

1 Supporting information

2 Anchoring Ultra-Small Mo₂C Nanocrystals on Honeycomb-Structured N- 3 doped Carbon Spheres for Efficient Hydrogen Evolution

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12 1. Experimental methods

13 Materials.

14 All chemicals were of reagent grade and used without further purifications. Tetraethyl
15 orthosilicate (C₈H₂₀O₄Si), Resorcinol (C₆H₆O₂), were purchased from Shanghai Aladdin Bio-
16 Chem Technology Co., LTD. Ammonia hydroxide (NH₃·H₂O), Ammonium molybdate
17 tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O, C₂H₅OH, CH₂O, HF were purchased from Sinopharm
18 Chemical Reagent Co., LTD.

19 Synthesis of silica nanospheres.

20 In a typical synthesis of the silica spheres, 2 mL of Tetraethyl orthosilicate and 3 mL of
21 aqueous ammonia solution (32 wt.%) was added to 50 mL of ethanol and stirred for 24 h at 25 °C.
22 The obtained white solid product was collected by centrifugation, washed with water and ethanol,
23 and then air-dried at 70 °C for 10 h.

24 **Synthesis of Mo-silica-RF precursor.**

25 Firstly, 0.4 g of silica nanospheres were dispersed into 50 mL of deionized (DI) water under
26 supersonic ultrasound for 10 minutes. Then, 0.4 g of resorcinol was added into the above solution
27 under magnetic stirring for 10 mins. After that, 0.8 g of ammonium molybdate tetrahydrate was
28 added under stirring for 10 minutes. Next, 0.56 mL of formaldehyde (36 wt.%) was added and
29 stirred at room temperature (RT) for 30 minutes. After that, the mixture solution was added in a
30 PTFE hydrothermal reactor and treated at 100 °C for 24 h. Finally, the Mo-silica-RF precursor
31 was collected by centrifugation, washed with water and ethanol, and dried at 70 °C for 10 h.

32 **Synthesis of Mo₂C-HNCS.**

33 Firstly, the Mo-silica-RF precursor was heated at 1100 °C for 2 hours in the Argon
34 atmosphere (with a heating rate of 10 °C/min). Subsequently, the silica spheres in the carbonized
35 product were removed by etching for 24 h in hydrofluoric acid (15 wt. %) solution. After that, the
36 product was further heated at 800 °C for 1 hours with Argon gas flowing through the 2 M KOH
37 solution. After the KOH activation process, the Mo₂C-HNCS were obtained.

38 **Synthesis of Mo₂C-CS.**

39 Firstly, the Mo-RF precursor was synthesized under the identical condition as the above-
40 mentioned Mo-silica-RF precursor but without silica as a hard template. The Mo₂C-CS was
41 obtained after calcination of the Mo-RF precursor at 1100 °C for 2 hours in Argon atmosphere
42 (with a heating rate of 10 °C/min).

