

Electronic Supplementary Information

**Synergistic zinc doping and defect engineering toward MoS₂
nanosheet arrays for highly efficient electrocatalytic
hydrogen evolution**

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Experimental Section

Reagents and materials

Carbon cloth (CC) was purchased from PINE Technology Holdings Co., Ltd., Hongkong, China. $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{CH}_4\text{N}_2\text{S}$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China. These chemical reagents were of analytical reagent grade and used without further purification. Deionized water with a resistivity of $18\text{ M}\Omega\cdot\text{cm}$ was used in our work.

Pretreatment of CC

A piece of CC with a size of $2 \times 2\text{ cm}$ was immersed in concentrated nitric acid at room temperature for 30 min, and then transferred into a 50 mL Teflon-lined autoclave and heated at $120\text{ }^\circ\text{C}$ for 30 min. After cooling to room temperature, the pretreated CC was cleaned in deionized water and ethanol for several times under ultrasonication for 30 min, respectively. Finally, it was dried under a $60\text{ }^\circ\text{C}$ oven for further use.

Synthesis of Zn-doped and defect-rich MoS_2 nanosheet assembled on CC (Zn/defect-rich MoS_2/CC or the typical samples)

In the typical experiments, 0.177 g $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 0.381 g $\text{CH}_4\text{N}_2\text{S}$ and 0.018 g $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were dissolved in 35 mL deionized water under magnetic stirring for 30 min. Subsequently, the above solution and the pretreated CC were transferred into a 50 mL Teflon-lined autoclave, which was maintained at $180\text{ }^\circ\text{C}$ for 18 h. After cooling to room temperature, the as-obtained samples were washed with deionized water and

ethanol for several times, respectively. Then, these samples were dried in a vacuum oven at 60 °C for 12 h. Meanwhile, the molar ratios of molybdenum and sulfur precursors, and molybdenum and zinc precursors were controlled as 1:5 and 1:0.06 in the typical experiments, respectively.

For comparison, defect-rich MoS₂ nanosheet arrays on CC (defect-rich MoS₂/CC or the Zn-undoped samples) were synthesized at the same experimental conditions as Zn/defect-rich MoS₂/CC except for the absence of Zn(NO₃)₂.

Zn-doped and defect-poor MoS₂ nanosheet arrays on CC (Zn/defect-poor MoS₂/CC) were synthesized at 0.152 g CH₄N₂S under otherwise the same conditions. Meanwhile, the molar ratio of molybdenum and sulfur precursors was controlled as 1:2.

Zn-doped and defect-rich MoS₂ nanosheet (Zn/defect-rich MoS₂) were synthesized at the same experimental conditions as Zn/defect-rich MoS₂/CC except for the absence of CC.

Characterization

Powder diffraction data (XRD) of all samples were obtained by using a Bruker AXS D8-Advance, a diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) in 2θ ranging from 5 ° to 80 ° at a scanning step of 0.01 °. Morphologies of these samples were observed by a field emission scanning electron microscope (FESEM; Hitachi S-4800) operated at an accelerating voltage of 5.0 kV. Elemental composition was characterized by an energy-dispersive spectrometer (EDX) associated with FESEM. Transmission electron microscope (TEM)

images, high-resolution TEM (HRTEM) images as well as the corresponding selected area electron diffraction (SAED) patterns of the samples were further investigated by a JEOL JEM-2100F HRTEM, and the accelerating voltage was 200 kV. Before TEM analysis, MoS₂ nanosheet was prepared by depositing a single drop of diluted sample dispersion in ethanol onto a copper grid coated with an amorphous carbon film. X-Ray photoelectron spectroscopy (XPS) measurements were employed by a VG Multilab 2000 X XPS system equipped with the Al K α source. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. An Optima 4300DV inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to analyze Mo or Zn contents of electrocatalysts.

Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode system on a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments, China) at room temperature with Zn/defect-rich MoS₂/CC (area: 0.5 × 0.5 cm²) as the working electrode, a graphite rod as the counter electrode and a Ag/ AgCl (2.5 M KCl solution) as the reference electrode. All experiments were done in the electrolyte of 0.5 M H₂SO₄ bubbled with N₂. Unless otherwise specified, all potentials in electrochemical measurements were converted to the potentials versus the reversible hydrogen electrode (RHE) according to the following formula: $E \text{ (RHE)} = E \text{ (Ag/AgCl)} + 0.059 \times \text{pH} + 0.197 \text{ (25 } ^\circ\text{C)}$. Loading amounts of all samples about MoS₂ nanosheet assembled on

