

## Supporting information

### **An efficient WSe<sub>2</sub>/Co<sub>0.85</sub>Se/Graphene hybrid catalyst for electrochemical hydrogen evolution reaction**

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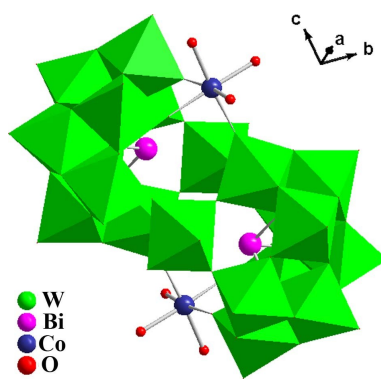
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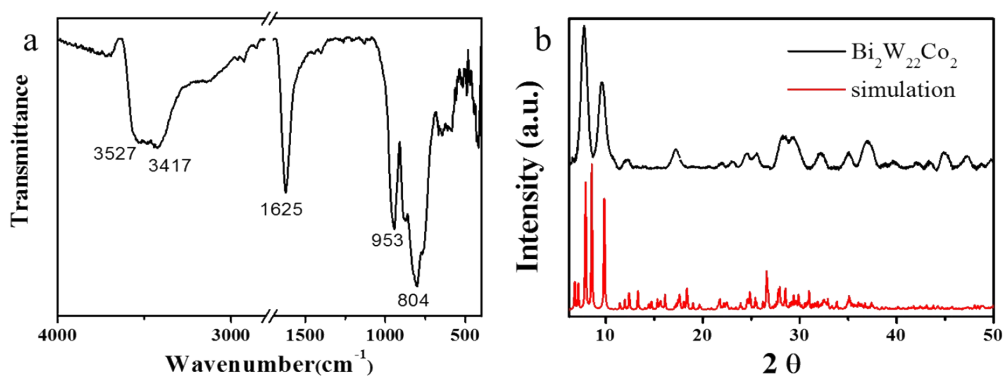
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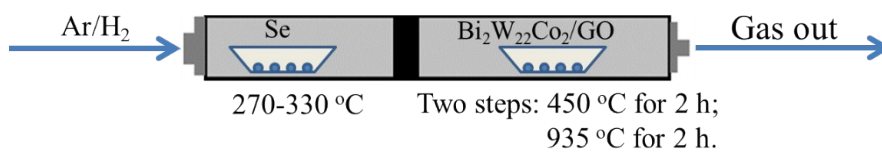
<sup>†</sup> These two authors made equal contributions.



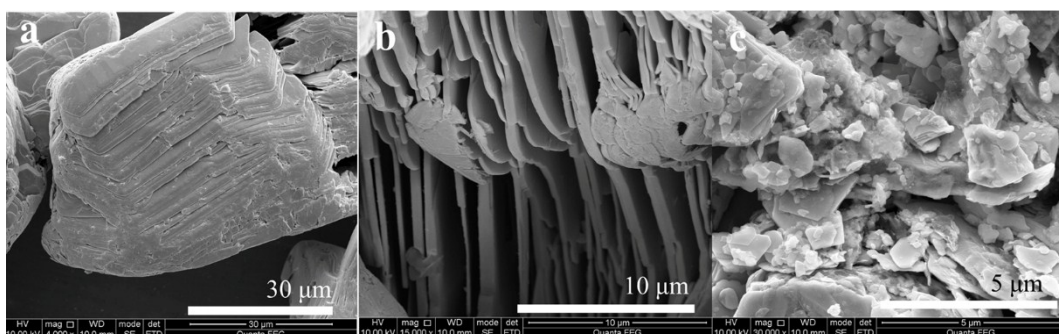
**Figure S1.** Crystal structure of  $\text{Na}_{12}[\text{Co}(\text{H}_2\text{O})_2(\text{OH})_2\{\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2\}]_{48}\text{H}_{20}$   
(Denoted as  $\text{Bi}_2\text{W}_{22}\text{Co}_2$ ).



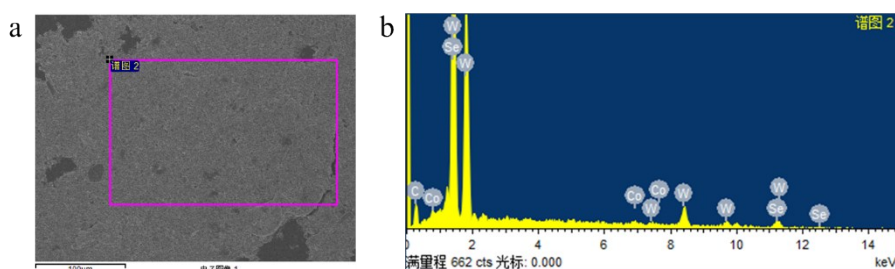
**Figure S2.** (a) FT-IR spectrum of  $\text{Bi}_2\text{W}_{20}\text{Co}_2$ ; (b) XRD patterns of  $\text{Bi}_2\text{W}_{20}\text{Co}_2$  powder and simulated curve from cif data.



