

Supporting Information

Experimental section

Ti foil, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and thiourea ($\text{CS}(\text{NH}_2)_2$) were obtained from Yitai Metal Materials *Co., Ltd*, Xi Long Hua Gong *Co., Ltd*, Sinopharm Chemical Reagent *Co., Ltd* and Tianjing Guangfu Technology Development *Co., Ltd*, respectively. $\text{CH}_3\text{CH}_2\text{OH}$ (~99 wt%), H_2SO_4 (~98 wt%) and HCl (~37 wt%) were purchased from Beijing Chemical Reagent *Co., Ltd*. All the reagents were of A. R. grade and used as received without further purification.

$\text{CoS}_2@/\text{MoS}_2$ hierarchical nanoarray/Ti foil was synthesized by a simple hydrothermal method. In a typical procedure, 0.119 g (0.5 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.0883 g (1/14 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 0.456 g (6 mmol) $\text{CS}(\text{NH}_2)_2$ were dissolved in 36.0 mL distilled water and stirred to form a pink and clear solution. Ti foil (4 cm \times 1 cm) was carefully cleaned with concentrated HCl solution (~37 wt%) in an ultrasound bath for 5 min, and then deionized water and absolute ethanol were used for 5 min each to ensure that the surface of the Ti foil was fully cleaned. The aqueous solution and Ti foil were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for 12 hours, and then allowed to cool to room temperature within 15 min using cooling water. The final product was taken out from the autoclave and subsequently rinsed with distilled water, and dried at 60 °C for 30 minutes.

CoS_2 nanopyramid array was prepared by the same hydrothermal method. 0.238 g (1 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.38 g (5 mmol) $\text{CS}(\text{NH}_2)_2$ were dissolved in 36.0 mL distilled water and stirred to form a red and clear solution. The aqueous solution and clean Ti foil were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for 12 hours.

MoS_2 nanosheet array was prepared by the same hydrothermal method. 0.1766 g (1/7 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 0.456 g (6 mmol) $\text{CS}(\text{NH}_2)_2$ were dissolved in 36.0 mL distilled water and stirred to form a clear solution. The aqueous solution and clean Ti foil were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for 12 hours.

Scanning electron microscopy (SEM) images were taken on a Zeiss SUPRA55 scanning electron microscope with two accelerating voltages of 200 kV and 50 kV. X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a

scan rate of 10 (°)/min in the range from 5 to 90°. X-ray photoelectron spectrum (XPS) and Raman spectrum were carried out by using a model of ESCALAB 250 and LabRAM Aramis. High-resolution transmission electron microscope (HRTEM) images and elemental mapping were obtained on a JEOL 2100 High-resolution TEM system with operating at 200 kV. The interaction force between the gas bubbles and electrode interfaces can be assessed by a high-sensitivity micro-electromechanical balance system (Dataphysics DCAT21, Germany).

CoS₂@MoS₂ hierarchical nanoarray/Ti foil as a binder-free cathode was measured for HER. All electrochemical measurements were performed on standard three-electrode setup under constant H₂ flow at room temperature at room temperature. Electrochemical measurements (using a CHI 660E from Shanghai Chenghua Instrument Co., Ltd, China) were conducted in an electrochemical cell using saturated calomel electrode (SCE, 0.262 V vs. reversible hydrogen electrode (RHE) in 0.5 M H₂SO₄ solution) as the reference electrode, a 1 cm² Pt plate as the counter electrode and the sample with 1 cm² electrode area as the working electrode. Prior to the test measurements, H₂ was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H⁺/H₂ redox couple. Linear sweep voltammetry with scan rate of 5 mV s⁻¹ was conducted in 0.5 M H₂SO₄ solution. AC impedance measurements were carried out in the same configuration at -0.15 V vs. RHE in the frequency range of 10⁻¹ to 10⁵ Hz with an AC voltage of 5 mV. The electrochemical double-layer capacitance (EDLC) measurements of CoS₂ electrodes were carried out by using cyclic voltammetry curves for two cycles between 0.1 and 0.2 V vs. RHE with scanning rates of 60, 80, 100, 120 and 150 mV s⁻¹. The current densities at 0.15 V vs. RHE and the corresponding scanning rates were used to calculate the EDLC value (the slope of current density-scan rate plots), which served as an estimate of the effective electrochemically active surface area (ECSA) of the solid-liquid interface. The cycling stability of CoS₂@MoS₂ hierarchical nanoarray/Ti foil electrode was carried out by using cyclic voltammetry curves for 2000 cycles between 0.2 and -0.3 V vs. RHE with scanning rate of ~30 mV s⁻¹.

