Supplementary Information

Tandem MoP nanocrystals with rich grain boundaries for efficient electrocatalytic hydrogen evolution

Xiaoxiao Liu, Lei Zhang, Mengxia Li and Xianluo Hu*

State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials

Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074,

China

*Corresponding author. Tel. +86 27 87558245.

E-mail address: huxl@mail.hust.edu.cn (X.L. Hu)

Experimental

Materials synthesis

Preparation of MoO$_2$·PO$_3$OH·H$_2$O. The MoO$_2$·PO$_3$OH·H$_2$O precursor for electrospinning was synthesized by a modified reflux method.[1] Firstly, 15 g of MoO$_3$ was dissolved in 45 mL of 85 wt% phosphoric acid by refluxing at around 180 °C for 2 h. After cooling down to room temperature, 200 mL of 16 M HNO$_3$ was added into the above solution. Then, the solution was again refluxed at 140 °C with constant strong stirring until large quantities of white solids were formed. The resulting solids were washed several times with cold water and ethanol, and finally dried in air. The detailed characterization results of the morphology and structure are shown in Fig. S1.

Preparation of N-MoP@C. The solution for electrospinning was prepared by dissolving 2 g of MoO$_2$·PO$_3$OH·H$_2$O and 1.5 g of polyvinylpyrrolidone (PVP, average Mw = 1,300,000) into a solvent mixed with 3 mL of deionized water and 14 mL of N, N-dimethylformamide. The obtained solution was loaded into a plastic injector with a normal 20-gauge stainless steel nozzle. To achieve well-proportioned as-spun precursor nanofibers, a constant flow rate of 30 μm m^{-1} and a high voltage of 17 kV were conducted, while a distance of 18 cm was set between the electrospinning jet and the grounded aluminum foil collector during electrospinning. The as-spun precursor nanofibers were put in a quartz boat and were separately heated up to 800 ºC for 3 h at a heating rate of 1.5 ºC min^{-1} in a flowing Ar gas.

For comparison, an irregular MoP/C hybrid prepared under the same conditions as described above except that the electrospinning method was omitted, and the sample

was denoted as I-MoP/C. In addition, carbon-free MoP nanoparticles were also prepared. After the electrospinning of the PVP/MoO$_2$·PO$_3$OH·H$_2$O solution, the achieved nanofibers were subjected to a calcination process at 400 °C for 10 h in a muffle furnace to remove the PVP, and they were then transferred to the carbon-free MoP particles in a flowing Ar/H$_2$ mixed atmosphere heating at 800 °C for 3 h. The sample of pure carbon was also prepared under the same conditions to the preparation of N-MoP@C except using MoO$_2$·PO$_3$OH·H$_2$O. The detailed characterization results are shown in Fig. S1.

Materials Characterization

The Powder X-ray diffraction (XRD) patterns were carefully collected for crystallographic analysis employing a PANalytical Multi-Purpose Diffractometer with high-intensity Cu Kα_1 irradiation (λ = 1.5406 Å) manipulating at 40 kV and 40 mA. Crystal structures were refined using the Rietveld method as implemented in the GSAS software package. A field emission scanning electron microscope (FE-SEM, FEI Sirion 200) together with a field emission transmission electron microscope (FE-TEM, Tecnai G2 F30, Holland) equipped with an energy spectrometer system were employed to investigate the microstructure and morphology of the samples. Nitrogen adsorption/desorption isotherms and pore size distributions were measured at 77 K (3H-2000PM1, Beishide Instrument Technology Co., Ltd). X-ray photoelectron spectroscopy (XPS) for surface element state analysis was carried out on a VG MultiLab 2000 system (Thermo VG Scientific) using a monochromatic Al Kα X-ray source. Thermogravimetric (TG) analysis was conducted using a PerkinElmer Diamond

apparatus in a flowing argon atmosphere. The carbon content is analyzed by the C/H/N/S/O elemental analyzer (Vario EL cube, Elementar Analysis System Company).