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44 **2. Characterization.**

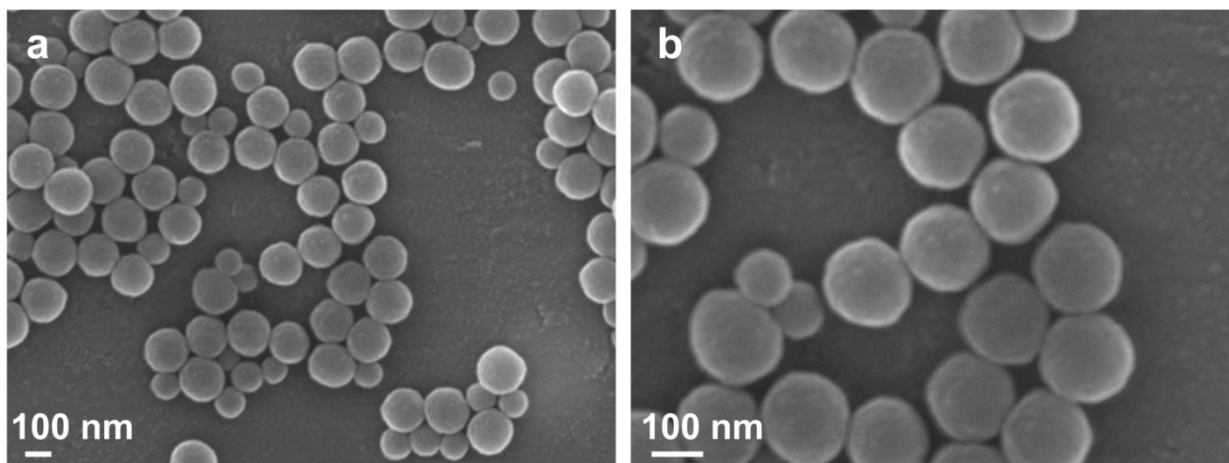
45 Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Discover X-
46 ray diffractometer equipped with a Co K α X-ray source ($\lambda = 1.5406 \text{ \AA}$). TGA was carried out on
47 a NETZSCH STA 449F5 with a temperature ramp of $10 \text{ }^\circ\text{C min}^{-1}$ under an air atmosphere. X-ray
48 photoelectron spectroscopy (XPS) analysis was performed using an ASAP 2020. Raman spectra
49 with a 514.5 nm laser Raman microscope by Renishaw INVIA. Field-emission scanning electron
50 microscopy (FESEM) images were recorded using a JEOL-7100F microscope. TEM, HRTEM,
51 and HAADF-STEM images were recorded using a STEM/EDS microscope with JEOL JEM-
52 2100F working at 200 kV.

53 **3. Electrochemical Measurements.**

54 To prepare the catalyst ink, 7 mg of the catalyst powder and 3 mg of XC-72R carbon were
55 dispersed in a mixture of 750 μL of isopropanol, 200 μL of water, 50 μL of 5 wt.% Nafion solution
56 at room temperature under ultrasonic stirring for 30 min. Then, 14 μL of the catalyst ink was
57 dropped on a glassy carbon electrode with a diameter of 5 mm and dried at room temperature for
58 1 h (catalyst loading $\sim 0.5 \text{ mg cm}^{-2}$).

