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# Electronic Supplementary Information

## Phosphorus-Doped $CoS_2$ Nanosheet Arrays as Ultra-efficient Electrocatalysts for the Hydrogen Evolution Reaction

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### Experimental Section

Commercial carbon fiber paper (HCP030) was purchased from Shanghai HeSen Electronic Co. Ltd. $Co(NO)_3 \cdot 6H_2O$ and S powder was purchased from a commercial company. All the chemical reagents were used without further purification. All solutions used in the experiments were prepared with DI water (18.25 MΩ).

**Preparation of $Co(OH)_2$ nanosheets on carbon fiber paper**: The carbon fiber paper was initially treated at 400 ℃ for 16h. A three-electrode system was used for electrodepositon with the pretreated CFP (1 $cm^2$) as the working electrode, a platinum mesh (1 cm × 1 cm) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The electrolyte solution of 20 mM $Co(NO)_3 \cdot 6H_2O$ was used for potentiostatic deposition of $Co(OH)_2$ nanosheets onto CFP. The electrodeposition experiments were carried out at a constant potential at -1 V (vs. SCE) for 20 min at (28 ± 1) ℃ using an Autolab electrochemical workstation (Autolab PGSTAT302N, Metrohm-Autolab BV, Netherlands). After electrodeposition, the deposited green CFP was taken out and washed with deionized water several times and finally dried in vacuum at 60 ℃ for 12 h.

**Preparation of $CoS_2$/P**: Firstly, the electrodeposited $Co(OH)_2$/CFP was placed in the center of the furnace tube while 500 mg S powder was placed in a quartz boat which sat at the upstream of the furnace tube. The $Co(OH)_2$ nanosheets then reacted with S powder at 400 ℃ for 1 h with a heating rate of 8 ℃ $min^{-1}$ under Ar (30 sccm) environment. Secondly, 0.1 g $NaH_2PO_2 \cdot H_2O$ in a quartz boat was placed in the center of the furnace tube and the quartz boat with obtained $CoS_2$/CFP was placed at the downstream of the furnace tube. The phosphorization reaction was performed at 300 ℃ for 1 h with a heating rate of 2 ℃ $min^{-1}$ under Ar (30 sccm) environment. After naturally cooling down to the room temperature, the $CoS_2$/P was obtained.

**Electrochemical measurements**: All the electrochemical measurements including CV and LSV were carried out using an electrochemical workstation (CHI 600E, CH Instrument, USA) with a typical three-electrode system. A platinum mesh was used as counter electrode and saturated calomel electrode (SCE) as reference electrode and the obtained samples ($CoS_2$/P and $CoS_2$) were used as the working electrode. The EIS test was performed at a potential of -0.363 V (vs SCE) using an Autolab electrochemical workstation (Autolab PGSTAT302N, Metrohm-Autolab BV, Netherlands). All the measurements were conducted in 0.5 M $H_2SO_4$ at room temperature. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of 0.273 V. All data was presented with IR correction.

**Characterization**: The crystal structures of the samples were characterized using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, Cu Kα1). The Raman spectra were collected on a Raman spectrometer (Labram-010) using 632 nm laser. The surface morphology and microstructure were observed by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, JEOL, JEM-2010). The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250Xi X-ray photoelectron spectrometer using Mg as the excitation source.

