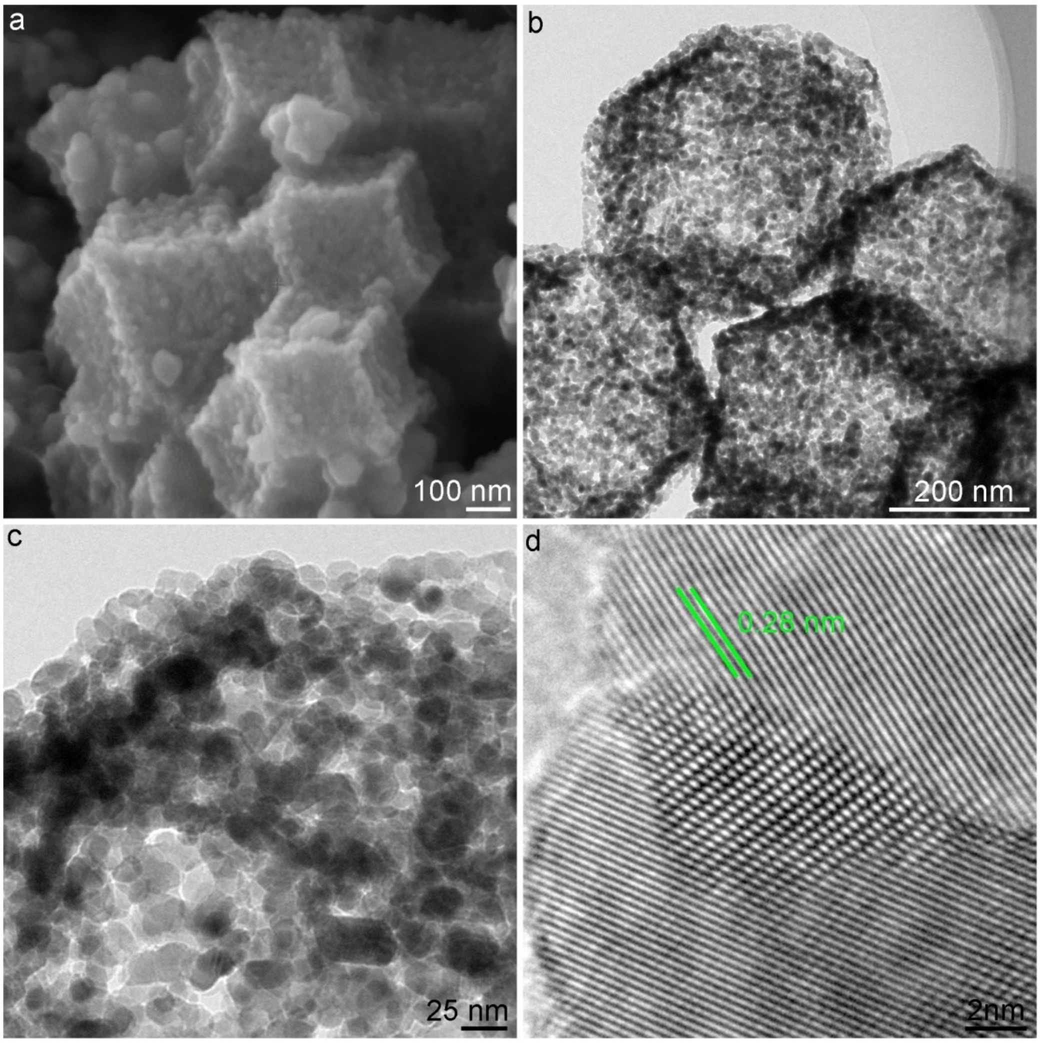


Figure S4. (a) SEM, (b and c) TEM and (d) HRTEM images of v-ZnO.

