Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Cobalt Metal Organic Framework (Co-MOF) derived $CoSe_2$/C hybrid nanostructures for Electrochemical Hydrogen Evolution Reaction Supported by DFT Studies

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Calculation of electrochemical active surface area (ECSA):

At first, the cyclic voltammograms at different scan rates in a non-Faradaic potential region were recorded and double layer capacitance (C_{dl}) has been calculated by linear fitting the plot of cathodic and anodic current against scan rates. Since the ECSA is directly correlated to the values of C_{dl}, thus the ECSA has been calculated as per the following equation,

$$ECSA = \frac{C_{dl}}{C_s} \quad \text{.............................} \quad (1)$$

Here, C_s is the specific capacitance of an atomically smooth nanostructure in acidic medium and its value is 35 μF/cm^2.

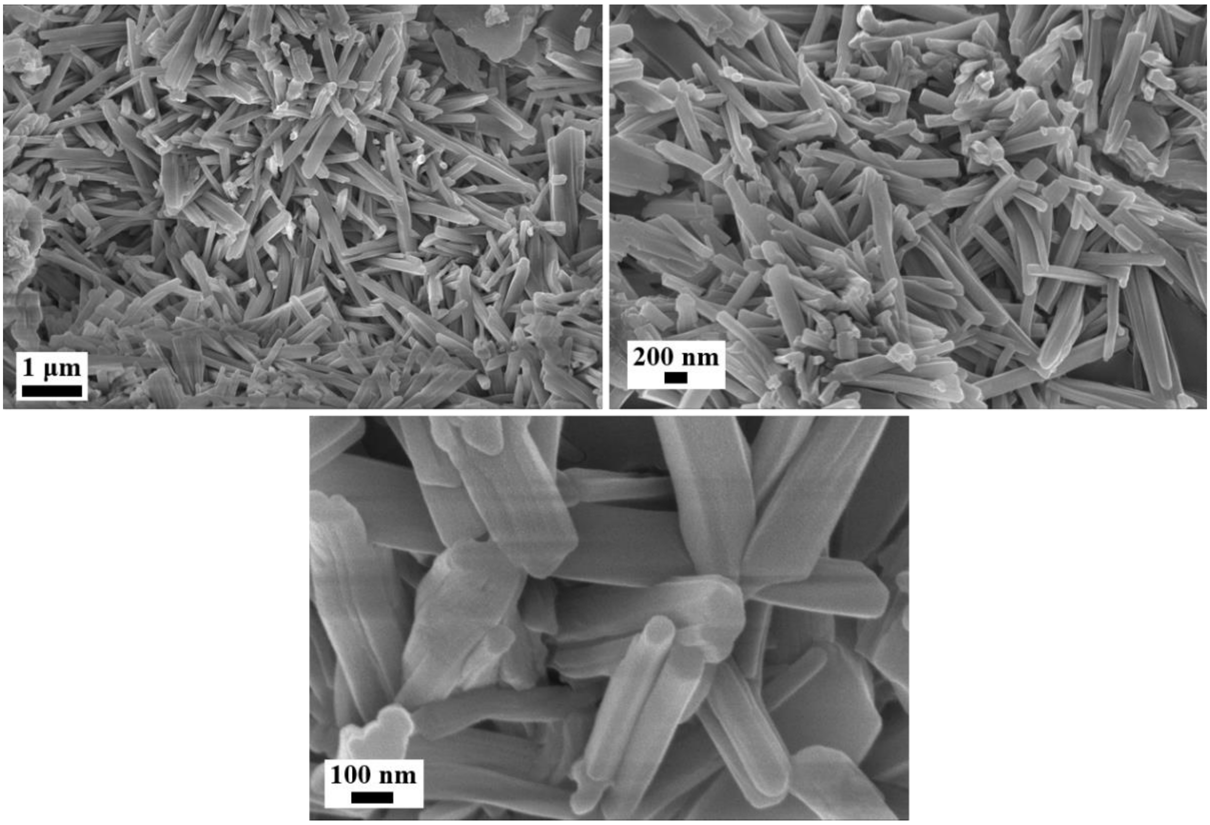


Fig. S1. FESEM images of Co-MOF.