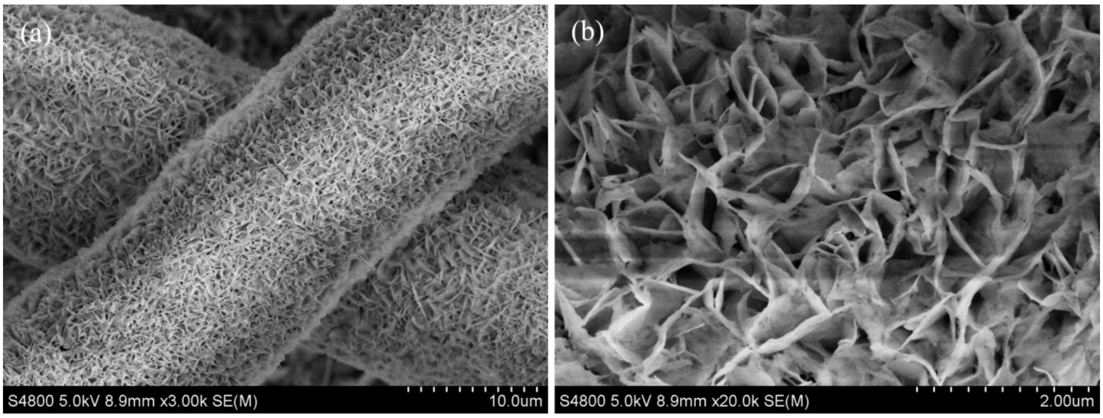

Figure S1. SEM of electrodeposited $Co(OH)_2$ nanosheets: low magnification (a); high magnification (b).

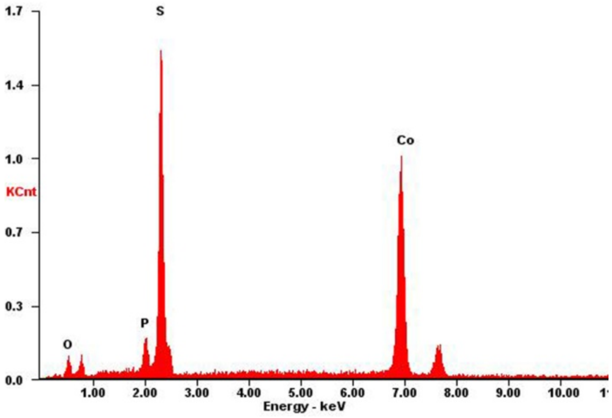

Figure S2. SEM-EDX of $CoS_2/P$

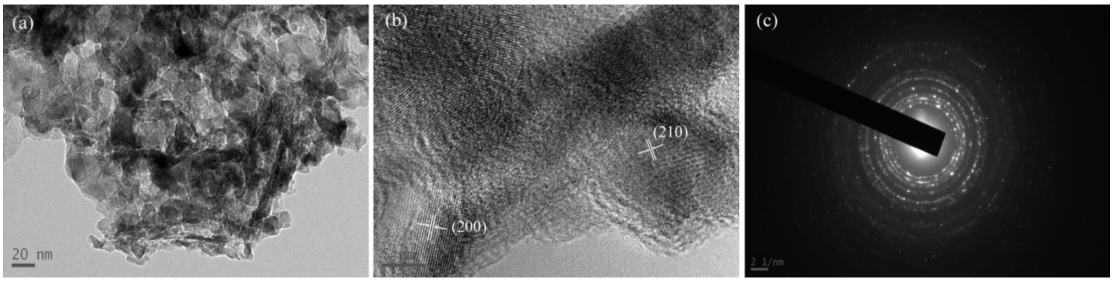

Figure S3. TEM image of $CoS_2$ (a); HRTEM image of $CoS_2$ with the d spacing of (210) (200) plane indicated (b); SAED spectrum of $CoS_2$ (c).

