Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information:

Assembled 3D Electrocatalysts for Efficient Hydrogen Evolution: WSe_2 Layers Anchored on Graphene Sheets

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

Contents

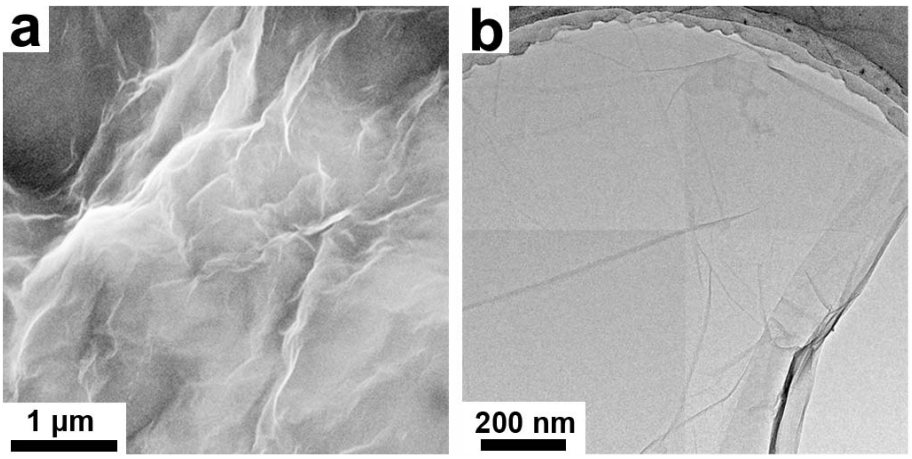

Fig.S1 (a) SEM and (b) TEM image of GO nanosheets fabricated by the modified Hummers method.

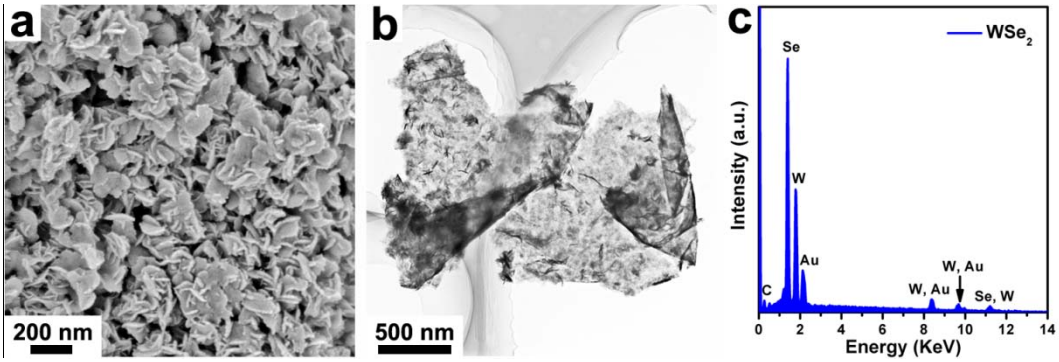

Fig. S2 (a) The SEM image of WSe_2 layers. (b) TEM image of WSe_2/rGO hybrid with no free WSe_2 can be observed. (c) Energy-dispersive X-ray analysis (EDS) spectrum of WSe_2 layers, the atomic ratio of W/Se = 1:2 The Au signals come from the WSe_2 sample treated by gold spraying to improve its electrical conductivity.

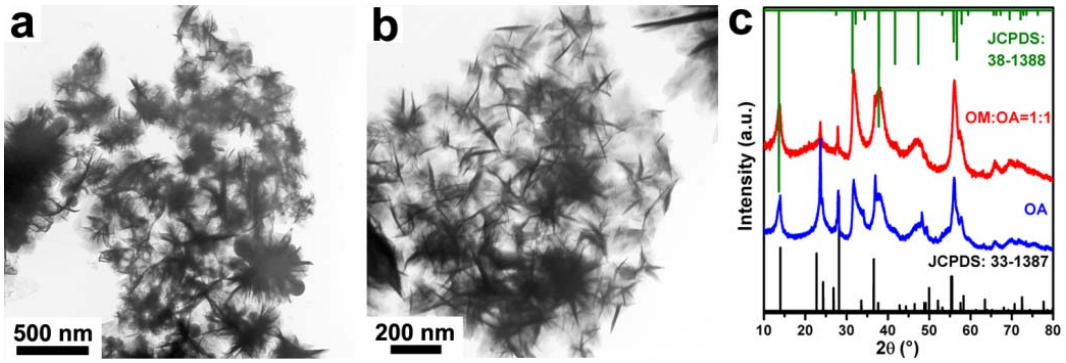

Fig. S3 TEM images of the WSe_2 products obtained from the reaction of 0.2 mmol $(NH_4)_2WO_4$ and 0.6 mmol Se in different surfactant composition (OM/OA) at 280 °C for 1 h: (a) OM (10 mmol)/OA (10 mmol) = 1/1, (b) pure OA (20 mmol). (c) XRD patterns of the (a) and (b) products, indicating the WO_3 is 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.