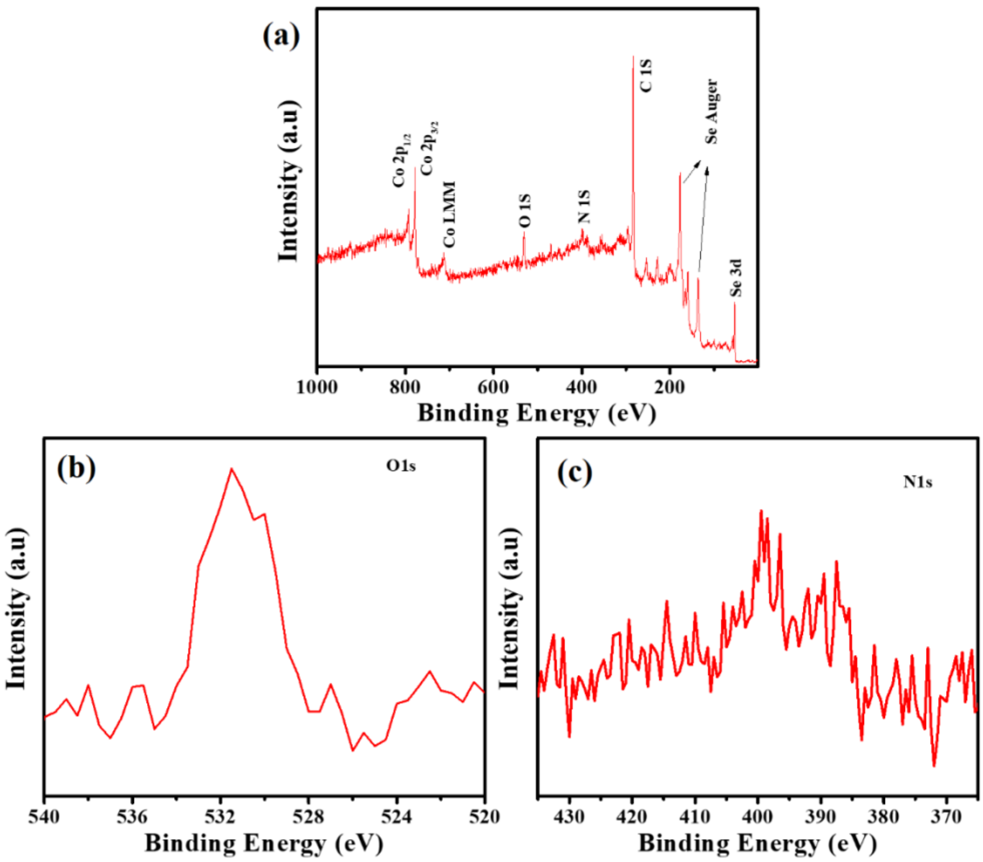


Fig. S 2 (a) Survey spectrum and high resolution XPS spectrum of (b) O1s and (c) N1s of $CoSe_2$/C hybrid.