Figure



Fig. S1 Optical image of Ti substrate.

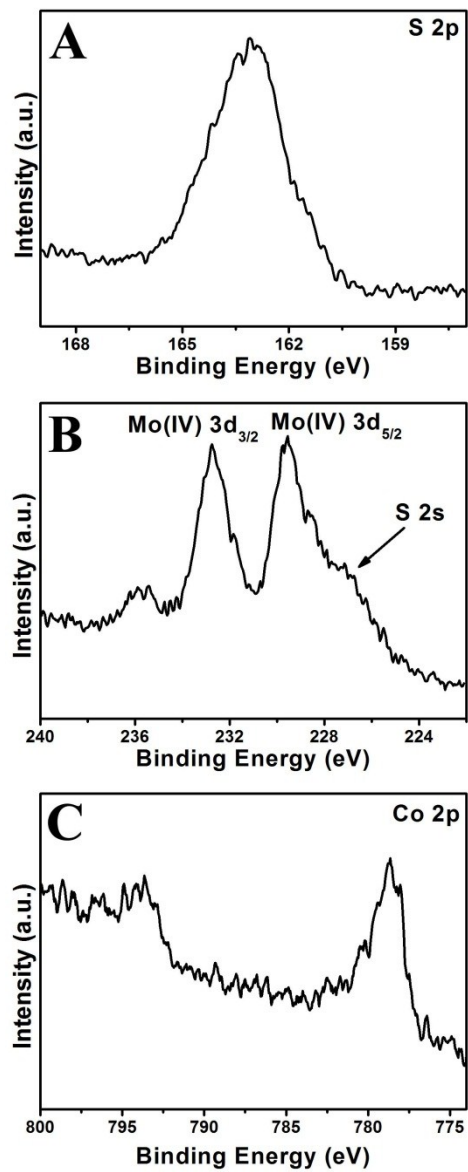


Fig. S2 XPS spectra of the (A) S 2p, (B) Mo 3d and (C) Co 2p regions for the CoS₂@MoS₂ hierarchical nanoarray material.

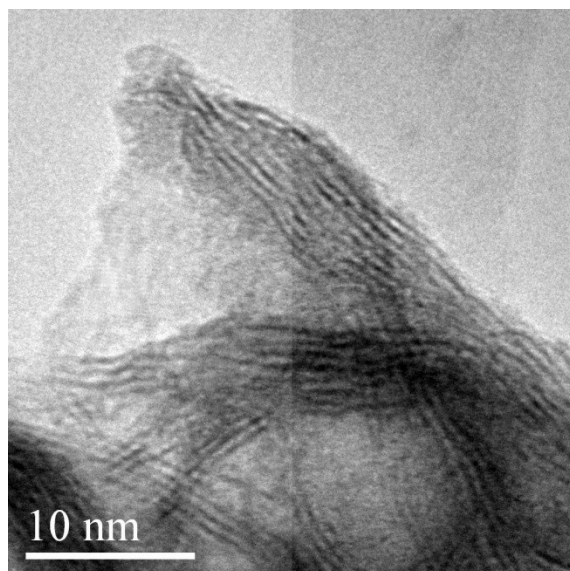


Fig. S3 High-resolution TEM image of CoS₂@MoS₂ hierarchical nanoarray.

