Electronic Supplementary Information

Highly active and durable self-standing WS_2/graphene hybrid catalysts for hydrogen evolution reaction**

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1. Material characterization

A Renishaw InVia Raman microscope was utilized to characterize the WS_2 and graphene samples using a 514 nm laser excitation with a power below 0.2 mW. X-ray photoelecton spectroscopy (XPS) (PHI Quantera XPS) was performed using a PHI Quantera SXM Scanning X-ray Microprobe with a base pressure of 5×10^{-9} Torr, and the MultiPak software was used for XPS data analysis. Scanning electron microscope (LEO 1525) was used to characterize the morphologies of the catalysts and graphene samples. WS_2/graphene samples were further transferred onto Cu grid and examined by high-resolution transmission electron microscopy (JEOL 2010F).

2. Electrochemical measurements

All the electrochemical tests were carried out in a typical three-electrode system at an electrochemical station (Gamry, Reference 600). Linear sweep voltammetry with a scan rate of 2 mV/s and step size of 1 mV was conducted in 82 mL of 0.5 M H_2SO_4 using a saturated calomel electrode (SCE) electrode as the reference electrode, a Pt wire (CH Instruments, Inc.) as the counter electrode, and three-dimensional graphene/Ni foam supported catalysts as the working electrode. Before all the measurements, high-purity N_2 gas was used to purge the system for at least 30 min, so as to ensure the saturation of N_2 in the electrolyte solution. N_2 purging continues throughout the whole electrochemical measurement. Prior

to all the HER measurements, the catalyst was cycled to electrochemically activate the material by applying 50 potential sweeps between 0.05 V to - 0.21 V vs. reversible hydrogen electrode (RHE) at a scan rate of 80 mV/s. Potentials were referenced to RHE by adding a value of 0.263 V after calibration. The electrochemical stability of the catalyst was evaluated by cycling the working electrode continuously 2000 times at a scan rate of 80 mV/s.