CC are determined by the weight difference between before and after their hydrothermal synthesis. Their loading amounts per area on CC are about 4.5 mg/cm². In addition, 10 mg Zn/defect-rich MoS₂ were dispersed into 1.0 mL mixed solution (volume ratio of water and ethanol = 3:1). Subsequently, 30 μL of 5 wt % Nafion were mixed under ultrasonication for about 30 min to prepare the corresponding working electrode. Then, 40 μL the above dispersion were gradually dropped onto the surface of the polished glass carbon electrode (GCE) of 3.0 mm in diameter, yielding the working electrode after air-drying at room temperature. Thus, loading amount of Zn/defect-rich MoS₂ is about 5.6 mg/cm². For the preparation of Pt/C electrode, 3 mg Pt/C (20 wt%)¹ electrocatalysts were dispersed into 500 μL solution (ratio volume of water to ethanol = 1:4). Subsequently, 25 μL of 5 wt % Nafion solution were mixed under ultrasonication for about 30 min to prepare the corresponding working electrode. Then, 5 μL of the electrocatalysts dispersion or ink were dropped onto the surface of the polished glass carbon electrode (GCE) of 3.0 mm in diameter, yielding the working electrode after air-drying at room temperature. Their loading amounts per area on GCE are about 4.25 mg/cm². For HER measurements, line sweep voltammetry (LSV) was measured at a scan rate of 5 mV/s. Polarization curves were recorded between 0 and -0.6 V versus RHE. For the investigation of electrochemical double-layer capacitances, cyclic voltammetry (CV) was measured at the scan rates of 5, 10, 15, 20, 25, 30, 35, 40 and 45 mV/s, respectively, in the potential ranging from 0.097 to 0.197 V vs. RHE. Chronoamperometric responses (*i* ~ *t*) methods was conducted to record the long-term durability.¹ Nyquist plots were measured with frequencies ranging from 100 kHz to 0.1

Hz at an overpotential of 350 mV. Impedance data were fitted to a simplified Randles circuit to extract the series and charge-transfer resistances.² All the experiments were carried out without an activation process and done at room temperature.

Table S1 Atomic ratio of the sum of Mo and 1/2 Zn to S ($[\text{Mo} + 1/2 \text{Zn}]/\text{S}$) of Zn/defect-rich MoS_2/CC synthesized at various molar ratios of molybdenum and zinc precursors (R) by XPS and EDX.

R	$[\text{Mo}^* + 1/2 \text{Zn}]/\text{S}$	$[\text{Mo}^* + 1/2 \text{Zn}]/\text{S}$
	by XPS	by EDX
1:0	1:2.12	1:2.09
1:0.04	1:2.20	1:2.18
1:0.06	1:2.32	1:2.35
1:0.08	1:2.24	1:2.26
1:0.10	1:2.17	1:2.15
1:0.25	1:2.14	1:2.11

*: Considering that oxygen element of existence form in Zn/defect-rich MoS_2/CC synthesized at various R is MoO_2 , the total molar number of Mo in these samples minus half of molar number of oxygen is molar number of Mo in this table.