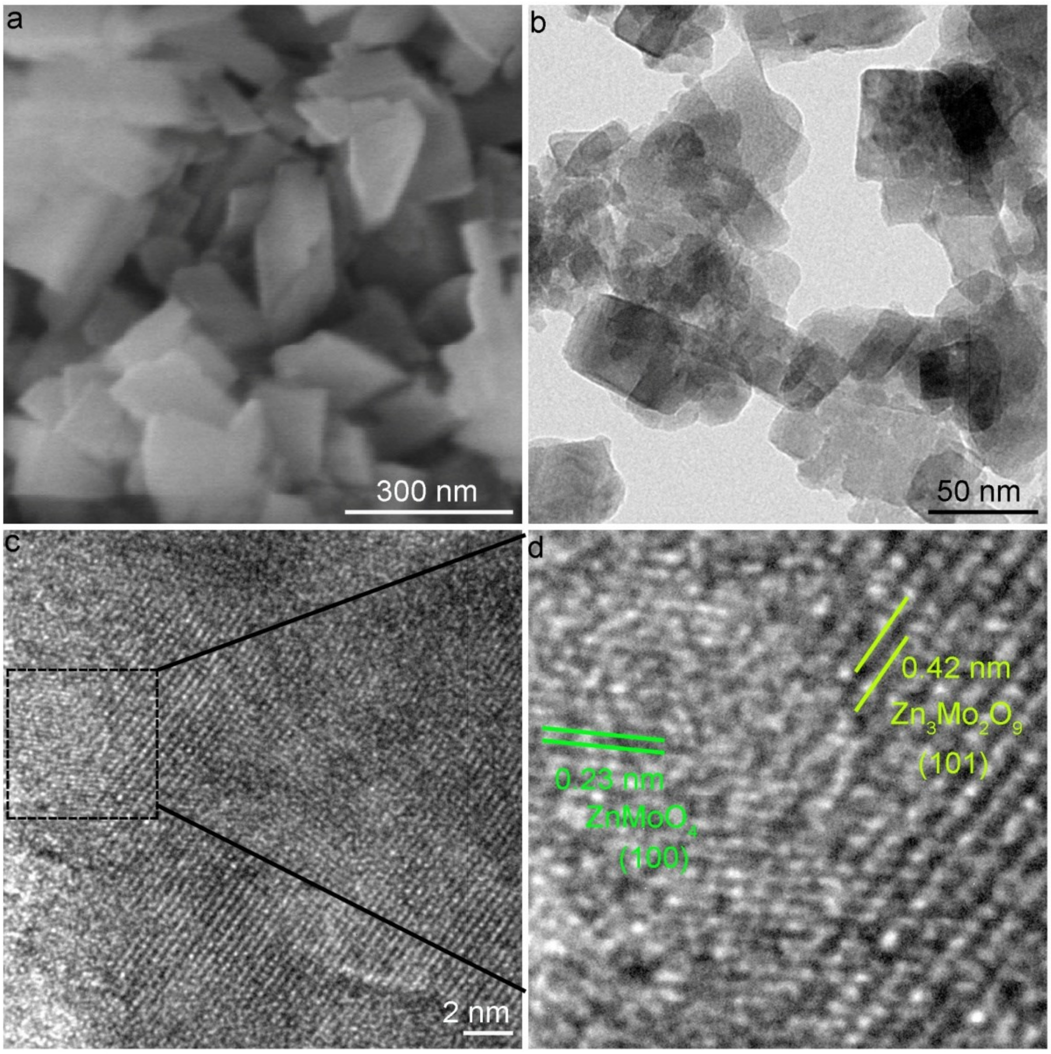


Figure S5. (a) SEM (b) TEM and (c and d) HRTEM images of PZMO.

