## **Supporting Information**

## In situ integration of cobalt diselenide nanoparticles on CNTs realizing durable hydrogen evolution

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Figure S1. SEM image of CNTs.



Figure S2. SEM image of pure CoSe<sub>2</sub>.



Figure S3. Grain size distribution of CoSe<sub>2</sub> nanoparticles of pure CoSe<sub>2</sub>.



Figure S4. (a) Polarization curves, and (b) histograms error bars of CoSe<sub>2</sub>/CNT with different ratios.



Figure S5. CVs were scanned at various rates from 20 to 200 mV s<sup>-1</sup>: (a)  $CoSe_2/CNTs$  and (b) pure  $CoSe_2$ .



Figure S6. Cyclic voltammetry cycling of Pure  $CoSe_2$  and  $CoSe_2/CNTs$  in pH = 7 phosphate buffer with a scan rate of 50 mV s<sup>-1</sup> range from -0.2 to 0.6 V vs. RHE.



Figure S7. Polarization curves at different temperatures (a) CoSe<sub>2</sub>/CNTs and (b) pure CoSe<sub>2</sub>.

The exchange current density was taken as a function of the reciprocal of temperature, and the activation energy was calculated using the Arrhenius formula<sup>1</sup>:

$$\log j_0 = \log A_i - E_a / (2.3RT)$$
 (S1)

Where  $A_i$  is the pre-Arrhenius factor. According to the slope of the Arrhenius curve, the  $E_a$  values of pure CoSe<sub>2</sub> and CoSe<sub>2</sub>/CNTs electrocatalysts are 48.043 kJ mol<sup>-1</sup> and 17.342 kJ mol<sup>-1</sup>, respectively.



Figure S8. (a) Co 2p, (b) Se 3d and Polarization curves, and (c) B 1s XPS spectra of CoSe<sub>2</sub>/CNT composite after cycling measurement.

In the Se 3d spectra, the  $SeO_x$  characteristic peak at 59.3 eV, caused by the oxidation of a slight excess of metallic selenium, disappears after the long cycle.<sup>2</sup>

Catalysts	$\eta_{10/\text{ mV}}$	Stability test conditions (mA cm <sup>-2</sup> )	Long cycle stability test time (h)	Ref
CoSe <sub>2</sub> @HC	171.7	10	12	3
CoSe2/GD	/	20	24	4
CoSe <sub>2</sub>	272	20	8	5
CoSe <sub>2</sub> /CNTs	153	30	48	Our work

Table S1. The stability of  $CoSe_2/CNTs$  in 0.5 M  $H_2SO_4$  solution compared with other HER catalysts.

## References

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