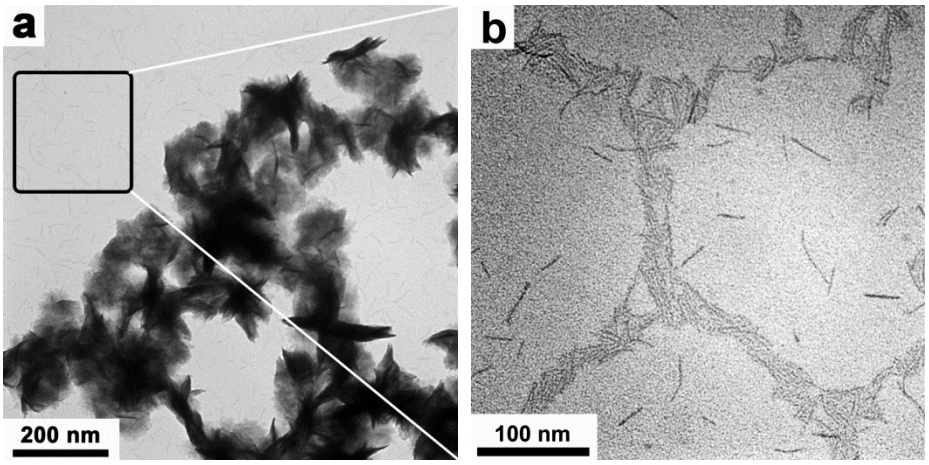

Fig. S4 (a) TEM image of the WSe_2 products obtained from the reaction of 0.2 mmol $(NH_4)_2WO_4$ and 0.4 mmol Se in pure OM at 280 °C for 1 h. (b) Magnified TEM image of the selected area showing in (a).

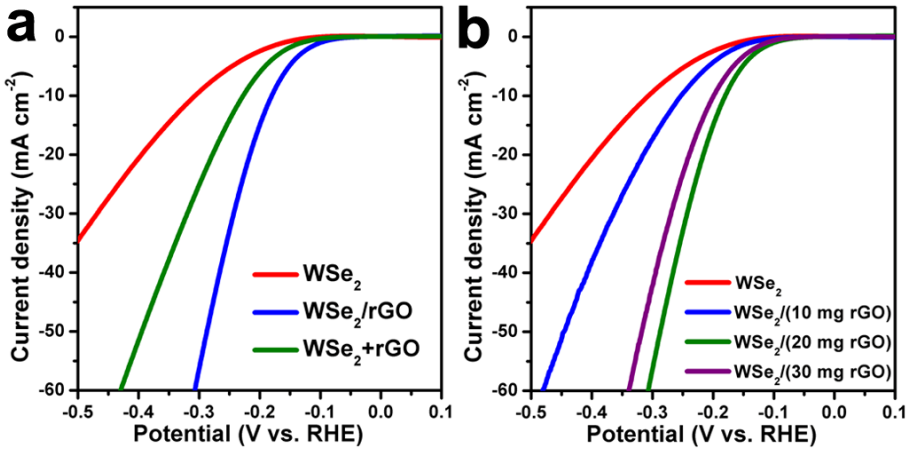

Fig. S5 Polarization curves recorded on glassy carbon electrodes with catalysts of (a) pure WSe_2 layers, WSe_2+rGO (0.2 mmol WSe_2 layers physically mixed with 20 mg rGO) and WSe_2/rGO hybrid, and (b) different content of rGO in WSe_2/rGO hybrid. The loading concentration is 0.285 mg cm^{-2}, potential scan rate is 2 mV s^{-1}, and electrode rotating rate is 1600 rpm.