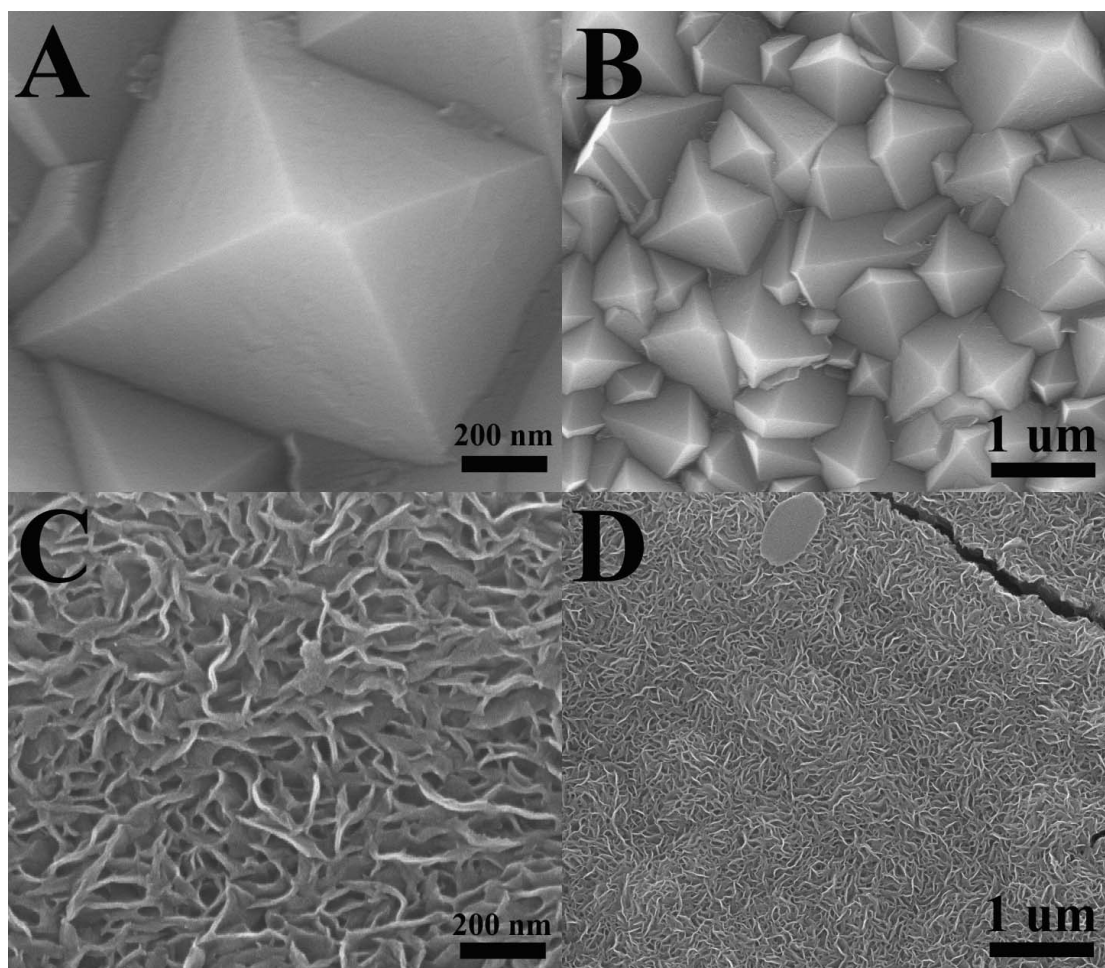


Fig. S4 High-resolution and low-resolution SEM images of (A and B) CoS₂ nanopyramid array and (C and D) MoS₂ nanosheet array.

