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A hybrid zeolitic imidazolate framework-derived ZnO/ZnMoO₄ heterostructure for electrochemical hydrogen production†

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Sustainable hydrogen fuel supply through electrochemical water splitting requires highly efficient, low-cost and robust electrocatalysts. Interface engineering is of key importance to improve the catalytic performance in a heterogeneous electrocatalytic system. Herein, a porous microcubic framework composed of a ZnO/ZnMoO₄ heterostructure (ZnO@ZnMoO₄) is prepared by a hybrid zeolitic imidazolate framework-derived oxidation method, and it shows much enhanced hydrogen evolution reaction (HER) activity in alkaline media. The overpotential (at 10 mA cm⁻²) for ZnO@ZnMoO₄ is significantly reduced by 30% and 20% compared with those for virgin ZnO (v-ZnO) and polycrystalline zinc molybdenum oxide (PZMO), respectively. The enhanced electrocatalytic activity should be attributed to the ZnO/ZnMoO₄ heterostructure, which can synergistically facilitate the charge transport. This work provides a more structured design strategy for electrocatalysts for future electrochemical energy conversion systems.

Electrocatalytic water splitting into hydrogen (H₂) is a promising alternative to realize renewable energy supply and mitigate environmental issues.^{1,2} Currently, Pt and Pt-based alloys are recognized as the state-of-the-art electrocatalysts for the hydrogen evolution reaction (HER).^{3,4} However, the high price and scarcity hamper their widespread utilization. Therefore, it is urgent to develop low-cost and exceptionally effective catalysts to replace Pt and Pt-based electrocatalysts. As an earth-abundant transition metal, molybdenum (Mo)-based compounds, such as sulfides,^{5,6} carbides,⁷ nitrides,^{8,9} phosphides,¹⁰ selenides¹¹ and oxides,^{12,13} have exhibited Pt-like catalytic activity for the HER. Particularly, Mo-based bimetallic compounds

show richer redox sites compared with their Mo-based monometallic counterparts, hence a significant enhancement of the electrochemical performance is observed.¹⁴ For instance, Tran *et al.* have reported that Cu₂MoS₄ shows higher HER activity over a wide pH range than MoS₂.¹⁵ Xiong *et al.* have synthesized Co covalently doped MoS₂ (Co-MoS₂) and used it as an effective electrocatalyst for alkaline water splitting.¹⁶ Despite the great achievements, limited work is available on Mo-based bimetallic oxide (MBO) electrocatalysts for the HER.

The low intrinsic conductivity of MBO electrocatalysts limits their widespread use.¹⁷ Construction of heterostructured electrocatalysts can serve as an efficacious approach to achieve high performance in the electrocatalytic HER.^{18–20} Compared with a single catalyst, heterostructured electrocatalysts could show a combination of the strengths of their parent phases.^{21,22} Moreover, the built-in electric fields or chemical potential differences at the heterostructure can provide a driving force for charge transfer.^{23–25} Co-aggregation and epitaxial growth are two common methods for the preparation of heterostructured electrocatalysts, but tend to lower their accessible active surface area.²⁶ Therefore, it is crucial to explore new methods for realizing the nano-sized heterostructure of MBO electrocatalysts.

Metal-organic frameworks (MOFs) have emerged as an interesting class of functional materials and precursors of inorganic materials for electrochemical energy-related applications.^{27–30} As a subfamily of MOFs, Zn, Mo-based hybrid zeolitic imidazolate frameworks (HZIF-Zn/Mo) with excellent stability and porous structures demonstrate great potential in the electrocatalytic field.^{31–33} The atomic-level structural uniformity of HZIFs can realize the intergrowth of different functional materials at the molecular level under desired conditions, resulting in the construction of a Mo-based heterostructured catalyst in a flexible and controllable manner.³⁴ Zhang *et al.* have constructed an ultrasmall MoC/MoS₂ heterostructure using HZIFs as the precursor and the obtained MoCS_x heterostructure exhibits much enhanced oxygen reduction activity.³⁵ In this regard, the HZIF-assisted

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strategy can be an economical strategy for preparing heterostructured MBO electrocatalysts.