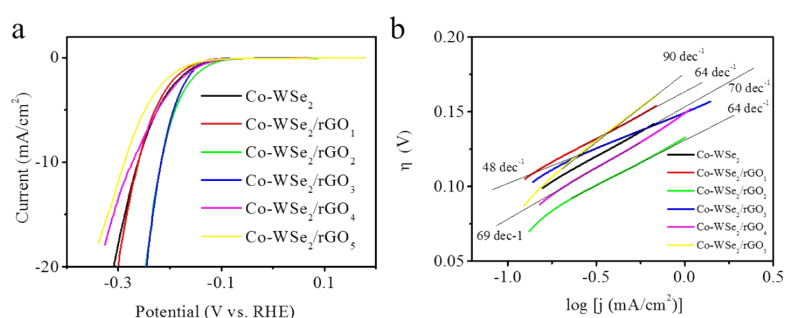
**Scheme S1.** Synthetic procedure of  $\text{Co-WSe}_2/\text{rGO}$  with different amount of rGO via CVD selenization.



**Figure S3.** SEM images of (a) as-synthesized Co-WSe<sub>2</sub>/rGO<sub>2</sub> and sonicated at (b) 10 and (c) 30 mins, respectively. The initial morphology is bulk aggregate with layered structures, and ethanol facilitated exfoliation took place during sonication. As shown in (b), sheet-like structures were formed, and the whole aggregated became loose. Finally, the as-synthesized was exfoliated into irregular sheet-like aggregates.



**Figure S4.** (a) Low magnification image of Co-WSe<sub>2</sub>/rGO<sub>2</sub>; (b) EDS profile of Co-WSe<sub>2</sub>/rGO<sub>2</sub> in the selected area of a.



**Figure S5.** (a) Polarization curves of Co-WSe<sub>2</sub>/rGO composites as a function of rGO contents. (b) Corresponding tafel curves of Co-WSe<sub>2</sub>/rGO composites.

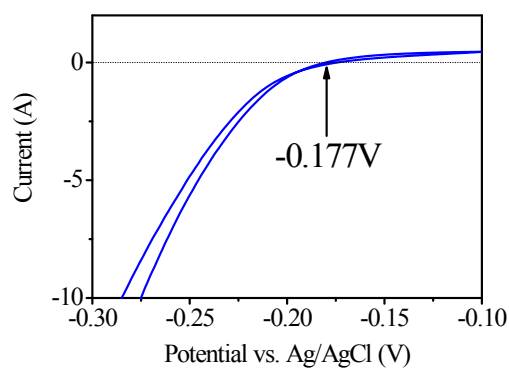
**Table S1.** Comparisons of our Co-WSe<sub>2</sub>/rGO composites and previous HER catalysts.

Sample	Loading mass (mg/cm <sup>2</sup> )	$\eta_{10}$ (mV)	Tafel slope (dec <sup>-1</sup> )	$j_0$ (mA/cm <sup>2</sup> )	reference
WSe <sub>2</sub> /W foil	—	350	—	—	1
WSe <sub>2</sub> /Si NWs	—	300	77.4	$\sim 4.5 \times 10^{-3}$	2
WS <sub>2(1-x)}</sub> Se <sub>2x</sub>	0.21	298	99	$29 \times 10^{-3}$	3
Exfoliated WSe <sub>2</sub>	0.057	800	120	$3.6 \times 10^{-5}$	4
3D dendritic WSe <sub>2</sub>	2.2-2.5	228	80	$15 \times 10^{-3}$	5
WS <sub>2(1-x)}</sub> Se <sub>2x</sub> nanoflakes on CF	—	158	98	0.240	6
thin films of tungsten selenides	—	245	98	—	7
Metallic WS <sub>2(1-x)}</sub> Se <sub>2x</sub> Nanoribbons	0.3	170	78	0.025	8
Monolayer WS <sub>2(1-x)}</sub> Se <sub>2x</sub>	—	80 (onset potential)	85	—	9
Co-WSe <sub>2</sub> /rGO <sub>1</sub>	0.56	260	64	$4.81 \times 10^{-3}$	This work
Co-WSe <sub>2</sub> /rGO <sub>2</sub>	0.56	217	64	$15.3 \times 10^{-3}$	This work
Co-WSe <sub>2</sub> /rGO <sub>3</sub>	0.56	217	48	$0.7 \times 10^{-3}$	This work
Co-WSe <sub>2</sub> /rGO <sub>4</sub>	0.56	273	68	$11.6 \times 10^{-3}$	This work
Co-WSe <sub>2</sub> /rGO <sub>5</sub>	0.56	290	90	$6.98 \times 10^{-3}$	This work

$\eta_0$ : Onset potential was obtained at current density of 0.5 mA/cm<sup>2</sup>;

$\eta_{10}$ : Over potential was obtained at current density of 10 mA/cm<sup>2</sup>;

$J_0$ : Exchange current density for the catalysts were obtained from the Tafel curves by using the extrapolation method.



**Figure S6.** Cyclic voltammetry curve of the calibrated Ag/AgCl electrode.

## References

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