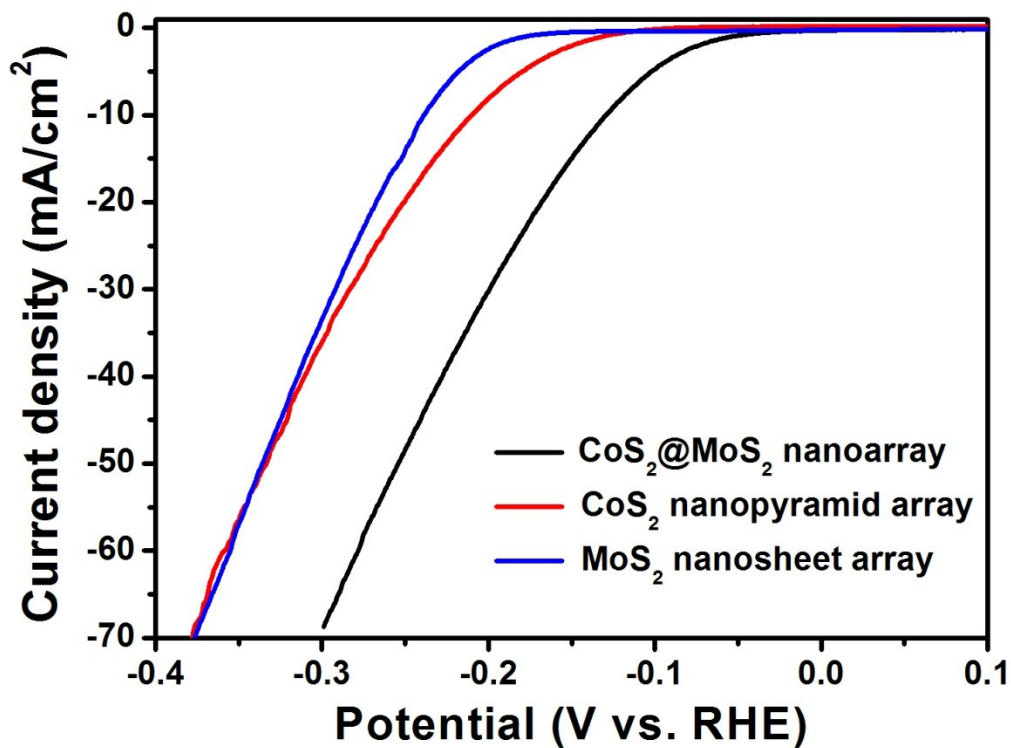


Fig. S5 Polarization curves of several electrocatalysts as indicated, including CoS₂@MoS₂ hierarchical nanoarray, CoS₂ nanopyramid array and MoS₂ nanosheet array.