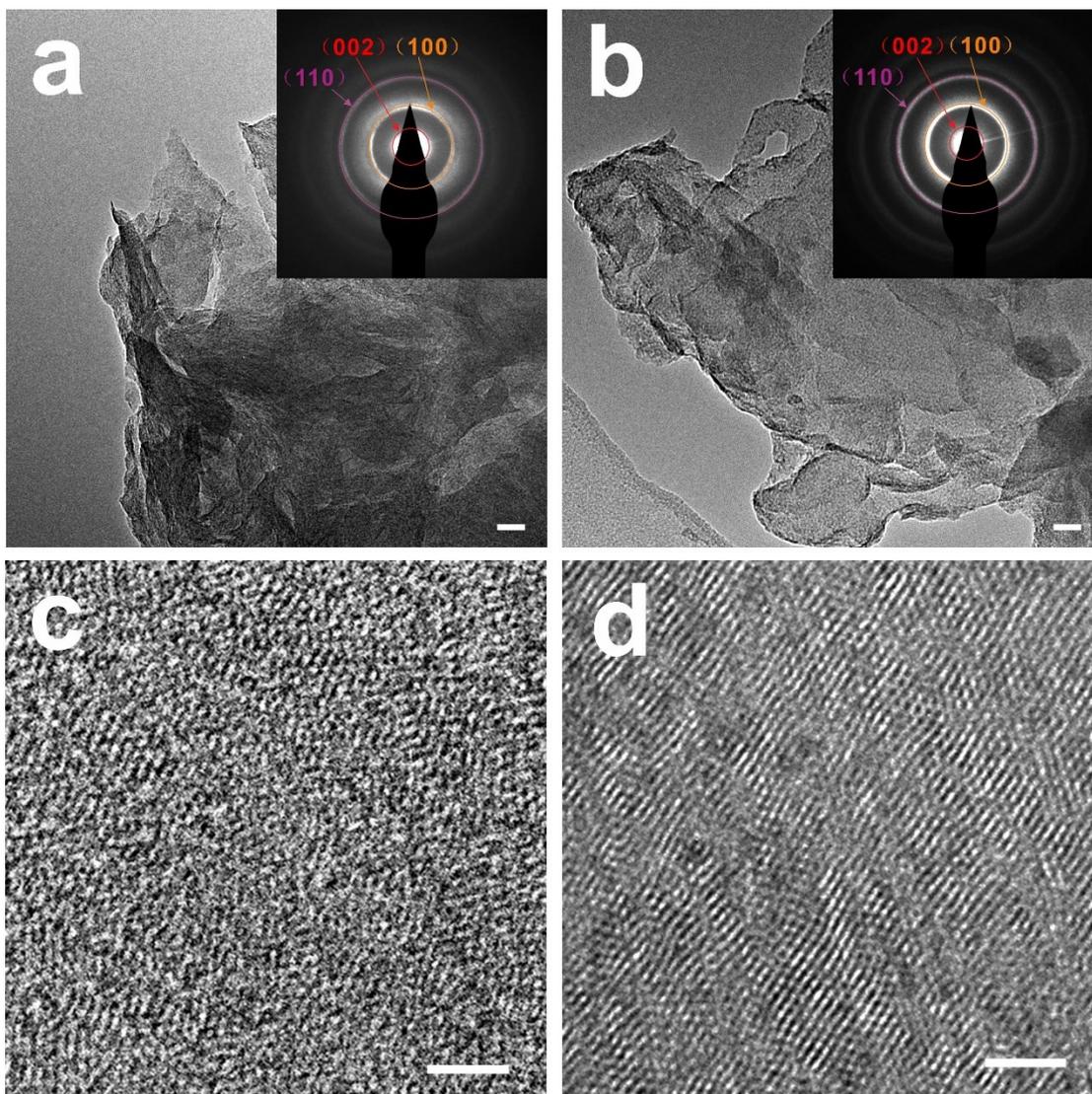


Fig. S1 TEM and HRTEM images of (a and c) Zn/defect-rich MoS₂/CC or the typical samples and (b and d) Zn/defect-poor MoS₂/CC. Insets of TEM images are SAED patterns of the related samples. Meanwhile, Zn/defect-rich MoS₂/CC were synthesized at $R = 1 : 0.06$. Scale bars of (a and b) and (c and d) are 20 and 2 nm, respectively.

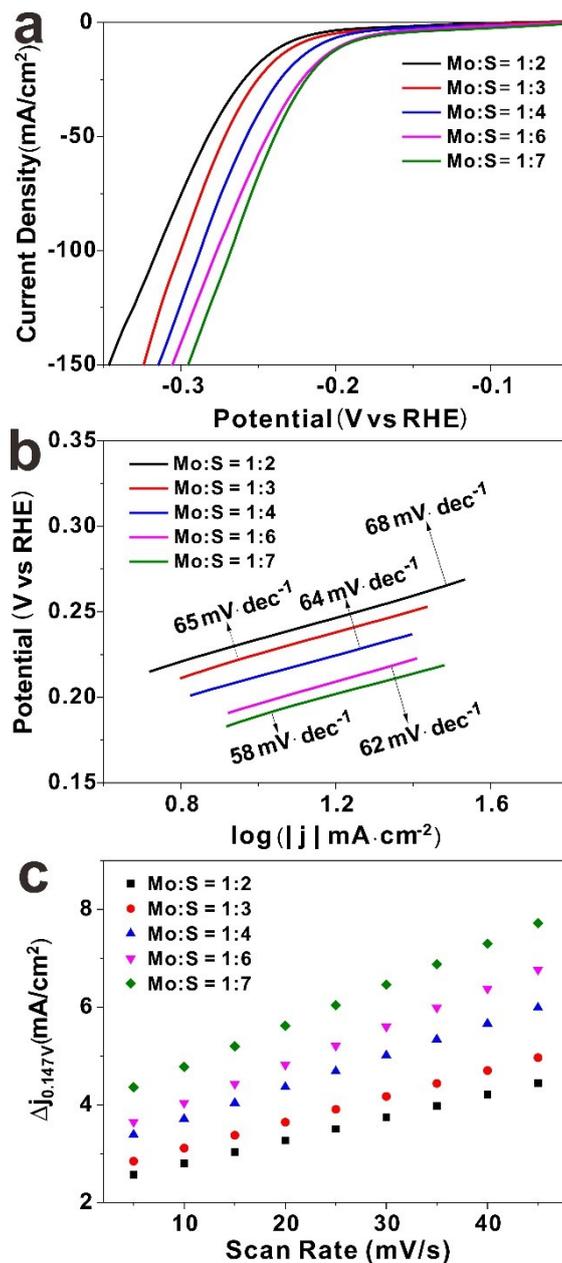


Fig. S2 (a) Polarization curves (b) Tafel plots (c) double-layer capacitances (C_{dl}) at different scan rates of Zn-doped MoS₂/CC synthesized at the various molar ratios of molybdenum and sulfur precursors. Defective MoS₂ nanosheet can be synthesized at low molar ratio of molybdenum and sulfur precursors, which can expose more active edge sites to improve HER activity.³ Meanwhile, all samples were synthesized at $R = 1 : 0.06$.

