## **Supporting Information**

Cobalt Sulphide Nanotubes ( $Co_9S_8$ ) Decorated with Amorphous  $MoS_x$  as Highly Efficient Hydrogen Evolution Electrocatalyst

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**Figure S1.** The effect of different counter electrodes on polarization curves of the  $Co_9S_8$  /  $MoS_x$  hybrid: red curve represents a Pt wire as counter electrode, and blue curve represents a graphite rod as counter electrode.

From the effect of different counter electrodes on polarization curves (Figure S1) of  $\text{Co}_9\text{S}_8$  / MoS<sub>*x*</sub> hybrid, it could be observed that the results did not show any obvious difference.



Figure S2. (a) XPS survey spectrum, (b) XP spectrum of Mo 3d-S 2s, and (c) S 2p of the pristine



**Figure S3.** FE-SEM figure of  $Co_9S_8 / MoS_x$ -1:2 hybrid.



**Figure S4.** Current-voltage characteristic of  $\text{Co}_9\text{S}_8 / \text{MoS}_x$  -2:1 and  $\text{Co}_9\text{S}_8 / \text{MoS}_x$  -1:2 at room temperature. Inset is the enlargement of current-voltage characteristic for  $\text{Co}_9\text{S}_8 / \text{MoS}_x$  -2:1. **Table S1.** Comparison of resistance R ( $\Omega$ ), parameters measured, resistivity  $\rho$  values for the  $\text{Co}_9\text{S}_8 / \text{MoS}_x$  -2:1 and  $\text{Co}_9\text{S}_8 / \text{MoS}_x$  -1:2.

sample	resistance R (Ω)	length L(cm)	cross-sectional area	resistivity ρ (Ω.cm)
			S (cm <sup>2</sup> )	
$Co_9S_8 / MoS_x - 2:1$	1.2	0.3	1.5×10 <sup>-2</sup>	0.06
Co <sub>9</sub> S <sub>8</sub> / MoS <sub>x</sub> -1:2	41.9	0.3	1.5×10 <sup>-2</sup>	2.10

In this case, we adopt the conventional four-point probe technique in the room temperature to measure electrical resistivity of the samples. Firstly, the powder samples were compressed into rectangular bulks with  $(10 \times 10 \times 0.15 \text{ mm}^3)$ . The electrical measurements were conducted using a 4-point test fixture (copper contact wires with a distance of 6 mm between the source electrodes and 3 mm between the measuring electrodes). I-V characteristics were measured by an electrometer Keithley 6220 (as a current source) and an electrometer Keithley 2182A (detecting voltage).



**Figure S5.** Cyclic voltammograms of the pristine  $MoS_x(a)$ , physical mixture ( $Co_9S_8$ -MoS<sub>x</sub>) (b), and  $Co_9S_8$  nanotubes (c).



Figure S6. Nyquist plots of the pristine  $MoS_x(a)$ , and  $Co_9S_8$  nanotubes (b), respectively.

**Table S2.** Comparison of charge transfer resistance ( $R_{ct}$ ) values for the pristine  $MoS_x$ ,  $Co_9S_8$  nanotubes, and  $Co_9S_8 / MoS_x$  hybrid.

Sample	η=-100mV(Ω)	η=-150mV(Ω)	η=-200mV(Ω)
$MoS_x$	7017	2964	971
Co <sub>9</sub> S <sub>8</sub>	4439	424.3	79.2
$\operatorname{Co}_9S_8$ / $\operatorname{MoS}_x$	474.7	216.2	69.5



Figure S7. Time dependent potential of  $Co_9S_8$  /  $MoS_x$  under a current density of 10 mA cm<sup>-2</sup>.



**Figure S8.** The durability test for the pristine  $MoS_x(a)$ ,  $Co_9S_8$ - $MoS_x(b)$ ,  $Co_9S_8$  nanotubes (c),  $Co_9S_8$ /  $MoS_x$ -3:1 (d),  $Co_9S_8$  /  $MoS_x$ -1:1 (e), and  $Co_9S_8$  /  $MoS_x$ -1:2 (f).