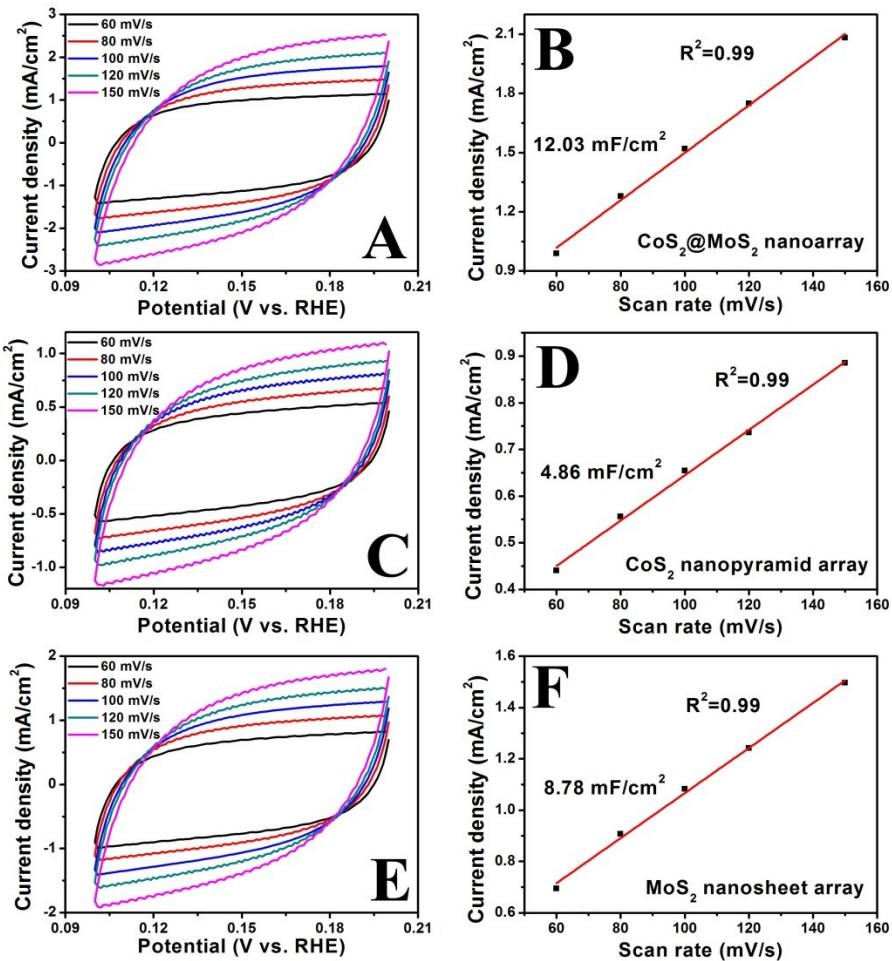


Fig. S6 EDLC measurements and the corresponding current density-scan rates curves of several electrocatalysts as indicated, including (A and B) $\text{CoS}_2@MoS_2$ hierarchical nanoarray, (C and D) CoS_2 nanopyramid array and (E and F) MoS_2 nanosheet array.

Table S1 Comparison of HER performances in 0.5 M H₂SO₄ solution for CoS₂@MoS₂ nanoarray electrodes with other HER electrocatalysts

Electrocatalyst	Onset potential (mV)	Tafel slope (mV dec ⁻¹)	Overpotential at -10 mA cm ⁻² (mV)
CoS ₂ @MoS ₂ nanoarray/Ti foil, this work	44	57.3	110.5
MoS ₂ nanosheet array/Ti foil, ref.4	150	51	225
MoS ₂ @MoO ₃ nanowires/FTO, ref.9	150	50	260
Co-doped MoS ₃ film/GC, ref.13	135	43	188
CoS ₂ nanopyramid array/Ti foil, ref.19	81	72	193
CoS ₂ nanowires/graphite, ref.6	75	51.6	145
CoS ₂ nanoparticles/graphite, ref.17	50	52	192