Herein, we prepared ZnO@ZnMoO₄ *via* direct oxidation of HZIFs and systematically evaluated its HER performance in an alkaline medium. The obtained ZnO@ZnMoO₄ integrates the structural advantages of different functional subunits. Specifically, the variable oxidation states of the elements in ZnMoO₄ ensure more active sites for the HER. The electrical coupling at the ZnO/ZnMoO₄ heterostructure is beneficial for electron transfer and structural stability. Moreover, benefiting from the mutual promoted action at the interface by the synergistic effect of two components, reconstructed active centers with higher intrinsic activity are established. Impressively, the obtained ZnO@ZnMoO₄ hybrid exhibits much boosted HER activity in alkaline media.

Post-annealing of the performed HZIF-Zn/Mo under air results in the formation of ZnO@ZnMoO₄. In this process, the organic moieties in HZIF-Zn/Mo are evaporated at a high temperature, whereas the Zn and Mo components react with O to form ZnO and ZnMoO₄. The X-ray diffraction (XRD) spectrum shows the coexistence of ZnO and ZnMoO₄ in ZnO@ZnMoO₄ (Fig. S1†).³⁶ Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images

show that the obtained ZnO@ZnMoO₄ retains the original cubic shape from the parent HZIF-Zn/Mo and exhibits a rougher surface (Fig. 1a–e and S2†). A closer observation of the cracked particle reveals that the interior of ZnO@ZnMoO₄ is composed of numerous loosely assembled nanoparticles (Fig. 1b and c). The formation of the loose structure probably originates from the consumption of the organic moiety in the pyrolysis process. The high-resolution TEM (HRTEM) image shows clear lattice fringes with lattice spacings of 0.28 and 0.23 nm, corresponding to the (100) and (130) crystal planes of ZnO and ZnMoO₄, respectively, revealing the formation of an intimate ZnO/ZnMoO₄ heterostructure (Fig. 1f).^{37,38} Energy-dispersive X-ray spectroscopy (EDS) investigation confirms that ZnO@ZnMoO₄ is composed of Zn, Mo and O (Fig. S3†). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) coupled with elemental mapping images show the homogeneous distribution of O, Zn and Mo in the ZnO@ZnMoO₄ framework (Fig. 1g–i). Virgin ZnO (v-ZnO) was fabricated by performing a similar synthetic process with ZnO@ZnMoO₄ except for using ZIF-8 as the precursor and polycrystalline zinc molybdenum oxide (PZMO) was also prepared and they were used as the references (Figs. S4 and S5†).