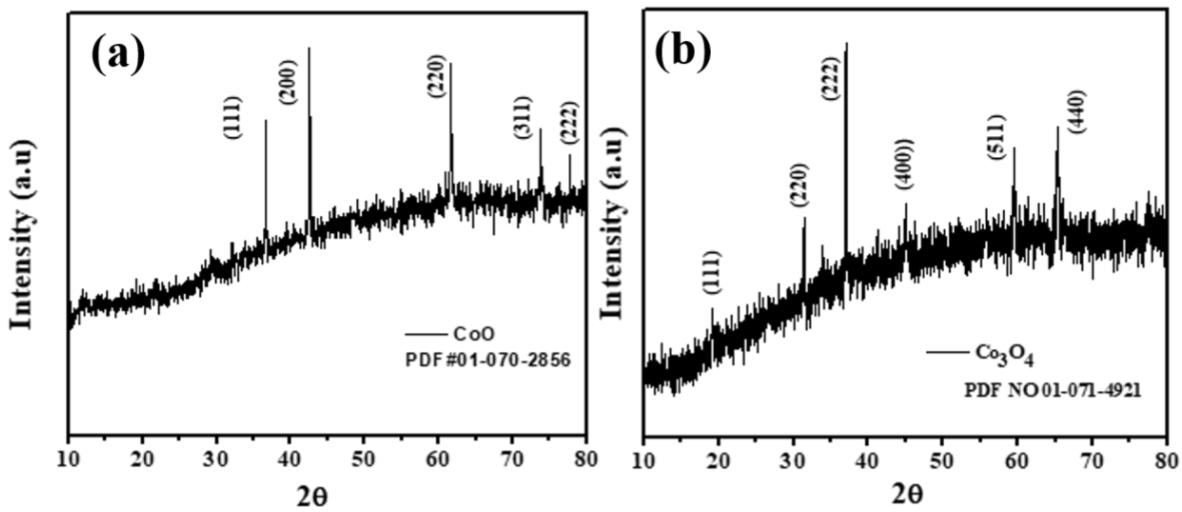
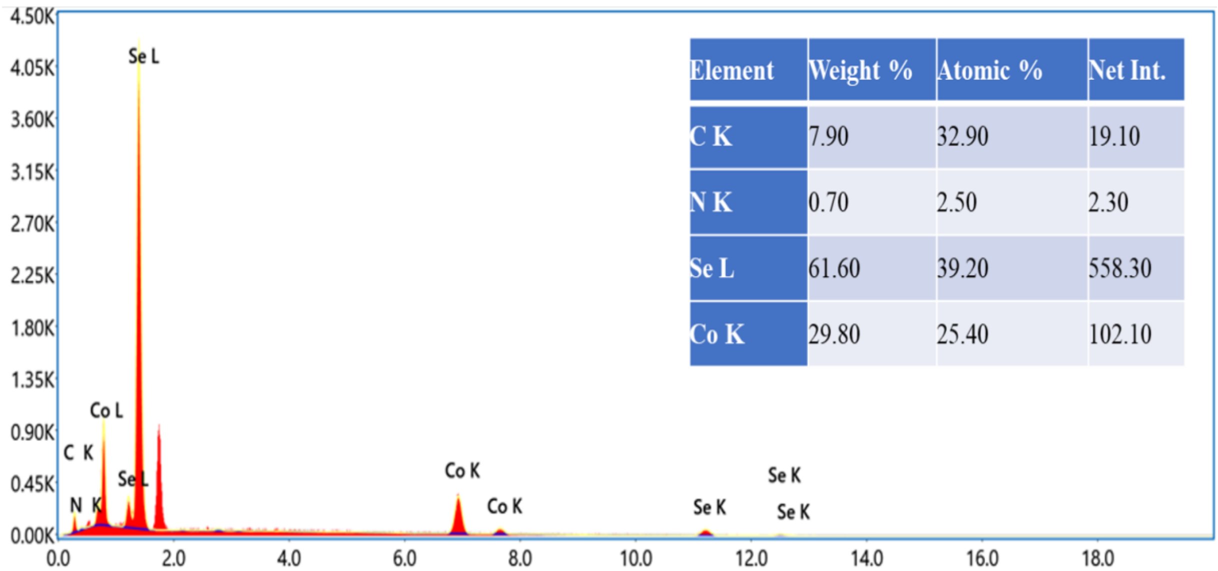


Fig. S3. Powder X-ray diffraction pattern of post TGA $CoSe_2$/C hybrid sample (a) under the flow of nitrogen and (b) oxygen gas.



Element	Weight %	Atomic %	Net Int.
C K	7.90	32.90	19.10
N K	0.70	2.50	2.30
Se L	61.60	39.20	558.30
Co K	29.80	25.40	102.10

Fig. S4. EDS spectrum of $CoSe_2$/C hybrid. The inset shows the weight and atomic percentage distribution of different elements.

