Electronic Supplementary Information:

Assembled 3D Electrocatalysts for Efficient Hydrogen Evolution:

WSe₂ Layers Anchored on Graphene Sheets

Zhengqing Liu, Hongyang Zhao, Na Li, Yi Zhang, Xinyu Zhang and Yaping Du*

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Fig. S1 (a) SEM and (b) TEM image of GO nanosheets fabricated by the modified Hummers method.

Fig. S2 (a) The SEM image of WSe$_2$ layers. (b) TEM image of WSe$_2$/rGO hybrid with no free WSe$_2$ can be observed. (c) Energy-dispersive X-ray analysis (EDS) spectrum of WSe$_2$ layers, the atomic ratio of W/Se = 1:2. The Au signals come from the WSe$_2$ sample treated by gold spraying to improve its electrical conductivity.
**Fig. S3** TEM images of the WSe$_2$ products obtained from the reaction of 0.2 mmol (NH$_4$)$_2$WO$_4$ and 0.6 mmol Se in different surfactant composition (OM/OA) at 280 °C for 1 h: (a) OM (10 mmol)/OA (10 mmol) = 1/1, (b) pure OA (20 mmol). (c) XRD patterns of the (a) and (b) products, indicating the WO$_3$ is present in as-harvested WSe$_2$ products. Where, WSe$_2$ space group: P63/mmc, $a = b = 0.329$ nm, $c = 1.298$ nm, JCPDS: 38-1388; WO$_3$ space group: P6/mmm, $a = b = 7.298$, $c = 3.899$ nm, JCPDS: 33-1387.

**Fig. S4** (a) TEM image of the WSe$_2$ products obtained from the reaction of 0.2 mmol (NH$_4$)$_2$WO$_4$ and 0.4 mmol Se in pure OM at 280 °C for 1 h. (b) Magnified TEM image of the selected area showing in (a).
Fig. S5 Polarization curves recorded on glassy carbon electrodes with catalysts of (a) pure WSe$_2$ layers, WSe$_2$+rGO (0.2 mmol WSe$_2$ layers physically mixed with 20 mg rGO) and WSe$_2$/rGO hybrid, and (b) different content of rGO in WSe$_2$/rGO hybrid. The loading concentration is 0.285 mg cm$^{-2}$, potential scan rate is 2 mV s$^{-1}$, and electrode rotating rate is 1600 rpm.

Fig. S6 XPS spectra of (a) W and (b) Se after 48 h continuous HER process, showing no obvious change of the chemical states, demonstrating the superior stability of the 3D WSe$_2$/rGO hybrid.
Fig. S7 Durability tests by continuous HER recorded on WSe$_2$-modified CFP electrode at a static overpotential of -0.7 V vs SCE. The catalysts were deposited on CFP with loading of 1 mg cm$^{-2}$. All the measurements were performed in N$_2$ saturated 0.5 M H$_2$SO$_4$ electrolyte. The WSe$_2$ layers catalyst exhibited fluctuation in HER activity, indicating the inferior stability of WSe$_2$ layers than the WSe$_2$/rGO hybrid catalyst.

Fig. S8 The equivalent circuit used for data fitting, where Rs is the solution (uncompensated) resistance, CPE is the electrode double-layer capacitance and Rct is the charge-transfer resistance.
Table S1 Comparison the present obtained WSe$_2$/rGO hybrid and other previously reported WSe$_2$-based catalysts for HER performance.

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References