Electrochemical Measurements

All the electrochemical measurements in this work were performed by applying a three-electrode configuration including a graphite rod serving as the counter electrode, a saturated calomel electrode (SCE) used as the reference electrode, and a working electrode. The ink for constructing the working electrode was confected by homogeneously dispersing 2 mg of active materials into a mixture of 10 μL 5 wt% Nafion® and 190 μL ethanol through sonication. 10 μL of ink was dripped onto a glassy carbon electrode with a diameter of 5 mm as the working electrode. Then, the working electrode was dried at ambient temperature for several hours under the protection of glassware. All the prepared samples had the same loading applied to ensure comparability. Linear sweep voltammetry (LSV), recorded on a computer controlled CHI 760E electrochemical workstation, was employed to measure the samples' catalytic hydrogen evolution reaction performance. The catalytic properties were tested at a scan rate of 2 mV s^{-1} in both acidic (0.5 M H$_2$SO$_4$) and alkaline (1 M KOH) solutions. Before testing, the electrolytes were bubbled with flowing argon/hydrogen for 30 min to remove the air inside.
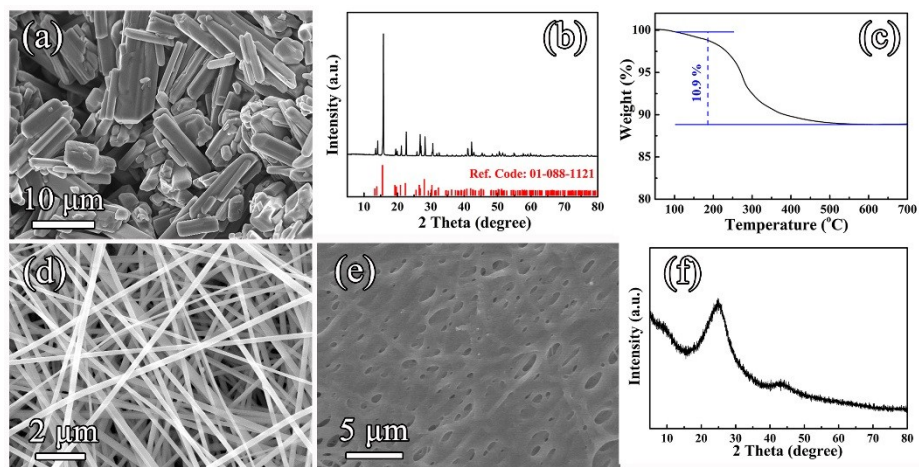
Fig. S1 (a) SEM image, (b) XRD pattern, and (c) TG curve of the precursor $MoO_2 \cdot PO_3OH \cdot H_2O$. (d) SEM image of pure PVP nanofibers. (e) SEM image and (f) XRD pattern of the pure carbon derived from the PVP nanofibers.