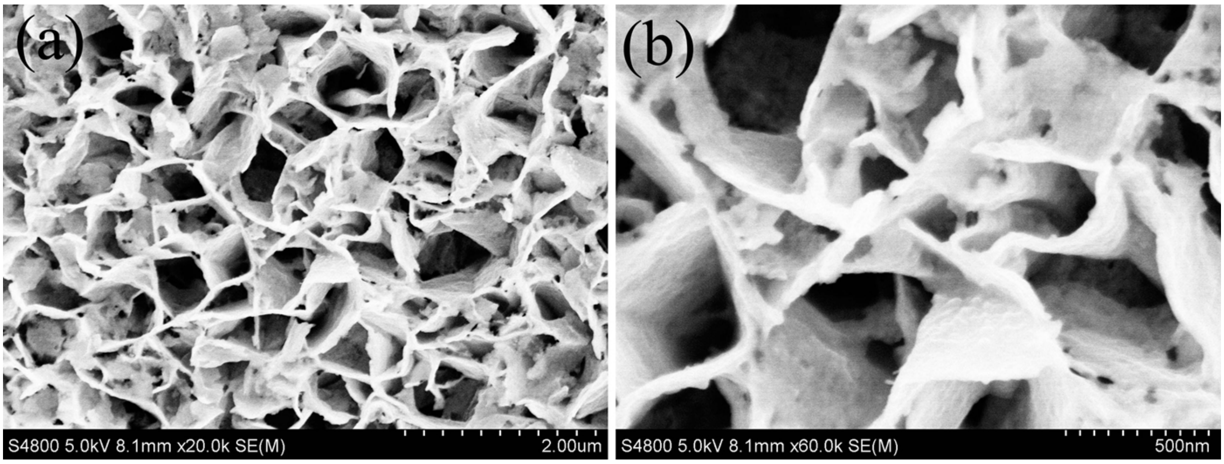

Figure S4. Magnifying SEM images of $CoS_2$/P.

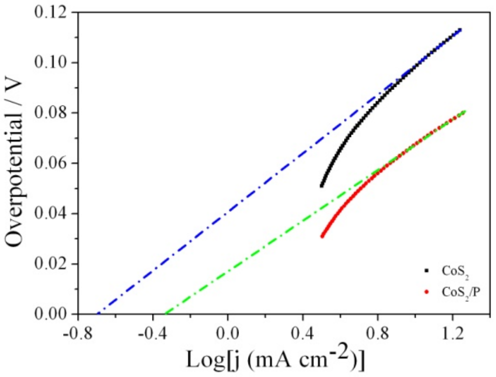

Figure S5. Calculation of exchange current density for $CoS_2/P$ and $CoS_2$.