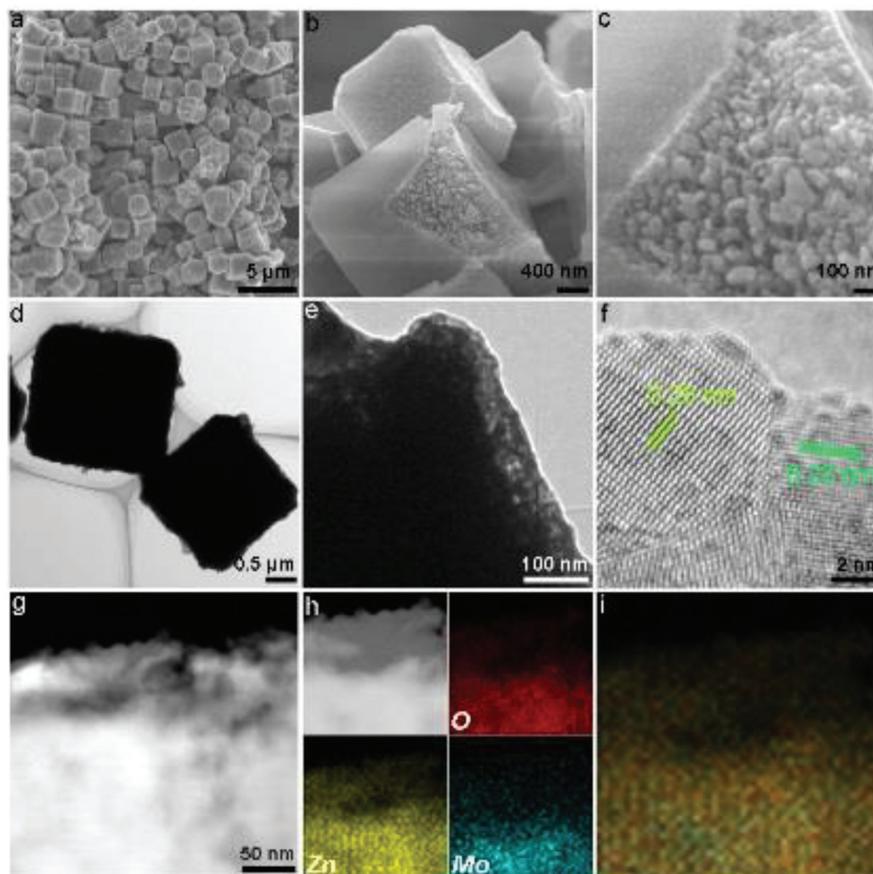


Fig. 1 (a–c) SEM images of ZnO@ZnMoO₄. (d and e) TEM images of ZnO@ZnMoO₄. (f) HRTEM image of ZnO@ZnMoO₄. (g–i) HAADF-STEM and elemental mapping images of ZnO@ZnMoO₄.



The surface chemical state of ZnO@ZnMoO₄ is investigated by X-ray photoelectron spectroscopy (XPS). Compared with v-ZnO, additional Mo 3d, Mo 3p_{3/2} and Mo 3p_{1/2} profiles are observed for ZnO@ZnMoO₄, suggesting the co-existence of Zn, Mo and O (Fig. 2a). The O 1s spectrum can be well divided into three peaks (Fig. 2b). The peaks at 529.8 and 530.8 eV correspond to the Mo–O and Zn–O bonds, respectively.³⁹ The higher energy peak at 532 eV is ascribed to chemisorbed oxygen.^{40–42} In Fig. 2c, the Zn 2p_{3/2} and Zn 2p_{1/2} peaks shift toward the higher binding energy after ZnMoO₄ modification, indicating the interaction of ZnO and ZnMoO₄.⁴³ In the high-resolution Mo 3d spectrum, the doublet located at the higher binding energy is attributed to the Mo⁶⁺ species, while the doublet with the lower binding energy originates from Mo^{δ+} ($\delta < 6$) (Fig. 2d).⁴⁴ The appearance of Mo^{δ+} could be due to the electronic redistribution at the ZnO/ZnMoO₄ nanointerface *via* charge transfer, strongly suggesting the chemical binding of the *in situ* formed ZnO and ZnMoO₄.⁴⁵ The structural information of ZnO@ZnMoO₄ is further analyzed using the Raman spectrum (RM). The E_{2L}–E_{2H} mode at 332 cm⁻¹ signifies the second order non-polar scattering arising from the ZnO zone boundary centre (Fig. 2e).⁴⁶ The peak at 437 cm⁻¹ is the

E₂(high) mode of ZnO owing to the vibration of the oxygen atom, indicating the high crystal quality of ZnO. The disappearance of E₂(high) for ZnO@ZnMoO₄ demonstrates the decreased *c*-axis growth and worse crystallization of the ZnO component, which could be attributed to the chemical bonding of ZnO with ZnMoO₄ because of their intergrowth during the annealing process.⁴⁷ The E₁(LO) mode observed at 583 cm⁻¹ means the existence of the oxygen vacancy and Zn interstitial in both v-ZnO and ZnO@ZnMoO₄. The N₂ adsorption and desorption isotherms show that the Brunauer–Emmett–Teller (BET) surface area of ZnO@ZnMoO₄ is 19.6 m² g⁻¹, higher than that of v-ZnO (15.5 m² g⁻¹) (Fig. 2f).

