Supporting Information

Confined growth of MoSe$_2$ nanosheets in N-doped carbon shell with hierarchical porous structure for efficient hydrogen evolution

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Experimental Section

Synthesis of MoSe₂/NDC composites

Typically, 0.2 g of ammonium molybdate and 1.0 g of dopamine hydrochloride were added to a mixed solution containing 80.0 mL of ethanol and deionized (DI) water and 4.5 mL of aqueous ammonia solution under vigorous stirring. The mixture was stirred for 8 h at room temperature. Subsequently, the Mo-precursor was centrifuged and washed for several times with ethanol and DI water. The Mo-precursor was synthesized by a freeze-drying process for 10 h. After that, the as-prepared Mo-precursors were further selenided to form the MoSe₂/NDC composites. Typically, 0.5 g of precursor and 0.3 g of selenium powder were placed at two separate positions of a porcelain boat in the tube furnace. The Mo-precursors were heated up to a temperature of 900 °C with a ramp of 5 °C min^{-1} in N_2 atmosphere and kept for 2 h. The obtained products were denoted as MoSe₂/NDC. For comparison, a series of catalysts labeled as NDC, and MoSe₂ were also prepared using the same procedures, which were prepared without ammonium molybdate and without dopamine, respectively.

Characterizations

The microstructure and phase composition of the as obtained samples were characterized by X-ray powder diffraction (XRD Bruker D8-ADVANCE) with an 18 kW advanced X-ray diffrac-tometer with Cu K$_\alpha$ radiation (λ=1.54056Å). The surface areas and pore sizes of the as-prepared samples were analyzed by the nitrogen adsorption-desorption isotherms method at 77 K (3H-2000PS2, BeiShiDe Instrument, China). Raman spectra were measured by Raman spectroscopy (inVia-Reflex, Renishaw, UK). X-ray photoelectron spectroscopy (XPS) was conducted with a Mg Kα achromatic X-ray source. Thermo-gravimetric analysis (TGA) measurements were performed on Diamond TG 6300 at a heating rate of 10 C min^{-1} in air atmosphere in the range of 30-900℃. Field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan), and Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) were used to investigate the structure information of materials.

Electrochemical tests

All electrochemical tests were performed with a three-electrode system in 1.0 M KOH or 0.5 M H_2SO_4 using a CHI 760E electrochemical workstation. A graphite rod and Ag/AgCl electrode were used as the counter and reference electrode, respectively. All potentials involved in this work were calibrated to the reversible hydrogen electrode. The electrode preparation was carried out as follows: 5 mg of catalysts were ultrasonically dispersed in a suspension containing 250 μL of isopropanol, 700 μL of DI water and 50 μL of 5 wt% Nafion solution. The as-prepared mixture was sonicated for 40 min to obtain a homogeneous catalyst ink. Subsequently, 8 μL of the ink was dropped onto a glassy carbon rotating disk electrode (RDE, 5 mm in diameter) and dried thoroughly at room temperature. The electrocatalytic activity for HER was evaluated by measuring polarization curves using Linear sweep voltammetry (LSV) at a sweep rate of 5 mV s^{-1}. Cyclic voltammetry (CV) tests were applied at different scan rates in 1.0 M KOH or 0.5 M H_2SO_4 to investigate electrochemical double-layer capacitances for estimating the effective electrochemical surface areas (ECSA). The stability of the catalyst was examined through CV scanning of 10000 cycles (300 mV s^{-1}). Time-dependent current density curves were operated by chronoamperometric measurements. Electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency range from 100 kHz to 0.01 Hz.

Calculation Details

We used the CASTEP code to perform our DFT+U calculations.[1] In this framework, we use the rotationally invariant (Anisimov type) DFT+U functional and the Hubbard U parameter self-consistently determined for the pseudized Mo 4d orbital by our new linear response method.[2] By that method, the Hubbard U parameters on the half-filled shell of 4d orbitals of Mo is self-consistently determined to be U_d =4.02 eV.