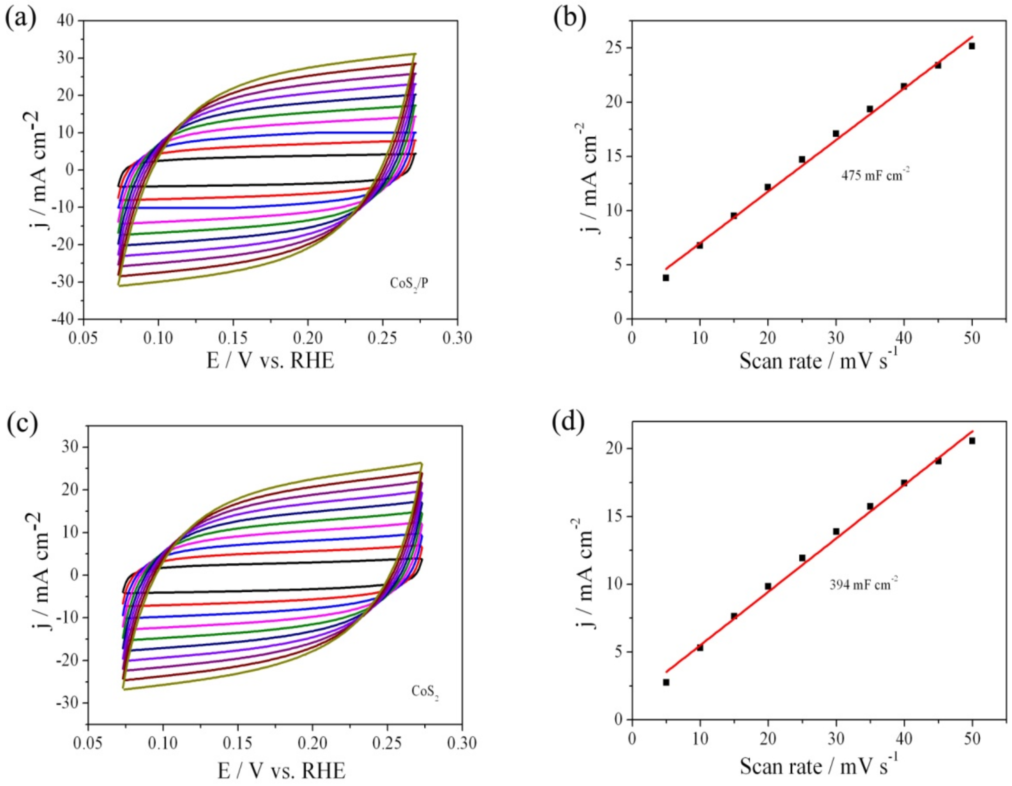

Figure S6. Cyclic voltammograms (CVs) for $CoS_2/P$ measured at different scan rates from 5 to 50 mV $s^{-1}$ (a); Plot of the current density at 0.173 V (vs. RHE) vs the scan rate for $CoS_2/P$ (b); Cyclic voltammograms (CVs) for $CoS_2$ measured at different scan rates from 5 to 50 mV $s^{-1}$ (c); Plot of the current density at 0.173 V (vs. RHE) vs the scan rate for $CoS_2$(d).

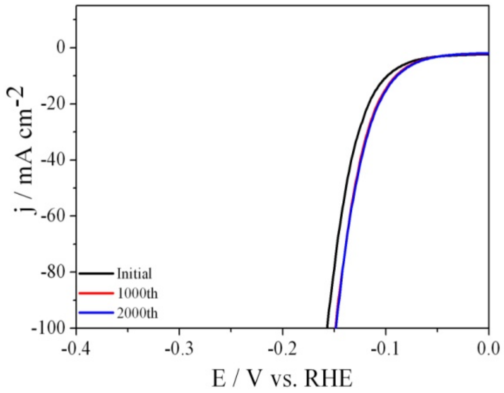

Figure S7.Polarization curves of $CoS_2$ initially and after 1000 and 2000 CV cycles with a scan rate of 100 mV $s^{-1}$ in 0.5 M $H_2SO_4$.

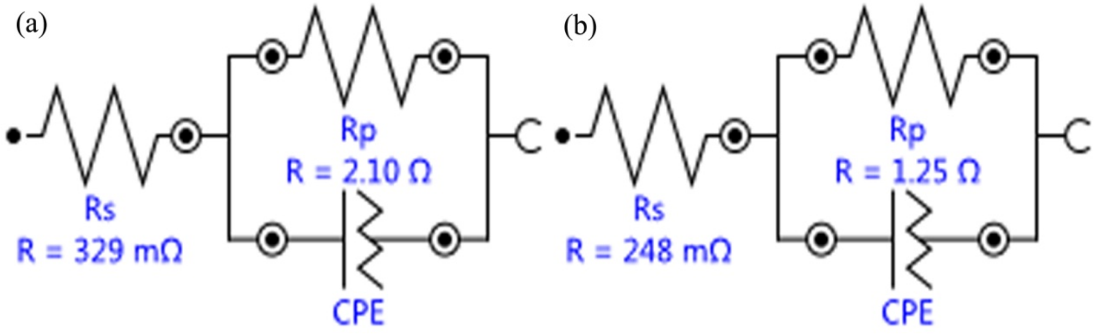

Figure S8.Electrochemical impedance spectroscopy (EIS) fitting results for $CoS_2$ and $CoS_2$/P recorded at 0.09 V vs. RHE. inset: the corresponding equivalent circuit consisting of an electrolyte resistance (Rs), a charge-transfer resistance (Rp) and a constant-phase element (CPE)

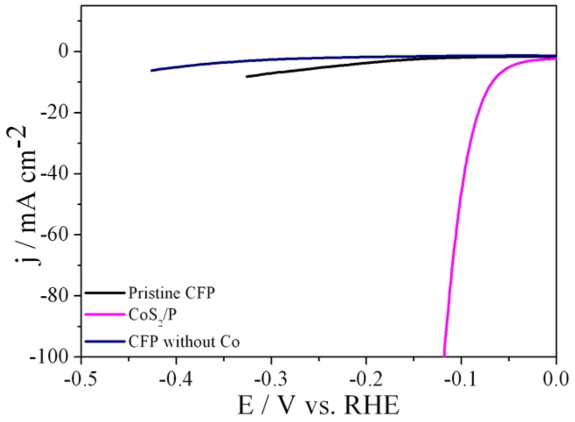

Figure S9. Polarization curves of pristine CFP, $CoS_2$/P and CFP without cobalt under the same experiments as $CoS_2$/P.