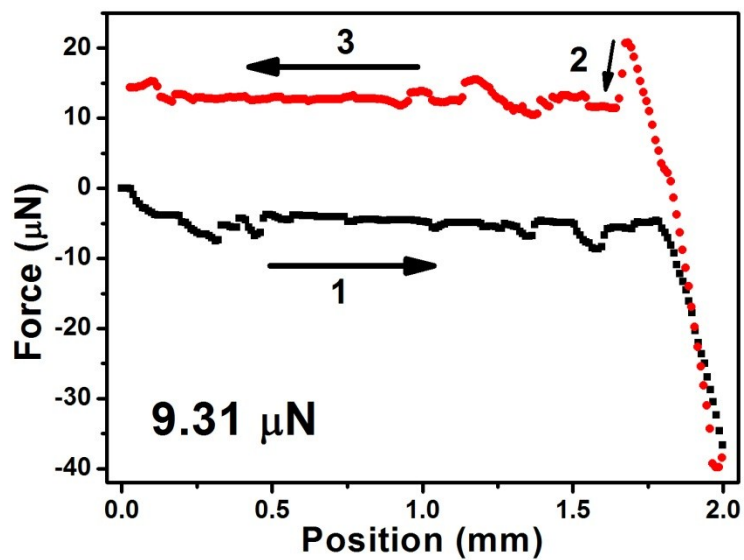


Fig. S7 The bubble adhesive force ($\sim 9.31\mu\text{N}$) of the $\text{CoS}_2@\text{MoS}_2$ hierarchical nanoarray material. For gas bubble adhesive force measurement, Process 1: the film surface approached to the air bubble; Process 2: the film surface left the air bubble; Process 3: the film surface broke away from the air bubble.

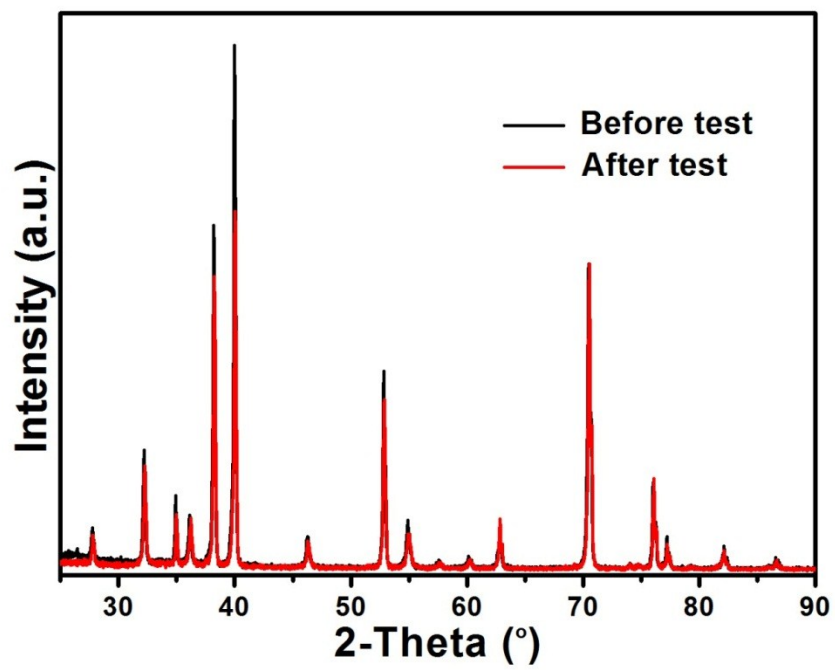


Fig. S8 XRD patterns of CoS₂@MoS₂ hierarchical nanoarray before and after test.