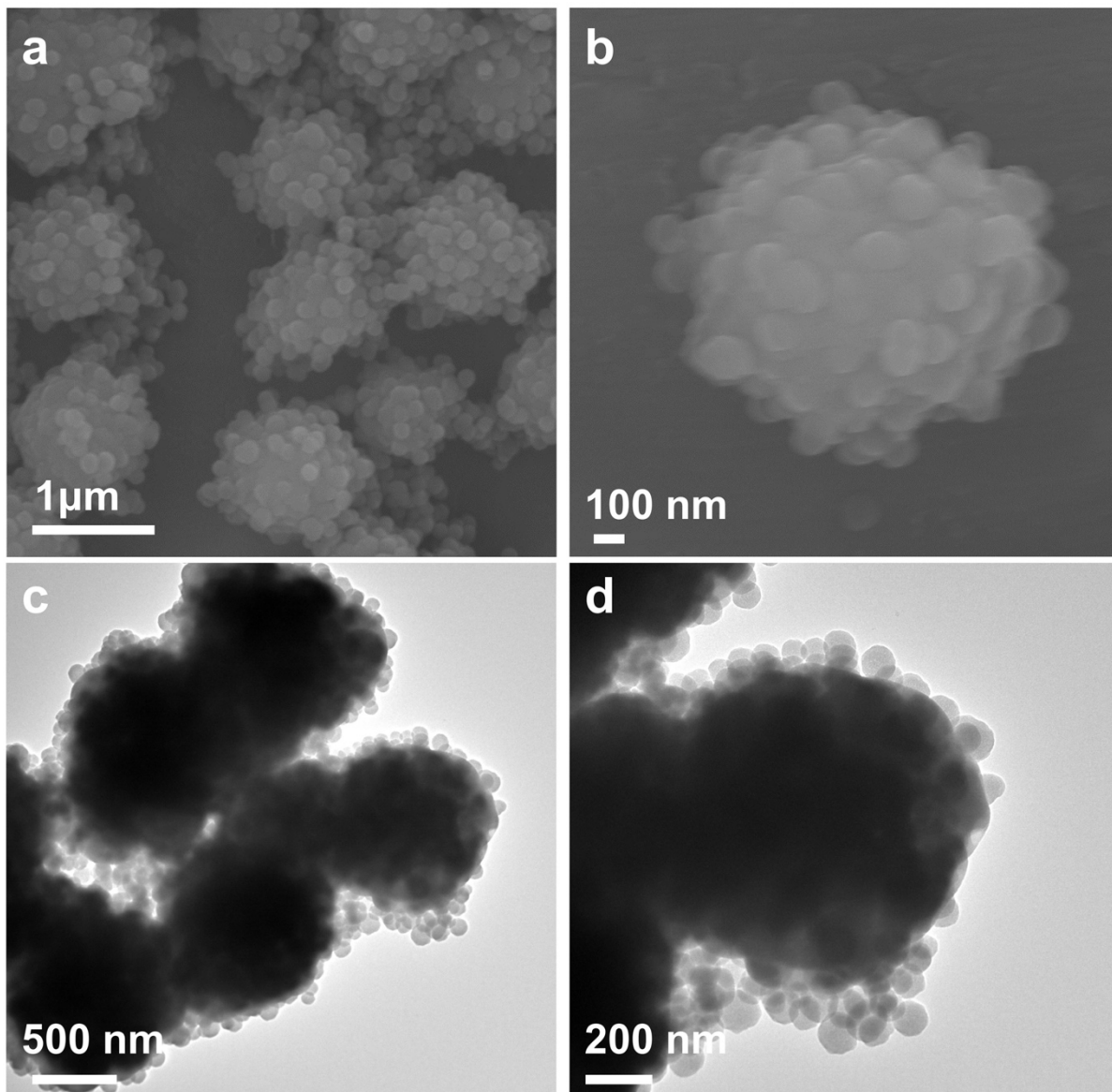
59 All the electrochemical measurements were carried out in a standard three-electrode cell
60 using the CHI760E workstations at room temperature. Hg/HgO electrode and graphite rod were
61 used as reference and counter electrodes, respectively. The reference electrode was corrected with
62 a reversible hydrogen electrode (RHE). The electrochemical experiments were carried out in 1 M
63 KOH electrolyte. Tafel plots were carried out at a scan rate of 5 mV s^{-1} . Electrochemical
64 impedance spectroscopy (EIS) was measured with a voltage of -0.128 V versus RHE from 100
65 kHz to 0.05 Hz with an AC voltage of 5 mV.

66 With the measurements of performing in a Windows of -0.24 and 0.76 V versus RHE, we
67 applied scan rates ranging from 20 to 180 mV s^{-1} to build a plot of the charging from current
68 density against the scan rate at a fixed potential of 0.17 V. The electrochemically active area
69 (ECSA) was estimated according to the slope of the obtained linear curve. Long-term stability tests
70 were conducted by two different evaluation methods were adopted to assess the. The amperometric
71 (i-t) stability was carried out in $\eta = 128$ mV. Additionally, the accelerated linear potential sweeps
72 (LSV) are conducted repeatedly on the working electrodes between -0.33 and 0.07 V at 50 mV
73 s^{-1} .
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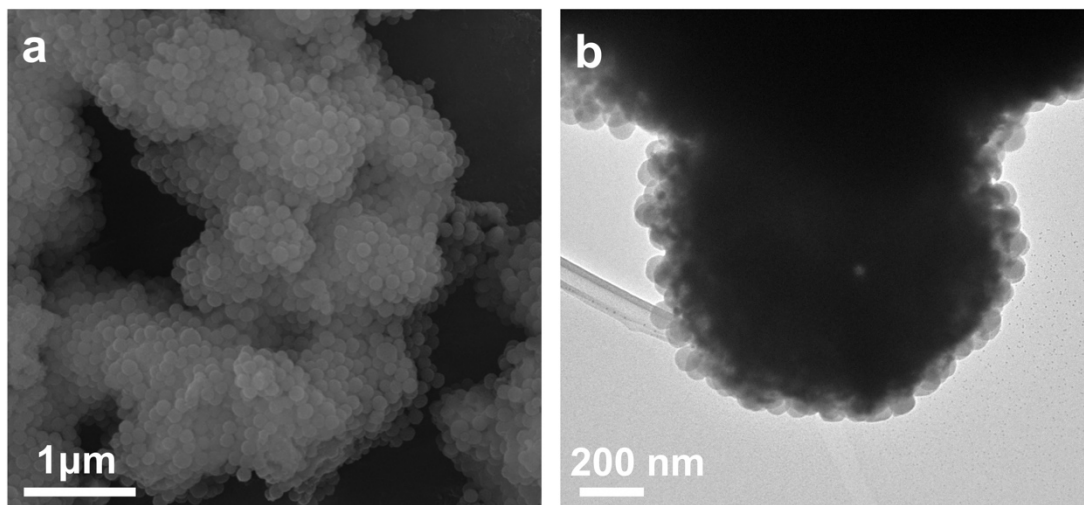
76 **Fig. S1** (a, b) SEM images of silica spheres.