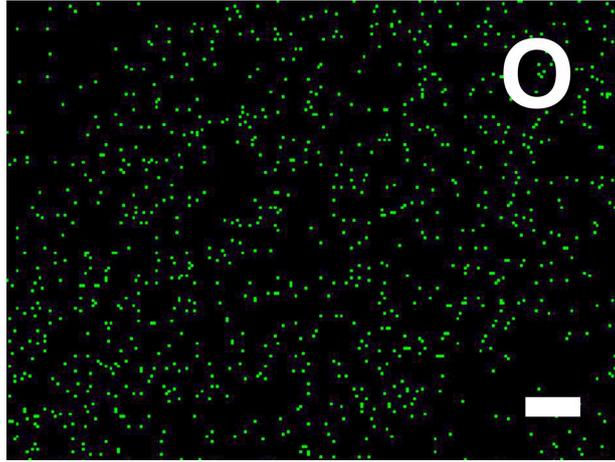


Fig. S3 Mapping EDX profile of O over the typical samples. Scale bar is 1 μm .

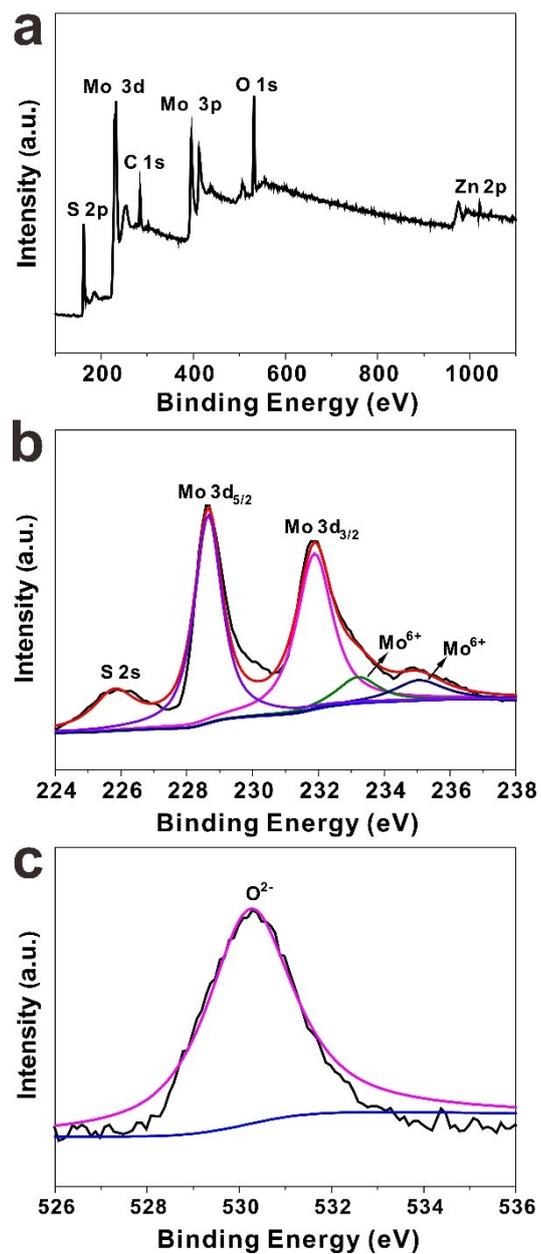


Fig. S4 (a) Full, (b) Mo3d and (c) O1s XPS spectra of the typical samples.