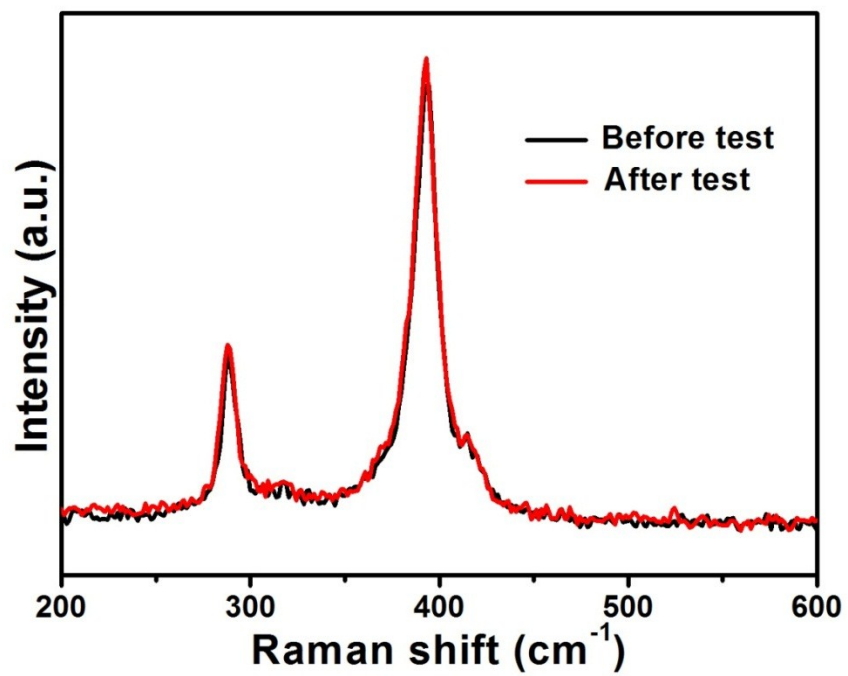


Fig. S9 Raman spectra of CoS₂@MoS₂ hierarchical nanoarray before and after test.

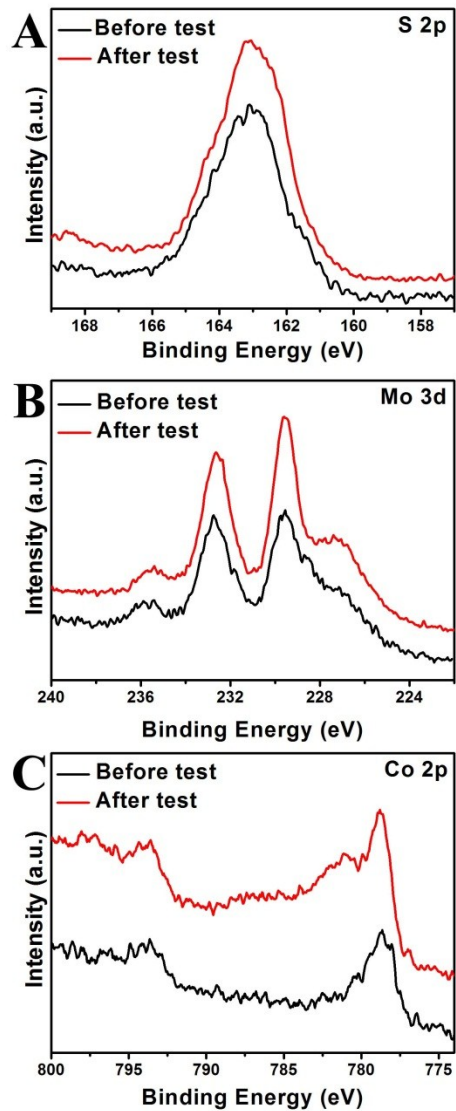


Fig. S10 XPS spectra of the (A) S 2p, (B) Mo 3d and (C) Co 2p regions for the $\text{CoS}_2@MoS_2$ hierarchical nanoarray material before and after 2000 CV cycles test.

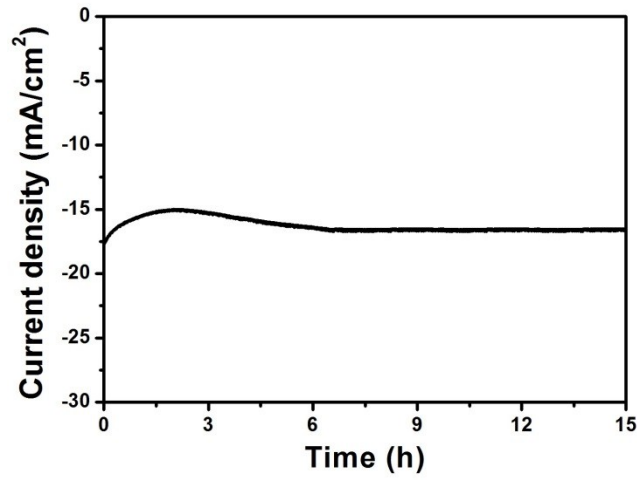


Fig. S11 Time-dependence of current density for the CoS₂@MoS₂ hierarchical nanoarray material.