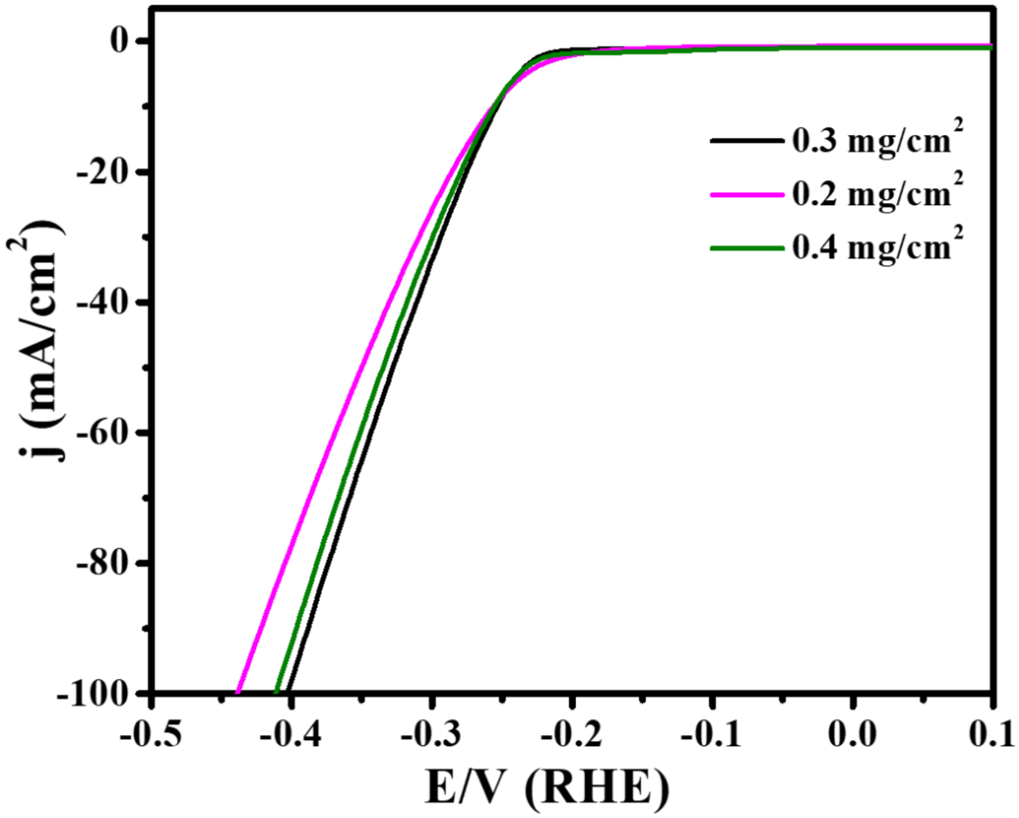


Fig. S 5 LSVs showing the HER activity of $CoSe_2$/C modified electrode at different mass loading in 0.5 M H_2SO_4 solution at a sweep rate of 5 mV/s.

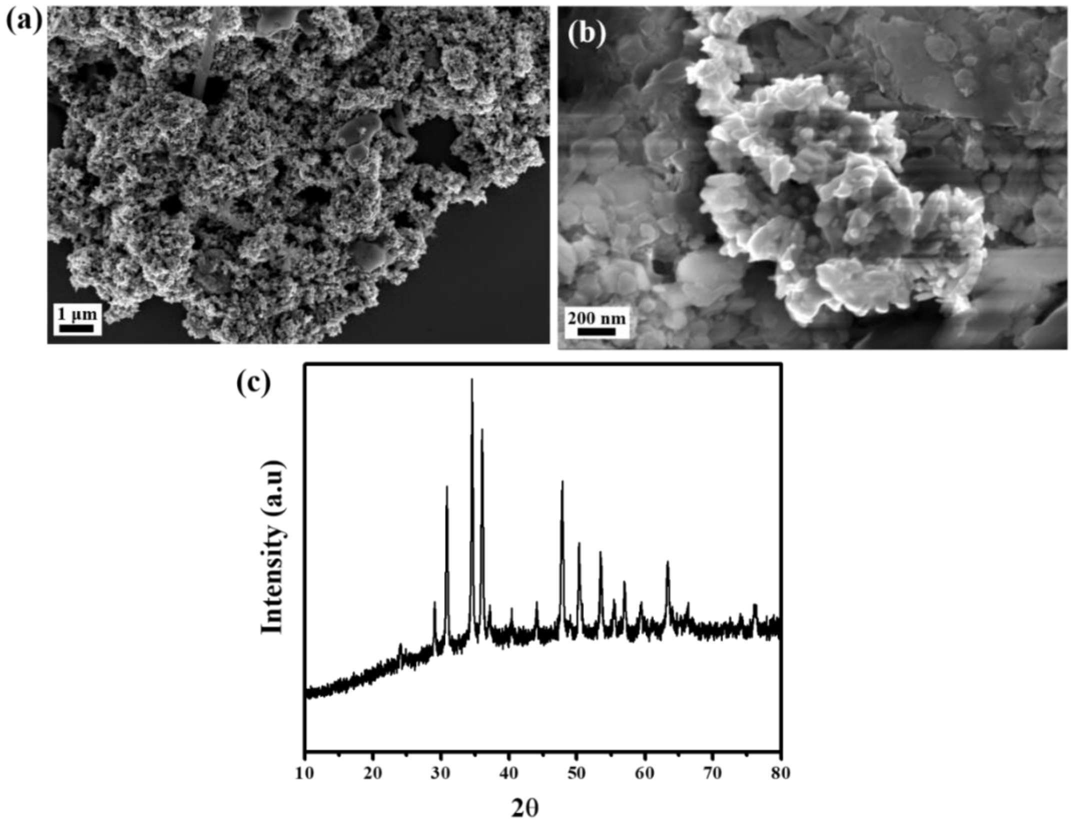


Fig. S6. FESEM (a, b) and PXRD of $CoSe_2$/C after HER stability test.