The generalized gradient approximation (GGA) of Perdew-Becke-Ernzerhof (PBE) was chosen for PBE+U calculations with a kinetic cutoff energy of 517 eV, with the valence electron states expressed in a plane-wave basis set.[3] All structures were optimized with a convergence criterion of 1×10^{-6} eV for the energy and 0.03 eV/Å for the forces. Brillouin

zone sampling was employed using a Monkhorst-Packing grid with 4×4×1. The Gibbs free energy change of adsorbing hydrogen atom is obtained by Eq.

$$\Delta G_{H*} = \Delta E_{H*} + \Delta ZPE - T\Delta S$$

Where ΔE_{H*}, ΔZPE and ΔS are the hydrogen adsorption energy, the difference in zero-point energy (ZPE) and entropy between the adsorbed hydrogen atom and gaseous hydrogen (H_2), respectively.[1]

As the contribution from the vibrational entropy of H in the adsorbed state is negligibly small, the entropy of hydrogen adsorption is $\Delta S_H \approx -\frac{1}{2}S_{H2}$, where S_{H2} is the entropy of H_2 in the gas phase at the standard conditions. Then the Gibbs free energy with the overall corrections is taken as $\Delta G_{H*} = \Delta E_{H*} + 0.24$ Ev.[1, 4]
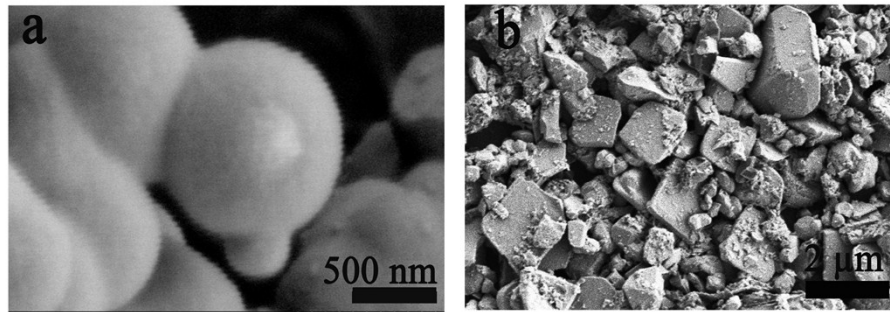

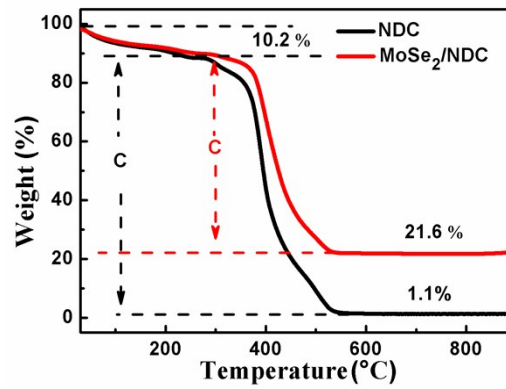**Fig. S1** Typical SEM images of (a) the NDC, and (b) the MoSe$_2$.

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Fig. S2 Thermogravimetric (TGA) curves of the of NDC and MoSe$_2$/NDC at a heating rate of 10 ℃ min^{-1} in a flowing air environment.
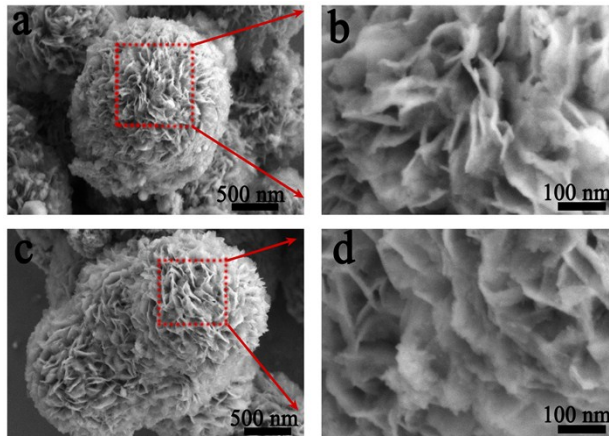

Fig. S3 SEM images of the MoSe$_2$/NDC electrocatalyst after 10000 cycles (a, b) in 1 M KOH and (c, d) 0.5 M H$_2$SO$_4$.

References

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