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78 **Fig. S2** (a, b) SEM images; (c, d) TEM images of Mo-silica-RF.

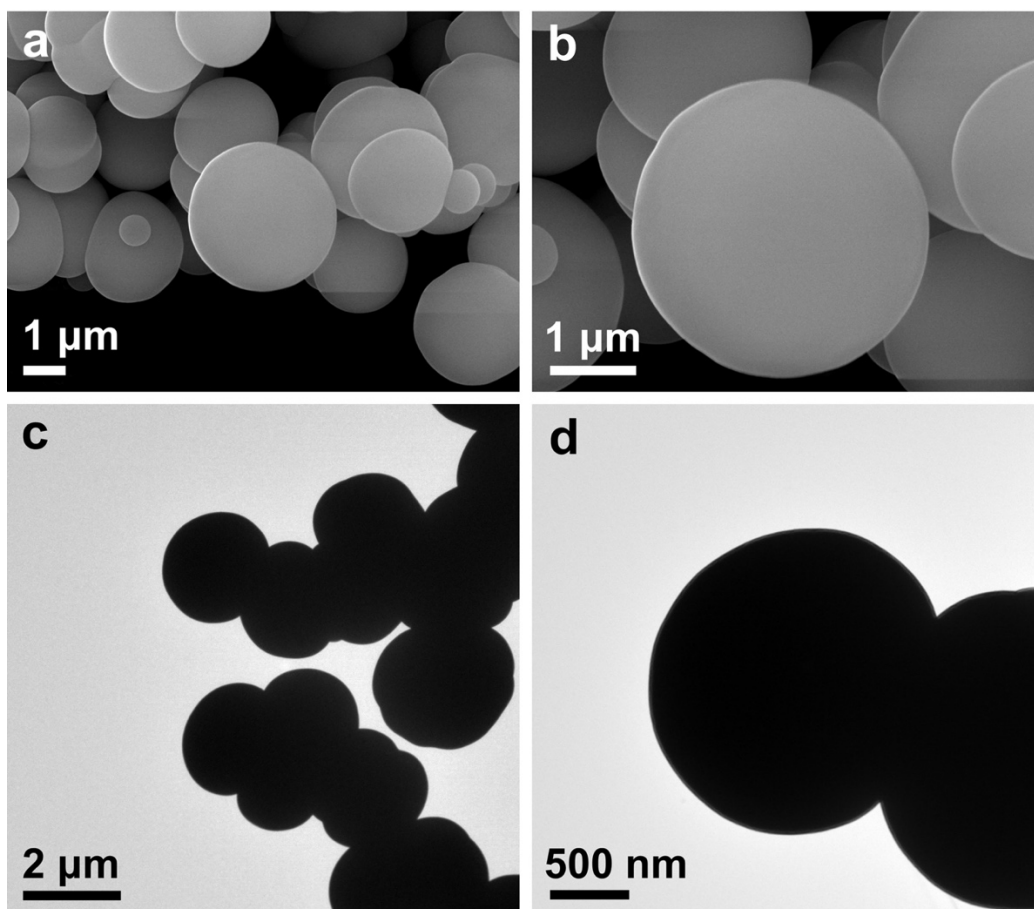
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81 **Fig. S3** (a) SEM image, (b) TEM image of Mo₂C-silica-CS.