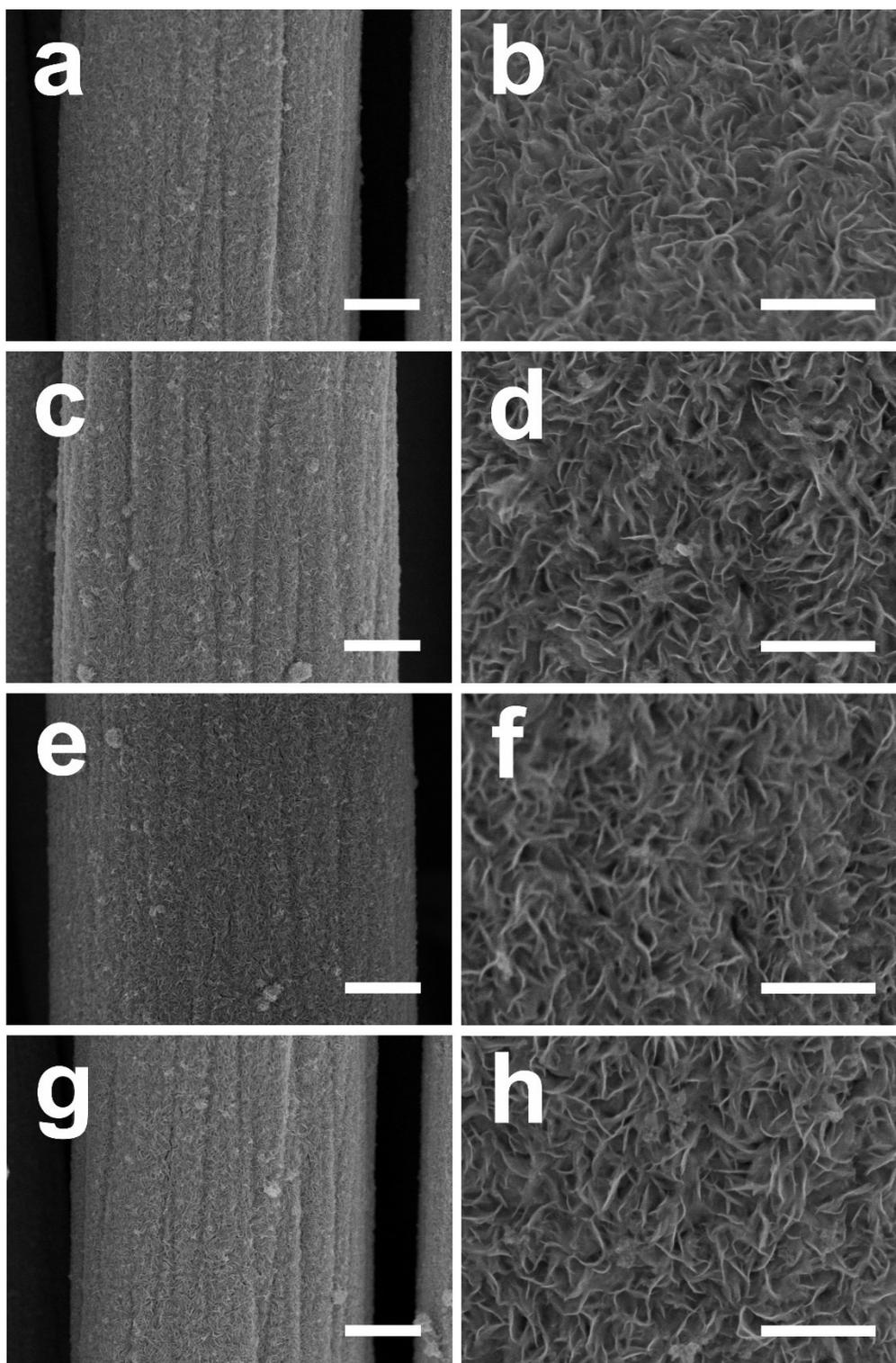


Fig. S5 SEM images of Zn/defect-rich MoS₂/CC synthesized at various R . R of (a, b), (c, d), (e, f) and (g, h) are 1 : 0.04, 1 : 0.08, 1 : 0.1 and 1 : 0.25, respectively. Scale bars of (a, c, e and g) and (b, d, f and h) are 2 μ m and 500 nm, respectively.

