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Electronic Supplementary Information for

Molybdenum phosphide：A new highly efficient catalyst for the electrochemical hydrogen evolution reaction

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1. Experimental

1.1 Catalyst preparation

The metal phosphide catalysts were prepared from precursor salts via a temperature programmed reduction (TPR) method. For the unsupported MoP and Ni_2P, the corresponding metal salt (2.472 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, or 8.148 g of $Ni(NO_3)_2 \cdot 6H_2O$) and a corresponding amount of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) was added into 30 ml distilled water, to yield a P/Mo molar ratio of 1/1, or a P/Ni molar ratio of 2/1. The precursor solution was aged in a covered beaker in a water bath at 353 K for 24 h, dried at 393 K and calcined at 773 K for 4 h. The calcined catalyst precursor was ground to powder and converted to the active metal phosphide by TPR in H_2 at a flow rate of 160 ml (STP)/min. A heating rate of 10 K/min to 573 K, followed by a heating rate of 2 K/min to 923 K was used during the TPR, with the final temperature held for 3 h. The catalyst was then cooled to room temperature in Ar. Commercial MoS_2 particles purchased from the JDC company of China was also selected as a comparison sample, marked as C-MoS_2.

1.2 Characterizations

XRD patterns were recorded using D/max-2500 system with a Cu Kα irradiation source (λ=0.154 nm). Scanning electron microscopy (SEM) images were obtained with a FEI Sirion 200 microscope. Transmission electron microscopy (TEM) studies were performed on a Tecnai G^2 20 microscopy operating at 200 keV. BET surface areas were measured by N_2 adsorption at 77 K using a volumetric unit (MicrometriticsFlowsorb II 2300).

1.3 Preparation of electrodes and electrochemical characterization

1 mg catalyst and 80 μL Nafion solution (5 wt.%) were dispersed in 1 mL of a solution composed of 4:1 (v/v) distilled water and ethanol. After sonication for 30 mins, 5 μL of the catalyst slurry was dropped on the surface of a GCE (glassy carbon electrode) (3 mm in diameter). Subsequently, the GCE was left to dry at room temperature. Each electrode was prepared with a loading of approximately 71 μg/cm^2.

The electrochemical measurements were carried out in a standard three-electrode setup. The electrocatalytic activity was examined through linear sweep voltammetry with a scan rate

of 2 mV/s in 0.5 M H_2SO_4 at room temperature using CHI 660E (Chenhua, China), and stable polarization curves were recorded after 20 cycles with a standard deviation within 5%. A saturated calomel electrode (SCE) was employed as the reference electrode and a Pt foil as the counter electrode. Electrode potentials were recorded vs SCE reference electrode, which was calibrated with respect to reversible hydrogen electrode (RHE).