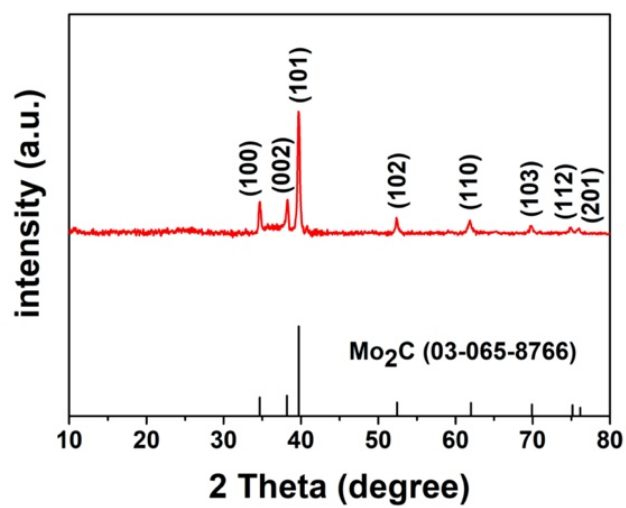
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84 **Fig. S4** (a, b) SEM images; (c, d) TEM images of Mo₂C-CS.

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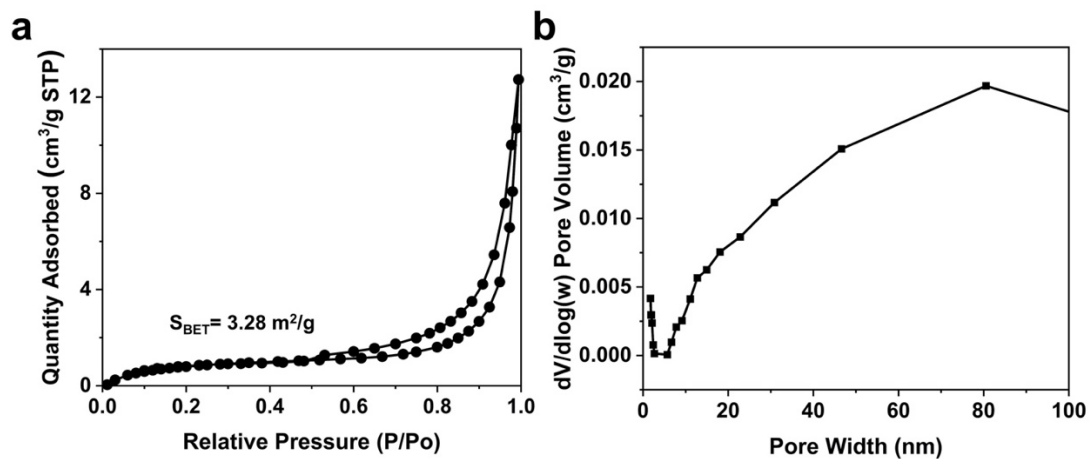


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87 **Fig. S5** XRD pattern of Mo₂C-CS.

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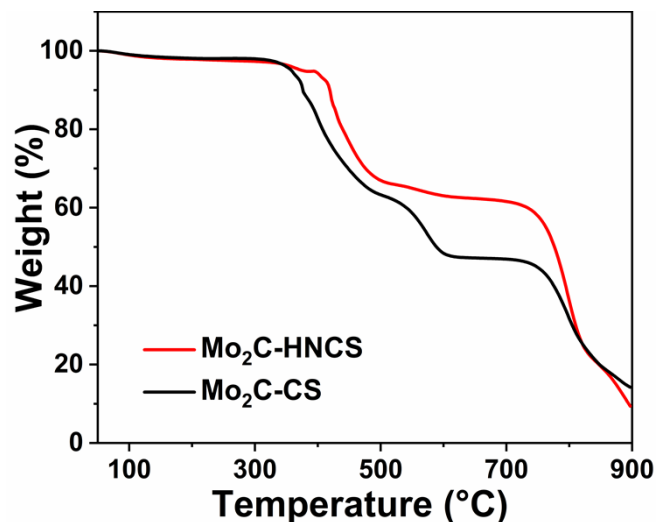
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91 **Fig. S6** (a) N₂ adsorption/desorption isotherms curve; (b) pore size distribution of Mo₂C-CS

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94 **Fig. S7** TGA curves of Mo₂C-HNCS and Mo₂C-CS.