The HER activities of the as-prepared catalysts are investigated in 1.0 M KOH. Fig. 3a shows the linear sweep voltammetry (LSV) curves of different electrode materials. Unsurprisingly, a commercial Pt/C (20 wt%) catalyst demonstrates the best HER activity, showing near ~0 V onset potential. v-ZnO exhibits inferior HER activity, requiring an overpotential (η_{10}) of 0.52 V at a current density of 10 mA cm⁻². A positively shifted η_{10} is observed for PZMO (0.45 V), indicating that more active sites existed in the constructed bimetallic oxide. The HER activity is further accelerated by the ZnO@ZnMoO₄ catalyst, the η_{10} value of which is reduced to 0.36 V, 30%, 20% and 18% lower than those of v-ZnO, PZMO and their mechanical mixture (ZnO/PZMO), respectively. These results indicate that the interface optimizing between ZnO and ZnMoO₄ can induce a synergistically enhanced HER activity.

The alkaline water-splitting kinetics of various catalysts is revealed by Tafel plots derived from the polarization curves. The Tafel slope of ZnO@ZnMoO₄ is confirmed to be 63 mV dec⁻¹ and smaller than those of PZMO (85 mV dec⁻¹), v-ZnO (479 mV dec⁻¹) and ZnO/PZMO (72 mV dec⁻¹), indicating the

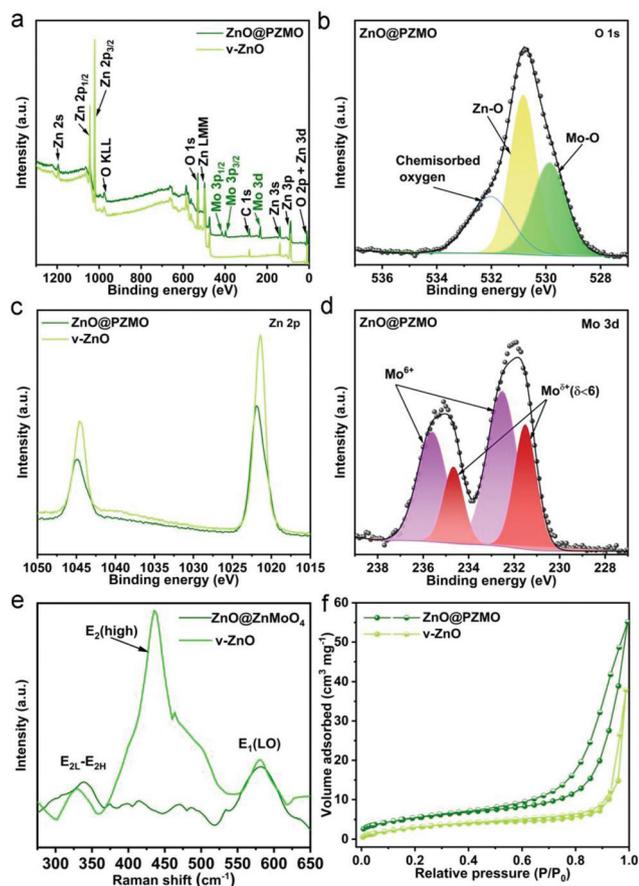


Fig. 2 (a) XPS survey spectra of ZnO@ZnMoO₄ and v-ZnO. The high resolution of (b) O 1s, (c) Zn 2p, and (d) Mo 3d of ZnO@ZnMoO₄ and v-ZnO, respectively. (e) Raman spectra and (f) N₂ adsorption–desorption isotherms of ZnO@ZnMoO₄ and v-ZnO.