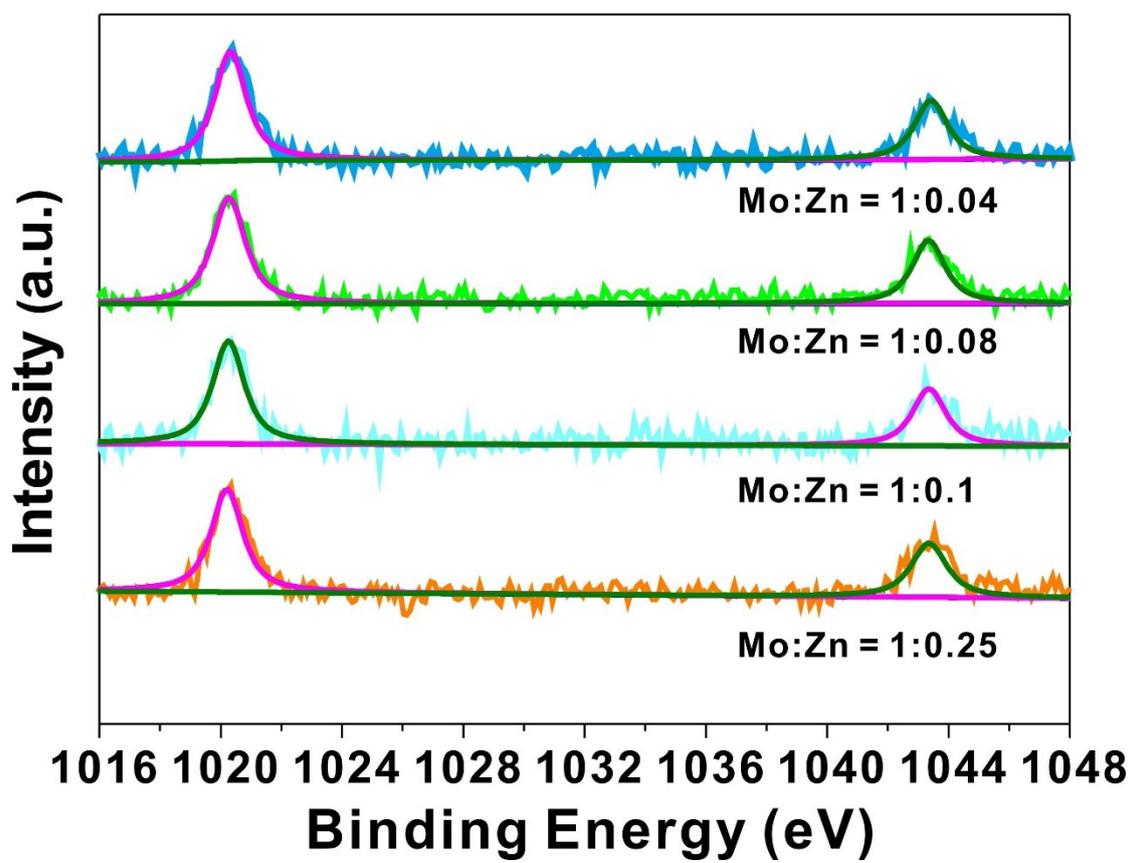


Fig. S6 Zn 2p XPS spectra of Zn/defect-rich MoS₂/CC synthesized at various *R*.

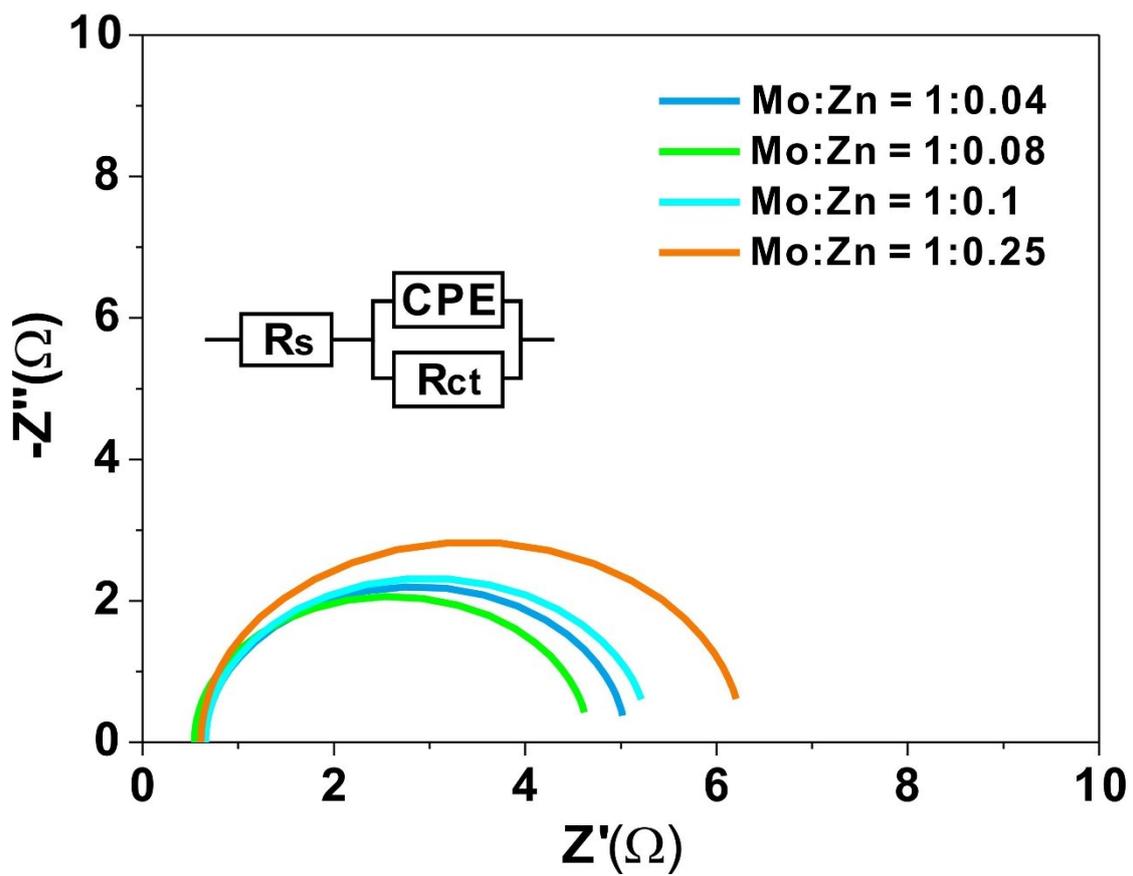


Fig. S7 Nyquist plots of Zn/defect-rich MoS₂/CC synthesized at various R .