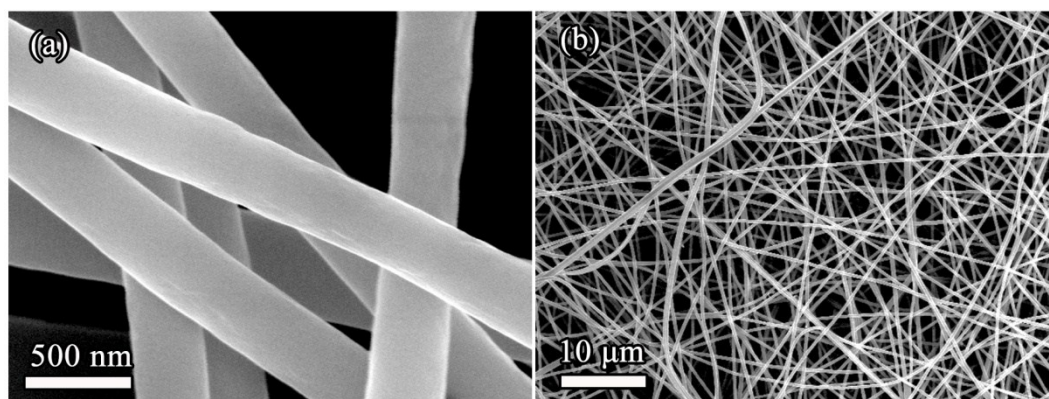**Fig. S2** (a, b) SEM images of the as-spun precursor of $MoO_2 \cdot PO_3OH \cdot H_2O$/PVP nanofibers. The average diameter is about 0.5 μm.
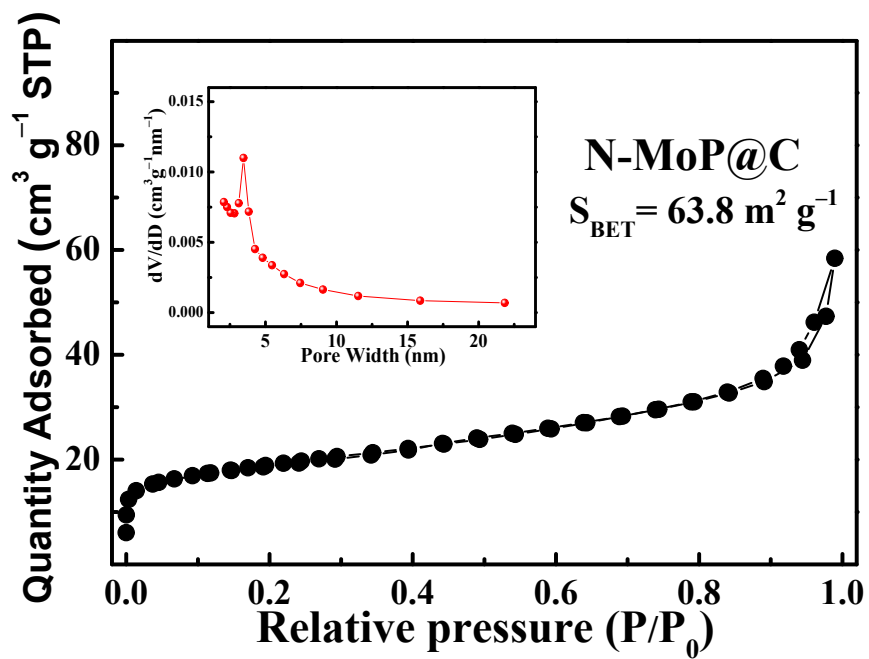
Fig. S3 N₂ adsorption/desorption isotherms and the corresponding pore size distribution for the as-prepared N-MoP@C product.
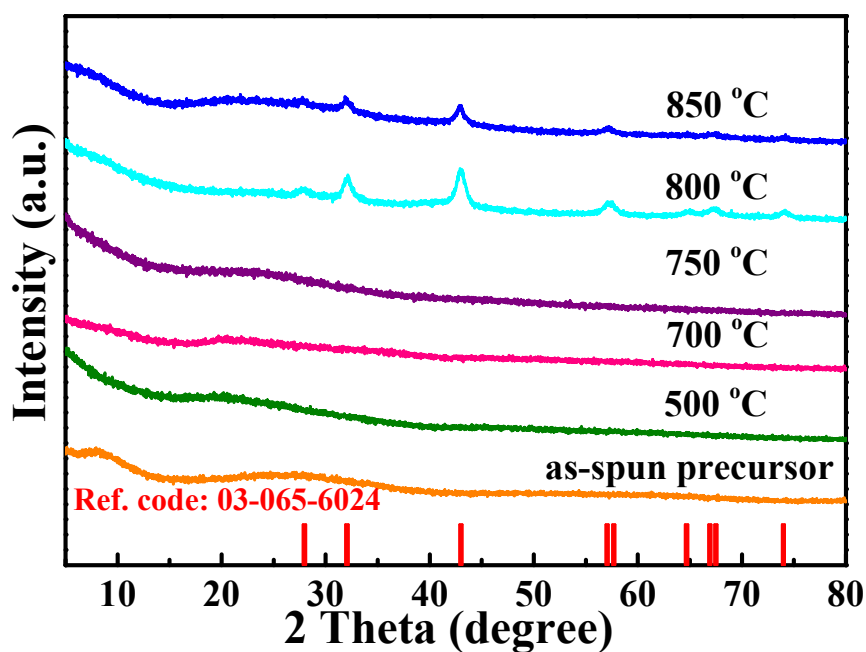
Fig. S4 XRD patterns of the products derived from the electrospun MoO$_2$·PO$_3$OH·H$_2$O/PVP precursor at different annealing temperatures from 500, 700, 750, 800, and 850 ºC.
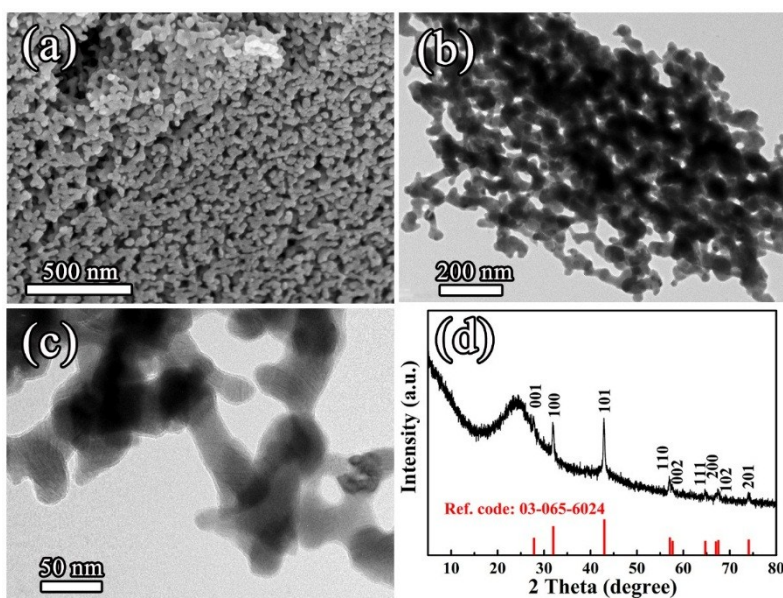