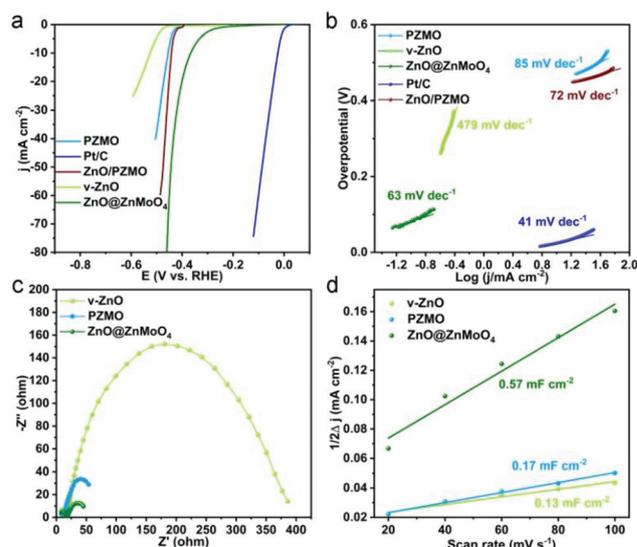


Fig. 3 (a–c) LSV curves, Tafel plots and EIS of various electrodes in 1.0 M KOH. (d) The capacitive currents as a function of scan rate for various electrodes.



higher HER rate of ZnO@ZnMoO₄ (Fig. 3b). This result suggests that the HER over ZnO@ZnMoO₄ proceeds *via* a Heyrovsky-dominated Volmer–Heyrovsky mechanism, which indicates that the sluggish dissociation of H₂O is the rate determining step.^{48,49} The electrode kinetics of ZnO@ZnMoO₄ in the HER process is evaluated by electrochemical impedance spectroscopy (EIS). The semicircle in the low-frequency range on the Nyquist plot derives the charge-transfer resistance (R_{ct}), which is highly related to the electrocatalytic kinetics. The EIS results show that ZnO@ZnMoO₄ has a smaller R_{ct} value than the other samples, indicating a faster charge transfer rate at the ZnO@ZnMoO₄/electrolyte interface (Fig. 3c).

The boosted HER activity of ZnO@ZnMoO₄ could originate from the high electrochemically active surface area (ECSA). To confirm this point, we investigate the double-layer capacitance (C_{dl}) which is positively proportional to the ECSA by performing cyclic voltammetry (CV) measurements. The current response in the CV test is ascribed to the exposed surface area of the electrode in the electrolyte. As shown in Fig. S6,[†] the highest C_{dl} value of ZnO@ZnMoO₄ indicates the most electrolyte-accessible surface area, which could originate from its interior porous structure. The chronoamperometric response at a fixed potential of -0.4 V is measured to investigate the stability of ZnO@ZnMoO₄ (Fig. S7[†]). During the testing, the minor fluctuations indicate the hydrogen gas generation, accumulation and desorption. A less than 20% degradation of the initial current after 40 000 s is observed, demonstrating the strong durability of ZnO@ZnMoO₄. The XRD, HRTEM and EDS characterization of ZnO@ZnMoO₄ after the HER reveals the decreased crystallinity of the ZnMoO₄ moiety, which may result from the etch in the alkaline medium during the HER process.

In summary, in this work we developed an effective strategy to accelerate the water-splitting activity of ZnMoO₄ by cooperating with ZnO to form an interfacial heterostructure. The experimental results demonstrate that the boosted HER activity derives from the modulated electronic states at the heterointerface, which offer abundant active sites and improve the conductivity of ZnMoO₄. Profiting from the aforementioned point, ZnO@ZnMoO₄ shows a low onset overpotential, small Tafel slope and good cycling stability. This work not only develops a low-cost and efficient HER electrocatalyst, but also delivers a HZIF-derived method, which could be extended to the synthesis of other multifunctional Mo-based catalysts for energy conversion and storage applications.

Conflicts of interest

There are no conflicts to declare.

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