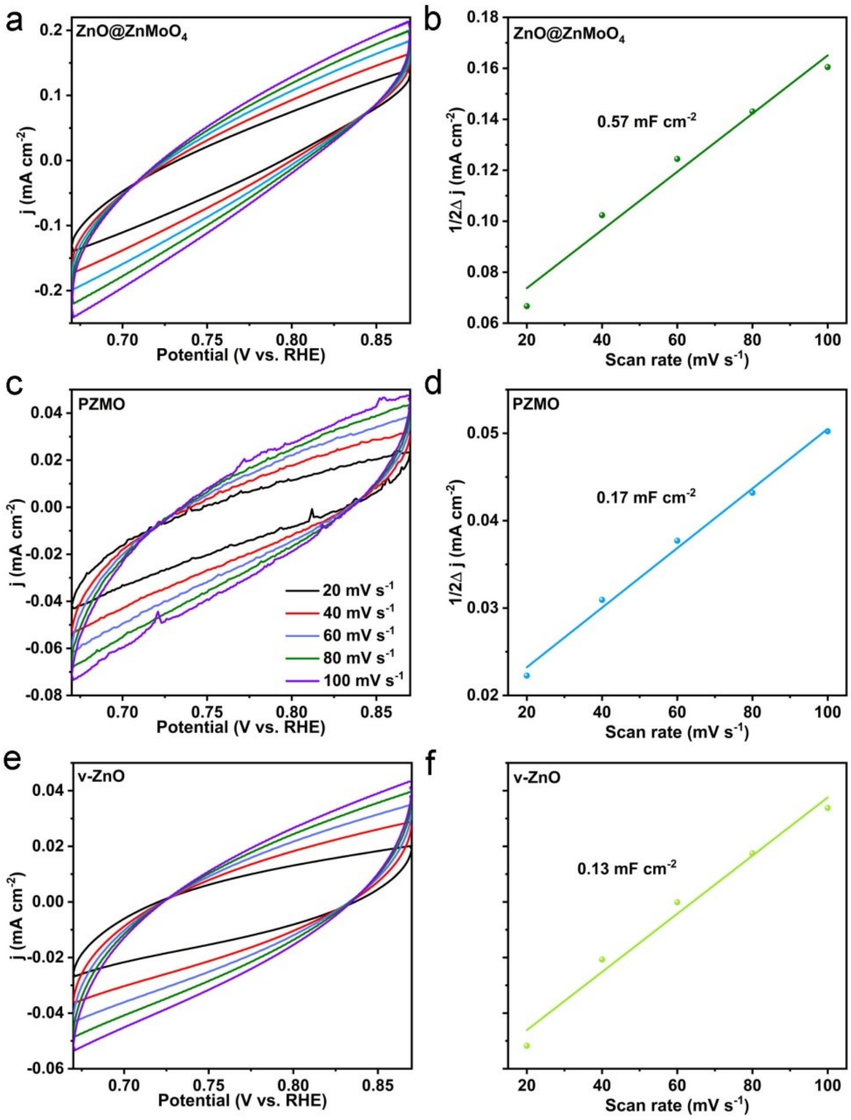


Figure S6. CV curves and calculated electrochemical double-layer capacitance of (a and b) $ZnO@ZnMoO_4$, (c and d) PZMO and (e and f) v-ZnO.

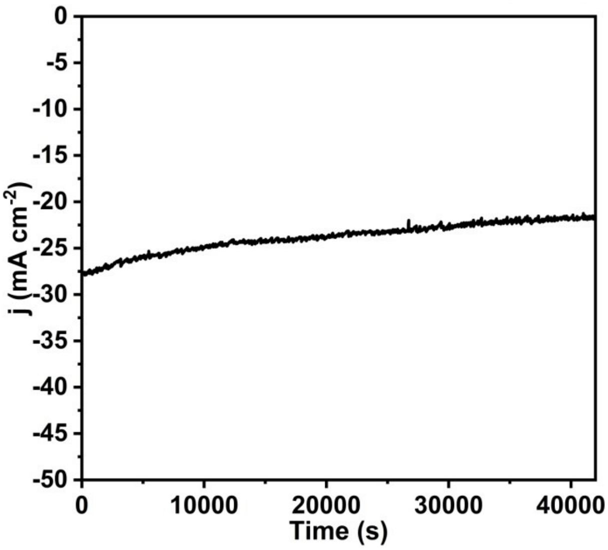
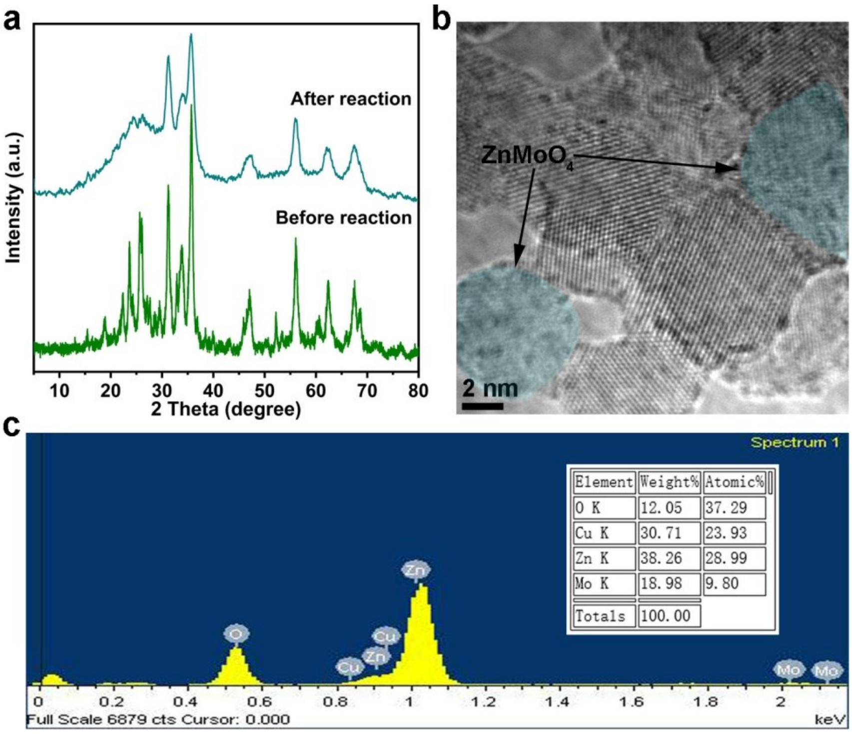


Figure S7. Time dependence of cathodic current density over ZnO@ZnMoO$_4$ during electrolysis at -0.4 V in 1.0 M KOH media.



Element	Weight%	Atomic%
O K	12.05	37.29
Cu K	30.71	23.93
Zn K	38.26	28.99
Mo K	18.98	9.80
Totals	100.00	

Figure S8. XRD, HRTEM and EDS of ZnO@ZnMoO$_4$ after durability tests.