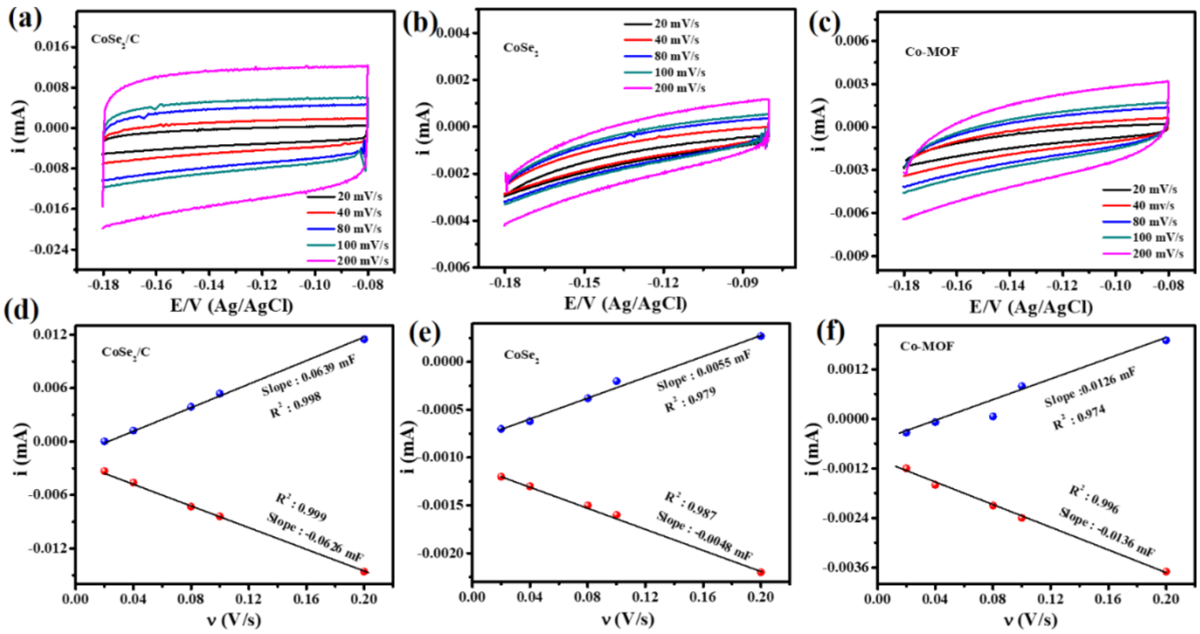


Fig. S7 (a-c) Cyclic voltammograms showing the charging currents measured in a non-Faradaic region at a scan rate of 25, 50, 100, 150, 200 mV/s respectively and (d-f) the plot of cathodic and anodic charging currents measured at −0.13 V (vs. Ag/AgCl) against scan rates for $CoSe_2$/C, $CoSe_2$ and Co-MOF respectively.