Fig. S5 (a) SEM image, (b, c) TEM images and the corresponding (d) XRD pattern of the irregular MoP/C hybrid (I-MoP/C).
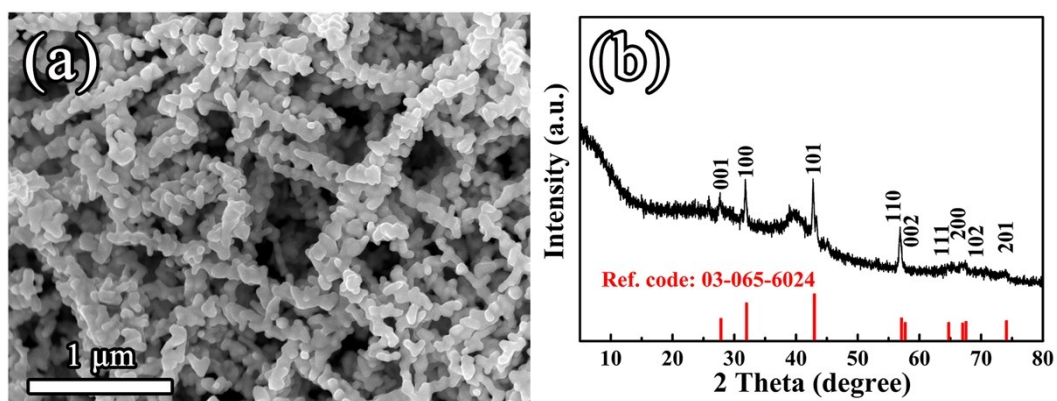
Fig. S6 (a) SEM image and the corresponding (b) XRD pattern of the carbon-free MoP product.
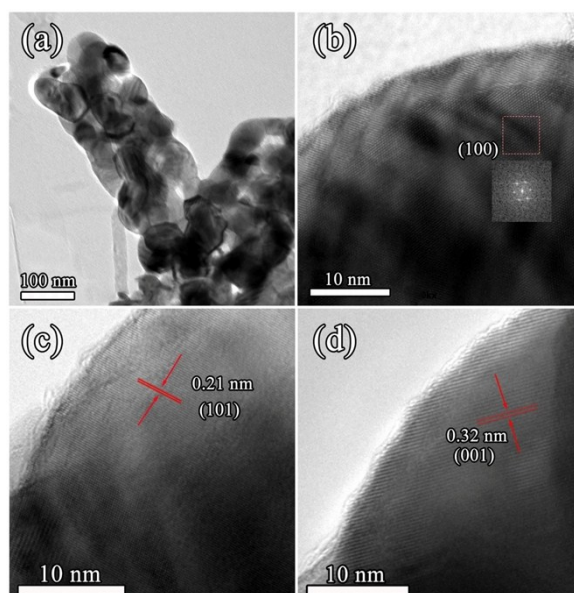

Fig. S7 TEM images of the N-MoP@C hybrid after stability measurement. The inset in (b) shows the fast Fourier transform pattern.

Reference

1 S.E. Lister, V.J. Rixom and J.S.O. Evans, *Chem. Mater.*, 2010, **22**, 5279-5289.