## Electronic Supplementary Information (ESI) Synthesis of Co-doped MoS<sub>2</sub>/graphene hybrids as an enhanced electrocatalyst for hydrogen evolution reaction

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Fig. S1 Calibration plot showing the potential of SCE with respect to RHE recorded in H<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.

In all measurements, we used saturated calomel electrode (SCE) as the reference electrode. It was calibrated with respect to reversible hydrogen electrode (RHE). In order to carry out such calibration, we used Pt as the working and counter electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, purged with high pure hydrogen gas during the measurement, and saturated calomel as the reference electrode. Linear sweep voltammetry (LSV) was carried out at a scan rate of 5 mV/s. The potential at which the current crossed zero

was taken to be the thermodynamic potential for the hydrogen electrode reactions. The LSV curve in Fig. S1 showed that the potential at the current crossed zero was - 0.272 V (vs. SCE), thus all the potentials referenced to the reversible hydrogen electrode (RHE) should be added a value of 0.272 V, namely, E (RHE) = E (SCE) + 0.272 V. Li *et al.* has also used similar method to carry out such correction.<sup>1</sup>



**Fig. S2**. (a) EDS pattern and (b) STEM image and corresponding elemental mapping of Co-MoS<sub>2</sub>/G-3 hybrid.

Fig. S2 illustrates the EDS pattern, STEM image and corresponding elemental mapping of Co-MoS<sub>2</sub>/G-3 hybrid. One can see from Fig. S2(a) that Co-MoS<sub>2</sub>/G-3 hybrid consists of Mo, S, C, O and Co elements. The element Mo and S are derived from MoS<sub>2</sub>, C and O are derived from reduced graphene oxide. Co is attributed to Co-doping. Fig. S2(b) shows the elemental mapping of Co-MoS<sub>2</sub>/G-3 hybrid. One can find from Fig. S2(b) that the Mo, S, C and O elements exhibit an homogeneous distribution. Despite the low content of Co element, one can still observe its relatively homogeneous distribution. The fact suggests that Co-doped MoS<sub>2</sub> sheets are well dispersed on the surface of reduced graphene oxides.



Fig. S3 Tafel plot of Co-MoS<sub>2</sub>/G-3 catalyst.

The onset potential for HER can be read from the Tafel plot.<sup>2</sup> For example, the Tafel plot of Co-MoS<sub>2</sub>/G-3 in the region of low current densities as displayed in Fig. S3 show a linear relationship above the overpotential of 142 mV but starts to deviate below 110 mV. Therefore, 142 mV was chosen as the onset potential.



Fig. S4 Current-time curve of Co-MoS $_2$ /G-3 catalyst at the overpotential of 194 mV for 10 h.

The current-time testing was carried out at the overpotential of 0.194 V (j=10 mA/cm<sup>2</sup>) for 10 h. As shown in Fig. S4, the current-time curve exhibits a typical serrate shape due to the alternate processes of bubble accumulation and bubble release.<sup>2</sup> The catalytic current experiences a slight degradation even after a long period of 10 h, indicating the excellent catalytic stability of Co-MoS<sub>2</sub>/G-3 catalyst.

## References:

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