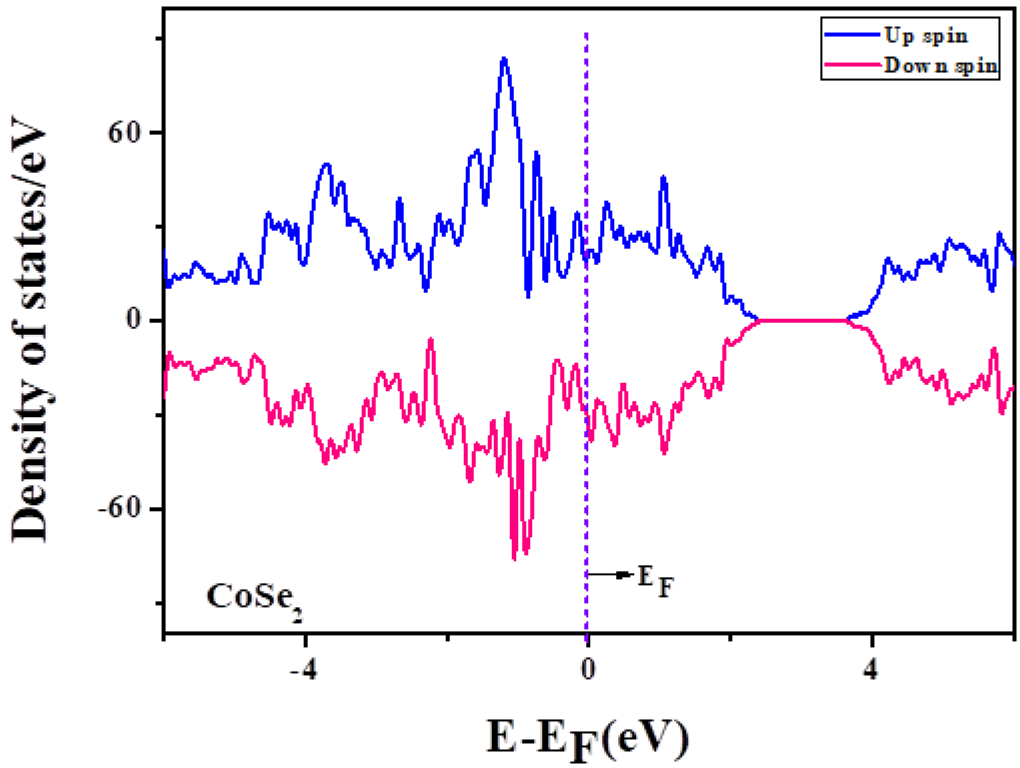


Fig. S8. TDOS plot for $CoSe_2$ (101) layer.

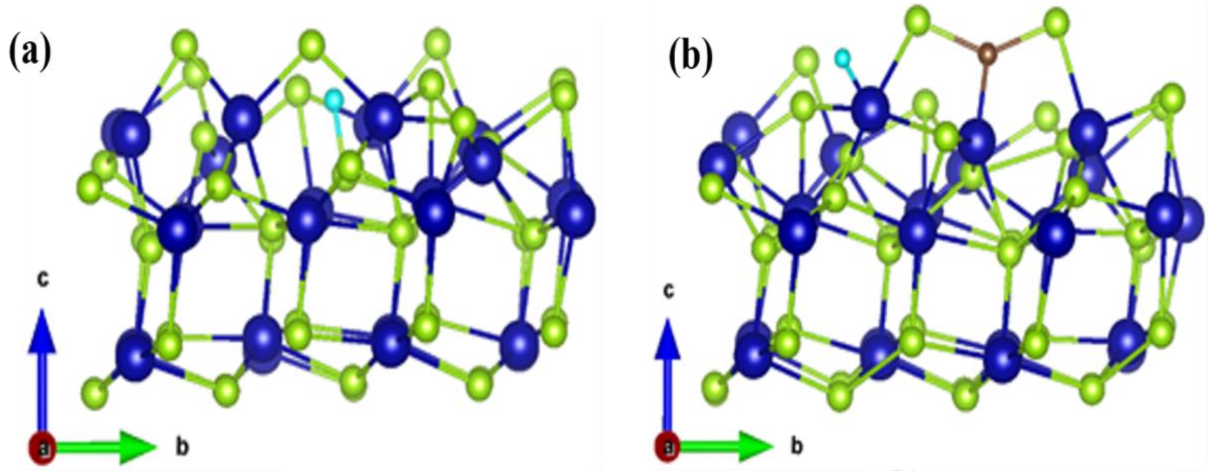


Fig. S9. DFT optimized structure after H adsorption for (101) layer of (a) $CoSe_2$ (b) $CoSe_2$ /C; blue, green, brown and cyan represent Cobalt, Selenium, Carbon and Hydrogen.

