Supporting Information

Few-layered Trigonal WS₂ Nanosheets Coated Graphite Foam as an Efficient Free-standing Electrode for Hydrogen Evolution Reaction

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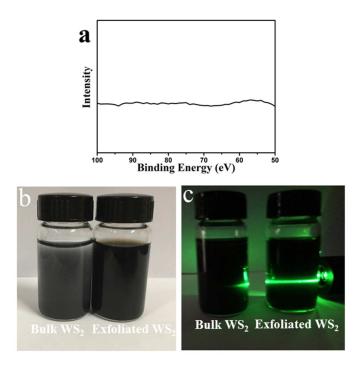


Figure S1. XPS spectra of the exfoliated WS_2 (a), optical image of aqueous solution of bulk WS_2 and exfoliated WS_2 (b,c).

The exfoliated WS₂ was analyzed by X-ray photoelectron spectroscopy (XPS) in the range of 50~100 eV. In the XPS spectrum (Figure S1a), no peaks were observed in the binding energy range of 50-100 eV, ^{S1} indicating the absence of lithium (53 eV, 55 eV and 56 eV) in the WS₂ nanosheets. As shown in Figure S1b, the dispersed exfoliated WS₂ nanosheets solution exhibits a homogeneous black colloid without any deposition in hours. Moreover, with a green laser irradiating from the vial right side, the obvious Tyndall phenomenon can be observed in Figure S1c, suggesting the uniform dispersion in water. ^{S2}

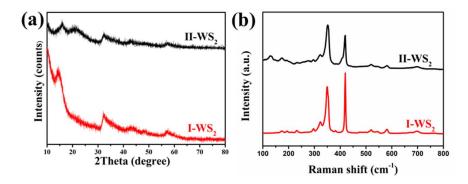


Figure S2. XRD (a) and Raman (b) spectra for the \Box -WS₂ and \Box -WS₂.

After the exfoliation, the intensities for all the diffraction peak of WS_2 nanosheets decrease obviously. As shown in Figure S2, the XRD pattern of II-WS₂ shows weaker peaks than I-WS₂, indicating the higher exfoliation ratio and thinner layer of the WS₂ nanosheets. For the Raman spectra, new peaks of J₁, J₂, and J₃ will appear after exfoliation. These new peaks of II-WS₂ are higher than those from I-WS₂, indicating the higher 1T-type percentage in the II-WS₂ nanosheets.

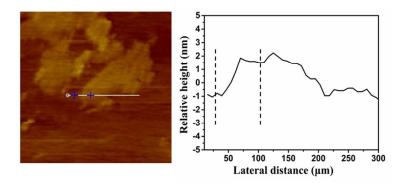


Figure S3. AFM image of the exfoliated WS_2 nanosheets.

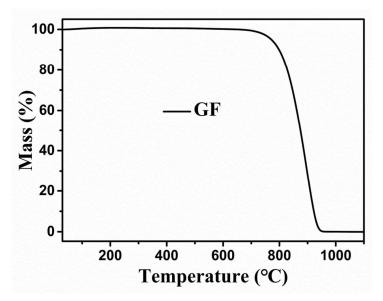


Figure S4. TGA thermogram of graphite foam.

The etched GF struts has been analyzed by TGA. After the calcination in air until $900 \,^{\circ}$ C, 100% of the GF could be burned, indicating that no residual nickel was left in the GF.

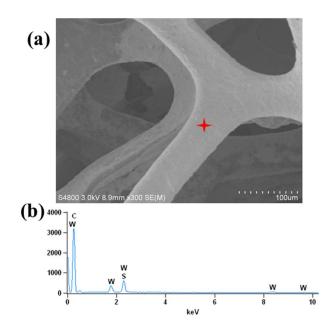


Figure S5. (a) SEM image of WS_2/GF composite; (b) EDS spectra of the red point selected from Figure S5a.

The WS₂/GF electrode has been tested by EDS, which possess only carbon, tungsten and sulfur. The absence of nickel indicates the successful and completely etching of Ni.

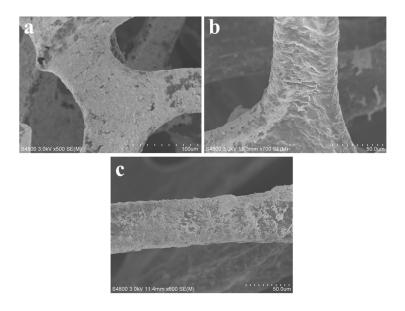


Figure S6. SEM images of WS₂/GF (a), WS₂/GF after 100 cycles (b) and 200 cycles (c).

The structure of the composite electrode and the electrode after 100 and 200 cycles has been analyzed by SEM. The WS_2 nanosheets were found tightly coated on the GF surface even after 100 and 200 cycles.

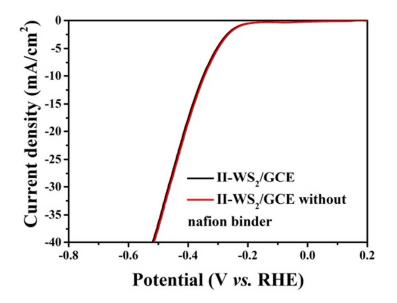


Figure S7.The electrochemical performance of the WS_2/GCE electrodes with and without binder.

The electrochemical performance of the II-WS₂/GCE without Nafion binder electrode was also investigated (Figure S7). No obvious difference could be observed with or without binder, indicating that addition of Nafion binder will not significantly decrease the activity of the electrodes. However, without the addition of Nafion binder, WS₂ nanosheets will peel off from the GCE substrate after several cycles during the experiment.

Materials	η ₁₀ (mV vs RHE)	Tafel slope (mV/dec)	Ref.
Free-standing NiO@C	-250	134	S3
THTNi 2DSP	-280	80.5	S4
(free-standing organic 2D nanosheets)			
3D ReS ₂ (chemical growth on free-standing	-336		S5
carbon foam)			
WS ₂ -CNT	-684	182	S 6
WS ₂ /GF	-190	84	This work

Table S1. Comparison of HER activities for the WS₂/GF and other HER electrocatalysts.

In Table S1, we listed some representative free-standing HER electrodes for comparison. All of these free-standing electrodes have larger overpotential and Tafel slopes than our electrodes. Specially, the organic THTNi 2DSP has a similar Tafel slope of ~80 mV/dec. Its η_{10} is however much larger than our electrode, and its preparation is difficult to perform on a large scale.

References

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