95 TGA of Mo₂C-HNCS and Mo₂C-CS catalysts was tested under air atmosphere from room
 96 temperature to 900 °C. It's assumed that there is no residual of carbon under 900 °C, the residual
 97 mass should be the content of MoO₃. Accordingly, the Mo₂C content was calculated from the
 98 following equation:

$$99 \quad \text{Mass\% (Mo}_2\text{C)} = \frac{\text{residual mass}}{2 \times M(\text{MoO}_3)} \times \frac{M(\text{Mo}_2\text{C})}{\text{Mass}_{\text{Original}}} = \frac{\text{residual mass (\%)}}{2 \times M(\text{MoO}_3)} \times M(\text{Mo}_2\text{C})$$

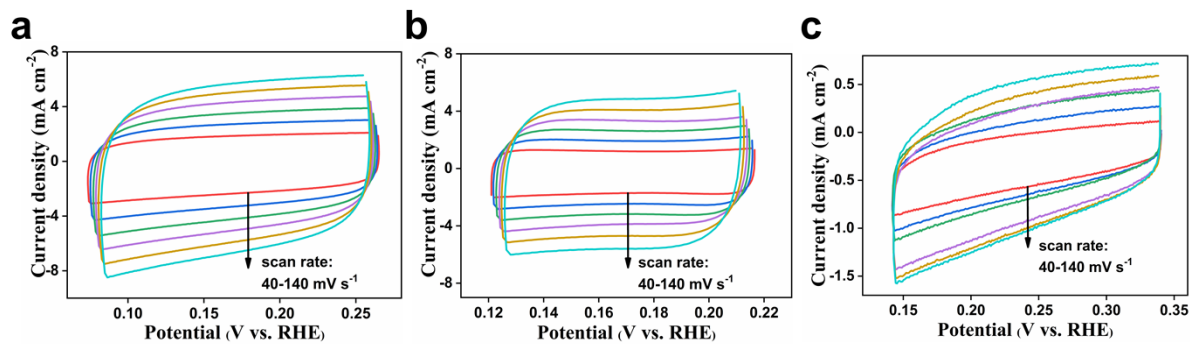
100 Where M represents the molar weight.

101 residual mass (%) of Mo₂C-HNCS= 8.87%; residual mass (%) of Mo₂C-CS=14.06%;

102 Mass% (Mo₂C) of Mo₂C-HNCS= 6.28%;

103 Mass% (Mo₂C) of Mo₂C-CS=9.96%.

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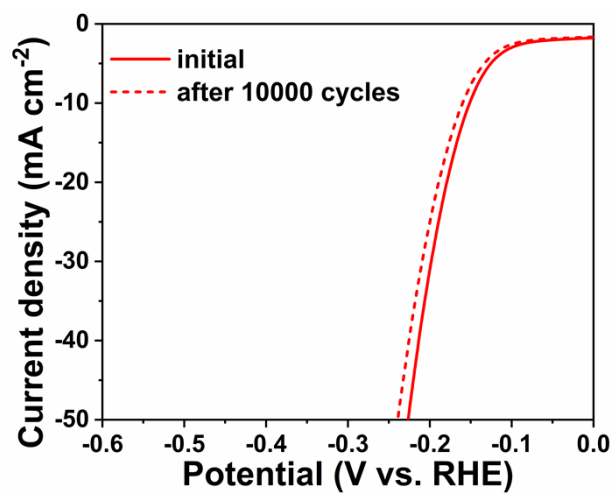


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107 **Fig. S8** CV curves of Mo₂C-HNCS, 20 wt.% Pt/C, and Mo₂C-CS at scan rates from 40 to 140 mV
108 s⁻¹ in 1M KOH.

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112 **Fig. S9** Polarization curve for Mo₂C-HNCS before and after 10000 cycles. The accelerated linear
113 potential sweeps (LSV) were conducted repeatedly between -0.33 and 0.07 V at 50 mV s⁻¹.

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