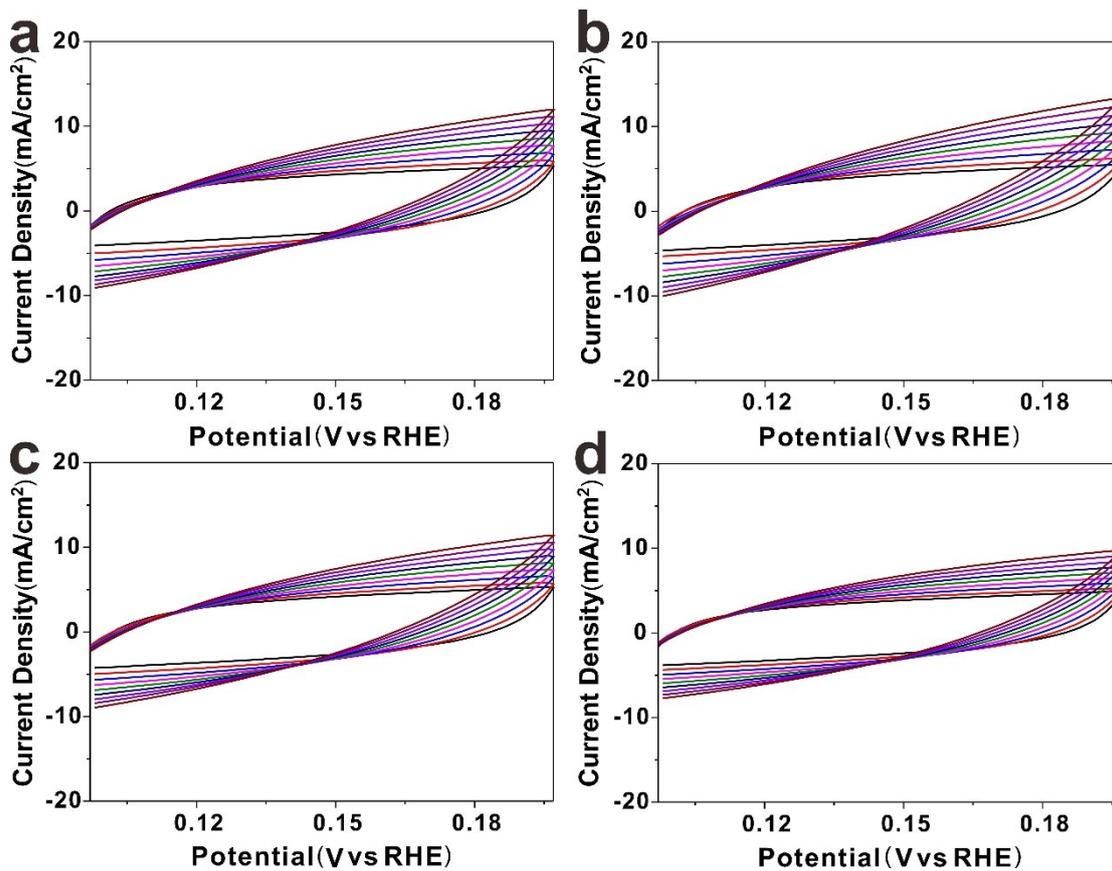


Fig. S8 CV curves of Zn/defect-rich MoS₂/CC synthesized at various *R* of (a) 1:0.04, (b) 1:0.08, (c) 1:0.10 and (d) 1:0.25. Scan rates are 5, 10, 15, 20, 25, 30, 35, 40 and 45 mV/s.