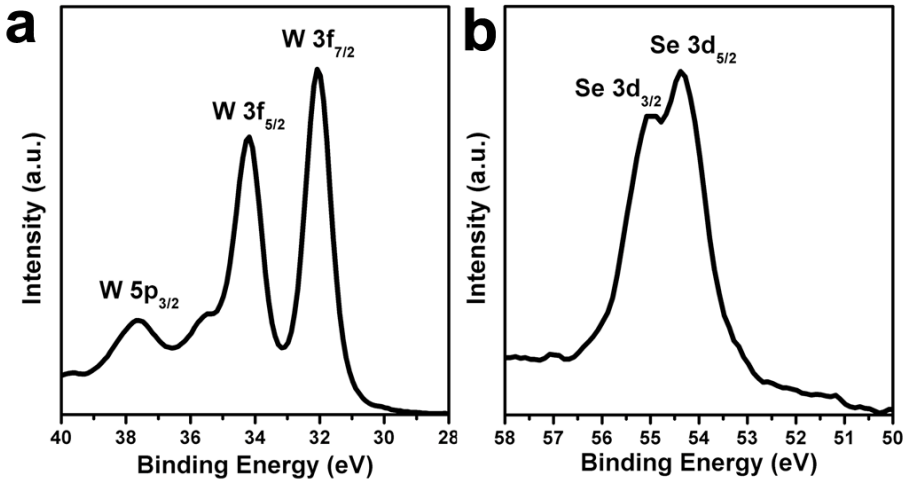

Fig. S6 XPS spectra of (a) W and (b) Se after 48 h continuous HER process, showing no obvious change of the chemical states, demonstrating the superior stability of the 3D WSe_2/rGO hybrid.

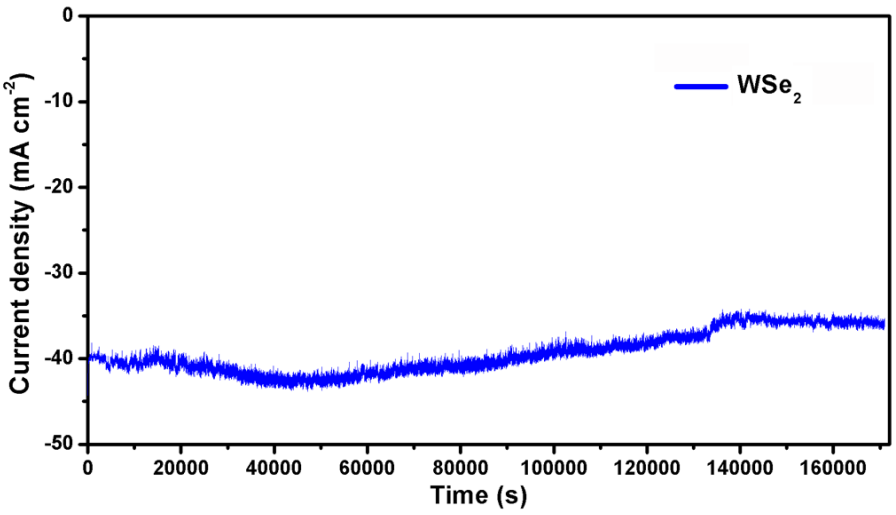

Fig. S7 Durability tests by continuous HER recorded on WSe_2-modified CFP electrode at a static overpotential of -0.7 V vs SCE. The catalysts were deposited on CFP with loading of 1 mg cm^{-2}. All the measurements were performed in N_2 saturated 0.5 M H_2SO_4 electrolyte. The WSe_2 layers catalyst exhibited 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.

Catalysts	Production Method	Onset Potential (mV vs. RHE)	Overpotential (mV vs. RHE) at 10 mA cm^{-2}	Tafel Slope (mV/dec)	Ref.
WSe_2/rGO hybrid	**Solvothermal**	**-100**	**180**	**64**	**Present Work**
WSe_2 nanotube on carbon fiber paper	**Selenylation**	**-**	**350**	**99**	**S1**
Vertically WSe_2 Aligned Layers on carbon fiber paper	**CVD**	**-**	**300**	**77.4**	**S2**
2D WSe_2 sheets	**Chemical exfoliation**	**-130**	**800**	**120**	**S3**
WSe_2 sheets on W foils	**Chemical-vapor transport (CVT)**	**-300**	**350**	**-**	**S4**
3D dendritic WSe_2 on carbon nanofiber	**CVD method**	**-150**	**228**	**80**	**S5**

References

S1 K. Xu, F. Wang, Z. Wang, X. Zhan, Q. Wang, Z. Cheng, M. Safdar and J. He, *ACS Nano*, 2014, **8**, 8468.

S2 H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, N. Liu and Y. Cui, *Nano Lett.*, 2013, **13**, 3426.

S3 A. Y. S. Eng, A. Ambrosi, Z. Sofer, P.˘Simek and M. Pumera, *ACS Nano*, 2014, **8**, 12185.

S4 J. M. Velazquez, F. H. Saadi, A. P. Pieterick, J. M. Spurgeon, M. P. Soriaga, B. S. Brunschwig and N. S. Lewis, *J. Electroanal. Chem.*, 2014, **716**, 45.

S5 M. L. Zou, J. F. Zhang, H. Zhu, M. L. Du, Q. F. Wang, M. Zhang and X. W. Zhang, *J. Mater. Chem. A*, 2015, **3**, 12149.