As shown in Figure S9, the activity of the carbon fiber paper without Co was almost the same as the pristine carbon fiber paper, hence, it could not be comparable to $CoS_2$/P. S or P species might not be doped into the carbon fiber paper during the preparation process because S or P doping needs much higher temperature than our experiment temperature (400 ℃ and 300℃). Hence, there is no synergistic effect of heteroatom doped carbon and $CoS_2$ to promote the HER activity.

# Tafel slope calculation :

$$\eta = a + b \, log|\mathrm{j}|$$

where $\eta$ is the overpotential, *b* is the Tafel slope and *j* is the current density

# Exchange current density calculation:

The exchange current density ($j_0$) was calculated using extrapolation method based on Tafel equation. When the overpotential value is 0, the log [j] values for $CoS_2$/P and $CoS_2$ are -0.33 and -0.69, respectively. $j_0$ for $CoS_2$/P and $CoS_2$ are calculated to be 0.47 and 0.20 mA $cm^{-2}$, respectively.

**Table S1 The comparison of HER performance of $CoS_2$ and $CoS_2/P$ with other cobalt based HER electrocatalysts in 0.5 M $H_2SO_4$**

| Catalyst | Mass loading (mg $cm^{-2}$) | Onset potential (mV) | $\eta$ at 10 mA $cm^{-2}$ (mv) | $\eta$ at 100 mA $cm^{-2}$ (mv) | Tafel slope (mV $dec^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| $CoS_2$ | 2 ± 0.1 | ~50 | 98 | 157 | 58 | This work |
| $CoS_2/P$ | 2.5 ± 0.1 | ~25 | 67 | 118 | 50 | This work |
| Metallic $CoS_2$ nanowire | 1.7 ± 0.3 | 75 | 145 | ~ | 51.6 | S1 |
| $CoSe_2$ | 2.8 | ~ | 137 | 180 | 42.1 | S2 |
| CoP nanowire | 0.92 | 38 | 67 | 204 | 51 | S3 |
| CoS | 0.91 | 59 | ~ | 196 | 56.2 | S4 |
| CoP | 0.91 | 32 | ~ | 107 | 54.8 | S4 |
| N-Co@G | 0.285 | 70 | 265 | ~ | 98 | S5 |
| $CoS_2$ | 0.037 | ~ | ~ | ~ | 44.6 | S6 |
| $CoSe_2$ | 0.037 | ~ | ~ | ~ | 42.4 | S6 |
| $CoSe_2$nanobelt | 2.3 | 96 | 141 | 200 | 68 | S7 |

S1 Faber M S, Dziedzic R, Lukowski M A, et al. High-performance electrocatalysis using metallic cobalt pyrite (CoS2) micro-and nanostructures[J]. Journal of the American Chemical Society, 2014, 136(28): 10053-10061.

S2 Kong D, Wang H, Lu Z, et al. CoSe2 nanoparticles grown on carbon fiber paper: an efficient and stable electrocatalyst for hydrogen evolution reaction[J]. Journal of the American Chemical Society, 2014, 136(13): 4897-4900.

S3 Tian J, Liu Q, Asiri A M, et al. Self-supported nanoporous cobalt phosphide nanowire arrays: an efficient 3D hydrogen-evolving cathode over the wide range of pH 0–14[J]. Journal of the American Chemical Society, 2014, 136(21): 7587-7590.

S4 Li J, Zhou X, Xia Z, et al. Facile synthesis of CoX (X= S, P) as an efficient electrocatalyst for hydrogen evolution reaction[J]. Journal of Materials Chemistry A, 2015.

S5 Fei H, Yang Y, Peng Z, et al. Cobalt Nanoparticles Embedded in Nitrogen-Doped Carbon for the Hydrogen Evolution Reaction[J]. ACS applied materials & interfaces, 2015, 7(15): 8083-8087.

S6 Kong D, Cha J J, Wang H, et al. First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction[J]. Energy & Environmental Science, 2013, 6(12): 3553-3558.

S7 Zheng Y R, Gao M R, Yu Z Y, et al. Cobalt diselenidenanobelts grafted on carbon fiber felt: An efficient and robust 3D cathode for hydrogen production†[J]. Chemical Science, 2015.