

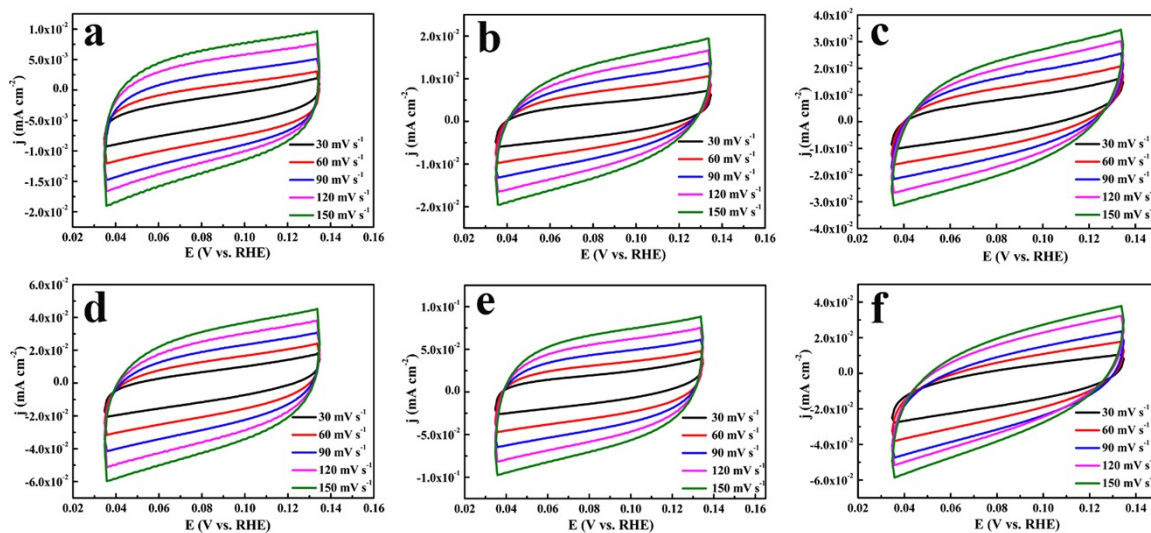
## Sulfur-doped Ni<sub>2</sub>P electrocatalyst for hydrogen evolution reaction

### Preparation of the electrode

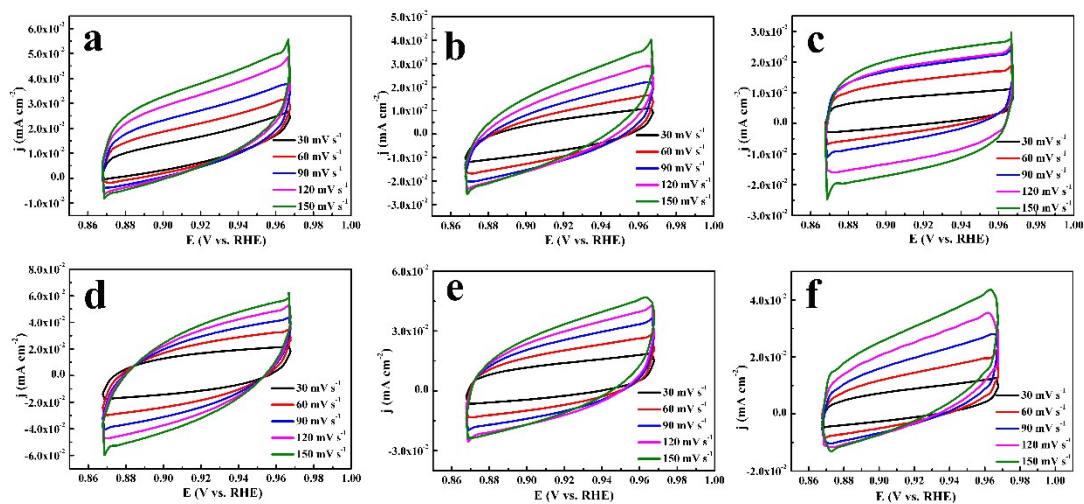
The sample (5 mg) was dispersed in the mixed solution of ethanol (480 μL) and water (500 μL), and then 20 μL of Nafion solution (5 wt%) was added. The mixture forms a uniform catalyst ink after ultrasonication for 30 minutes. 10 μL of catalyst ink was dropped on a glassy carbon electrode with a diameter of 5 mm, and dried at room temperature to obtain the electrode.

### Electrochemical measurements

All the electrochemical measurements were conducted on a three-electrode electrochemical cell by Autolab PGSTAT128N electrochemical workstation. S-Ni<sub>2</sub>P materials and other samples as controls were used as the working electrode. Ag/AgCl and Hg/HgO were used as the reference electrodes in acidic and alkaline electrolytes, respectively. The graphite rod was used as counter electrode. Electrochemical tests were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH electrolytes, respectively. The presented potentials in this work were all converted to reversible hydrogen electrode (RHE) via the equation:  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \text{ pH} + 0.197$  (in acidic electrolyte) and  $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.059 \text{ pH} + 0.098$  (in alkaline electrolyte). All of the polarization curves were recorded using linear sweep voltammetry (LSV). Electrochemical impedance spectroscopy (EIS) measurement was performed at the corresponding open circuit potential to the electrode. The frequency range is 50 KHz ~ 0.01 Hz. The charge-transfer resistance (R<sub>ct</sub>) was calculated by the diameter of the semicircular arc in the Nyquist plots. The double-layer capacitance (C<sub>dl</sub>) values were determined by performing cyclic voltammetry (CV) measurements at different scanning rates of 30 ~ 150 mV s<sup>-1</sup> under a non-Faradaic potential range.



**Fig. S1.** CV curves of the different samples in 0.5 M  $\text{H}_2\text{SO}_4$  solution. (a)  $\text{Ni}_2\text{P}$ , (b)  $\text{S}_3\%-\text{Ni}_2\text{P}$ , (c)  $\text{S}_5\%-\text{Ni}_2\text{P}$ , (d)  $\text{S}_7\%-\text{Ni}_2\text{P}$ , (e)  $\text{S}_{10}\%-\text{Ni}_2\text{P}$ , (f)  $\text{S}_{13}\%-\text{Ni}_2\text{P}$ .



**Fig. S2.** CV curves of the different samples in 1 M  $\text{KOH}$  solution. (a)  $\text{Ni}_2\text{P}$ , (b)  $\text{S}_3\%-\text{Ni}_2\text{P}$ , (c)  $\text{S}_5\%-\text{Ni}_2\text{P}$ , (d)  $\text{S}_7\%-\text{Ni}_2\text{P}$ , (e)  $\text{S}_{10}\%-\text{Ni}_2\text{P}$ , (f)  $\text{S}_{13}\%-\text{Ni}_2\text{P}$ .