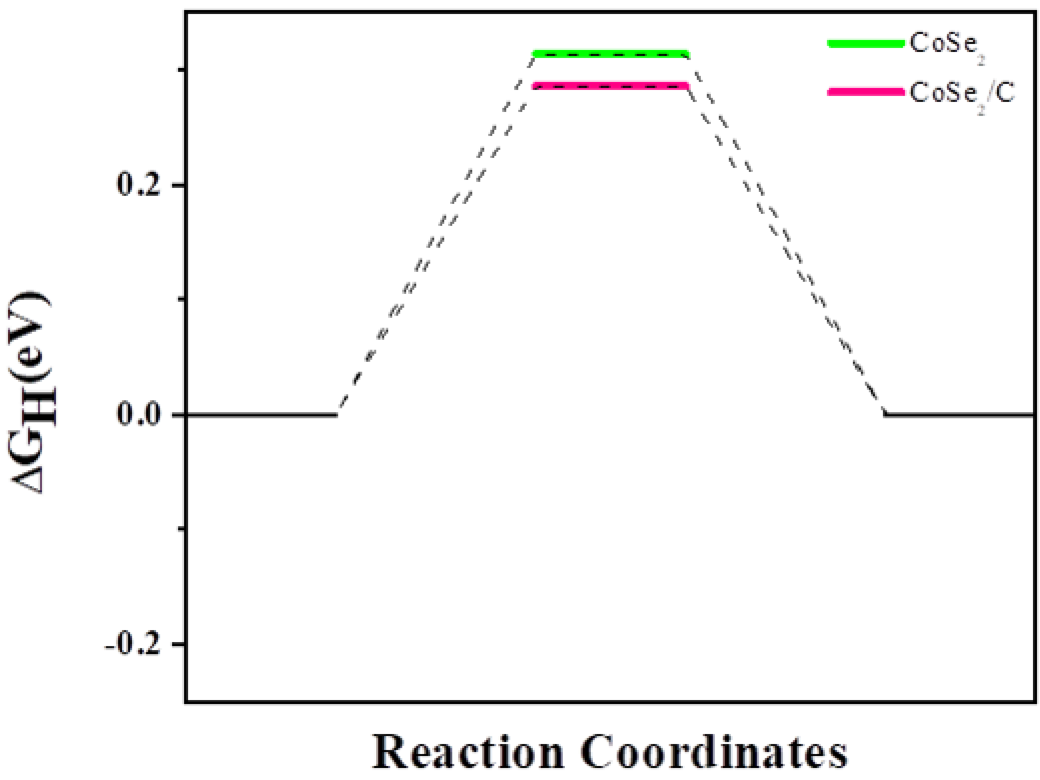


Fig. S10. Reaction coordinates for HER of (101) layer of $CoSe_2$ and$CoSe_2$ /C.

Table S1. Table showing the comparison of electrocatalytic activity of $CoSe_2$/C hybrid with other reported nanostructures.

Sl.No	Catalysts	Electrolyte (Conc.)	Overpotential(mV) @10 mA/cm^{-2}	Tafel slope (mV/dec)	Reference
1	$CoSe_2$	0.5 M H_2SO_4	-272	60	ACS Energy Lett. 2016, 1, 3, 607-611
2	$CoSe_2$/C	0.5 M H_2SO_4	-196	45.73	International journal of hydrogen energy, 2019, 4 4, 22787-22795
3	$CoSe_2$–CNT	0.5 M H_2SO_4	-174	37.8	Small, 2017, 13, 1700068
4	Co-NC/CNT	1M KOH	-263	125	J. Mater. Chem. A, 2016, 4, 16057
5	$CoSe_2$/CF	1M KOH	-95	52.0	Nano Research 2016, 9, 2234–2243
6	Carbon Supported Cobalt Di-selenide	0.1M KOH	-270	118.5	Journal of The Electrochemical Society, 2020 167 026507
7	$CoSe_2$/SDGC	0.5 M H_2SO_4	-203	58.0	International journal of hydrogen energy, 2019, 44, 1344-13431
8	$CoSe_2$	0.5 M H_2SO_4	-272.0	60.0	ACS Energy Lett, 2016, 1, 3, 607-611
9	$CoSe_2$/NC-170	0.5 M H_2SO_4	-159.	83.0	international journal of hydrogen energy 4 3 (2 0 1 8) 1 7 0 2 1 e1 7 0 2 9
10	$CoSe_2$/C	0.5 M H_2SO_4	-224.0	34.0	j. mater.sci,54.22 (2019): 14123-133
11	Fe-$CoSe_2$@NC	0.5 M H_2SO_4	-143	40.0	ACS Sustainable Chem. Eng. 2018, 6, 8672−8678
12	$CoSe_2$/C	0.5 M H_2SO_4	-253.0	46.0	Present work