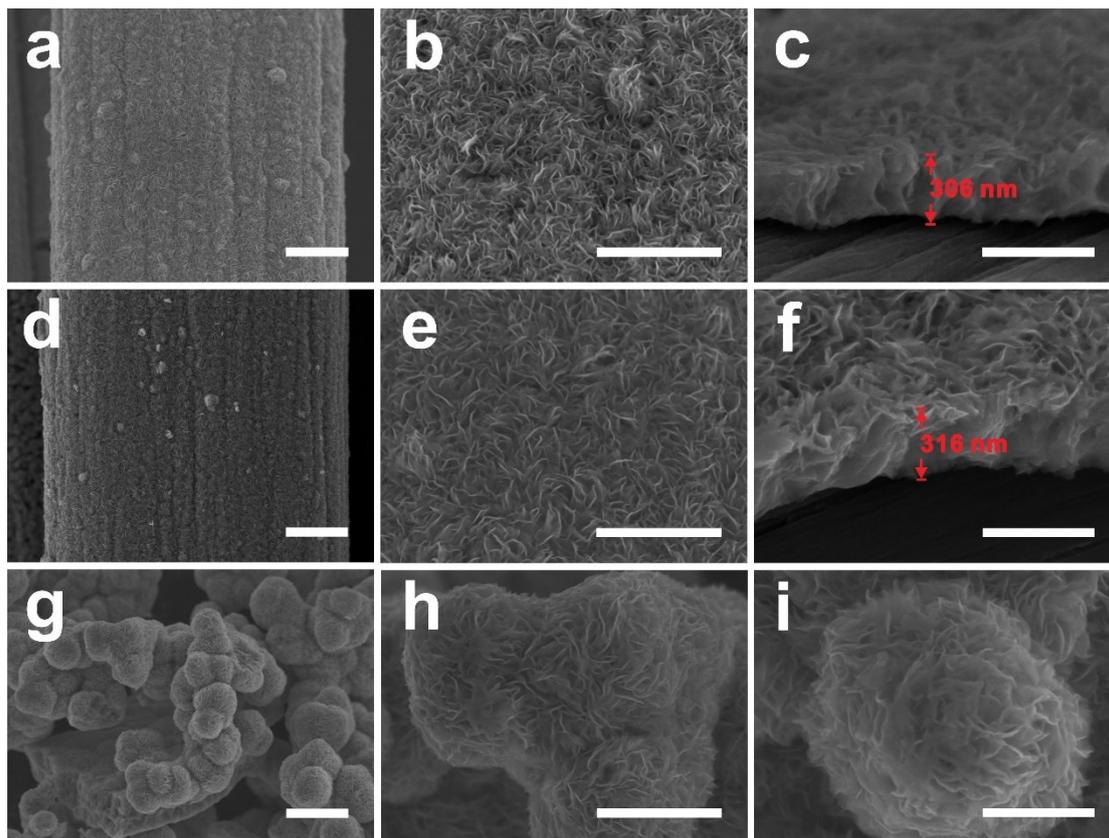


Fig. S9 SEM images of (a, b and c) defect-rich MoS₂/CC or the Zn-undoped samples, (d, e and f) Zn/defect-poor MoS₂/CC and (g, h and i) Zn/defect-rich MoS₂. Scale bars of (a, d and g), (b, e and h) and (c, f and i) are 2 μ m, 1 μ m and 500 nm, respectively.

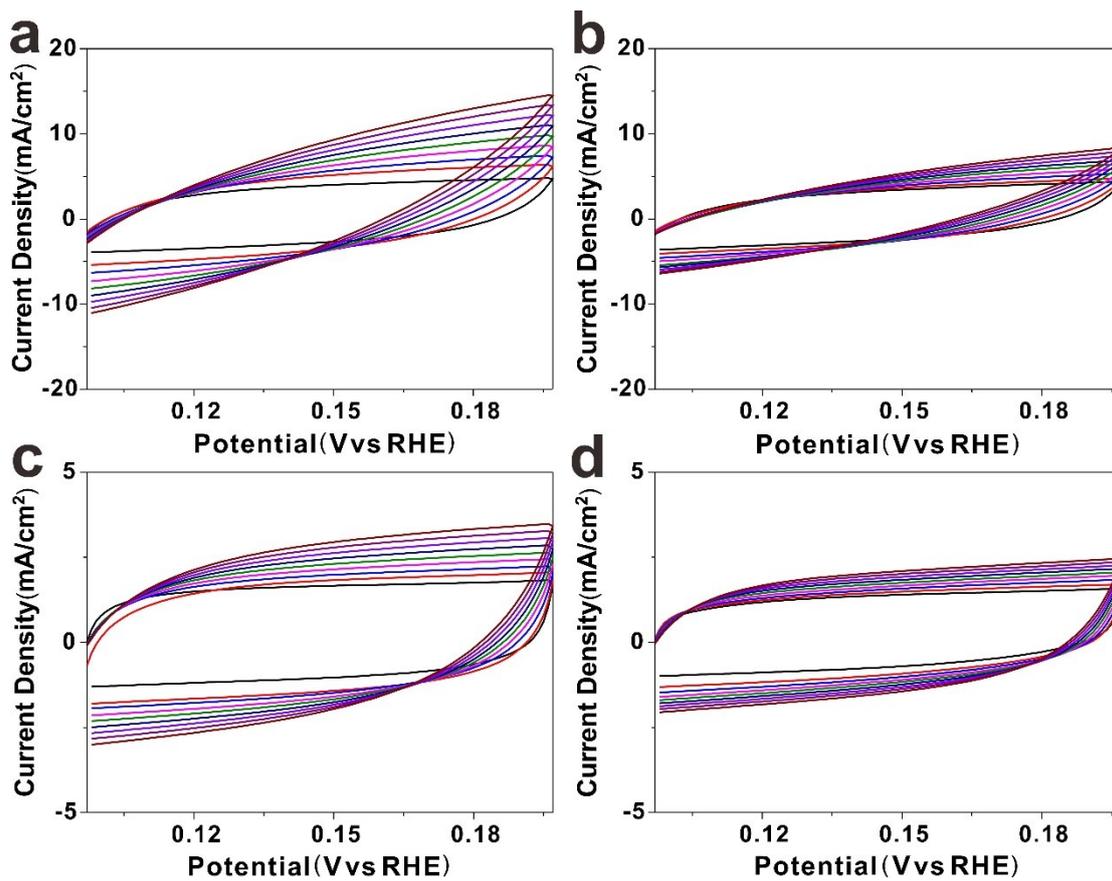


Fig. S10 CV curves of (a) Zn/defect-rich MoS₂/CC, (b) defect-rich MoS₂/CC, (c) Zn/defect-poor MoS₂/CC and (d) Zn/defect-rich MoS₂. Scan rates are 5, 10, 15, 20, 25, 30, 35, 40 and 45 mV/s.

References

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3. J. F. Xie, H. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807–5813.