3. A typical Raman spectrum of WS_2/graphene/Ni foam hybrid

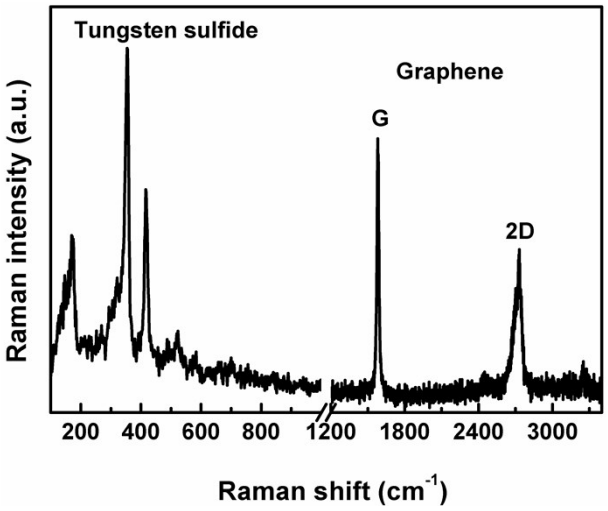

Figure S1. A typical Raman spectrum of WS_2 catalysts grown on graphene/Ni foam

4. Energy dispersive X-ray spectra of WS_2 catalysts on graphene/Ni foam

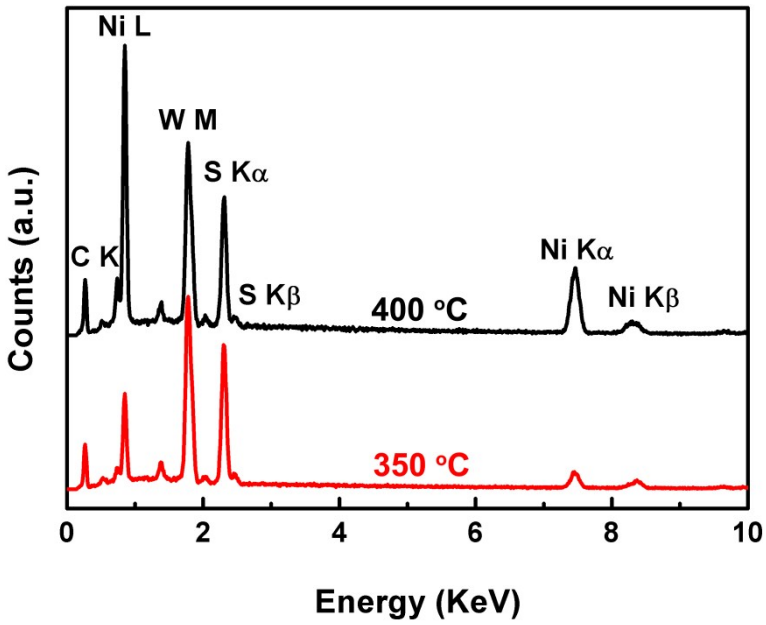

Figure S2. EDS analysis on the chemical composition of as-prepared WS_2 catalysts on three-dimensional graphene/Ni foam at different temperatures.

5. Neglible electrochemcal errosion for graphene-covered Ni foam in acid

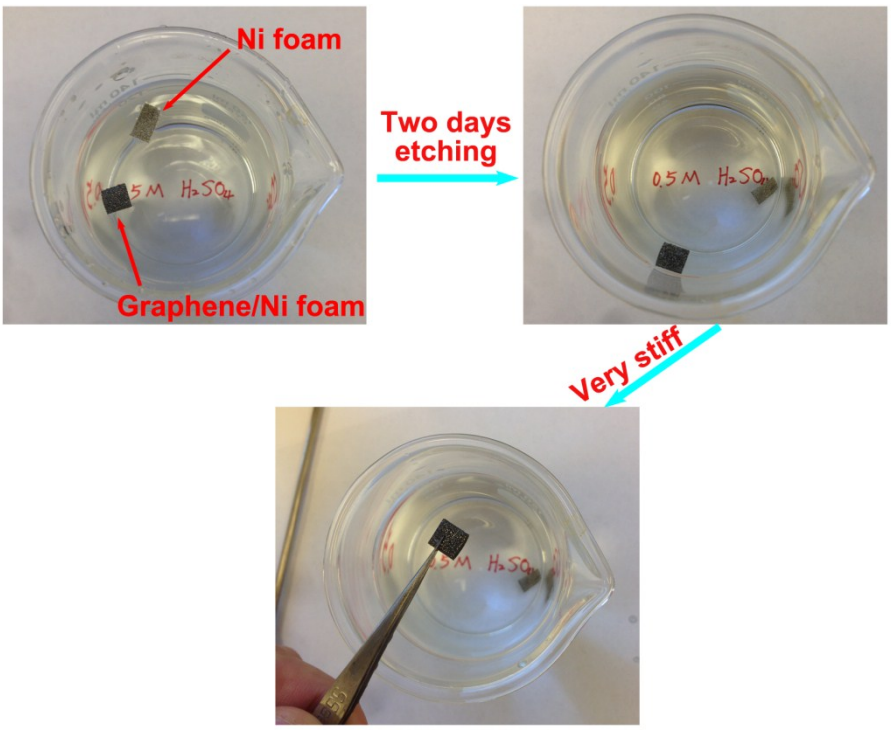

Figure S3. The protection of Ni foam from electrochemical errosion in 0.5 M H_2SO_4 solution. After two days etching, it is obvious that not only Ni foam, but also graphene-covered Ni foam are still there

without obvious changes. It is reasonable since graphene has the ability to protect Ni foam from chemical etching, and the surface of Ni foam has the tendency to be passivated in 0.5 M H_2SO_4 solution.

6. The summary of the HER performances for different WS_2 electrocatalysts

Table S1. The detailed parameters for the catalytic HER performance of different WS_2 catalysts on three-dimensional graphene/Ni foam. η *and* j_0 are the potential and exchange current density, respectively.

Temperature	Slope (mV/dec)	j_0 (μA/cm^2)	η (mV, j = 10 mA/cm^2)	j (mA/cm^2, η = 200 mV)
350 °C	46.0	17.6	139	54.0
400 °C	46.8	25.4	125	66.1
450 °C	43.0	18.3	119	77.0

7. Stability of the as-prepared catalysts on graphene/Ni foam at 350 °C

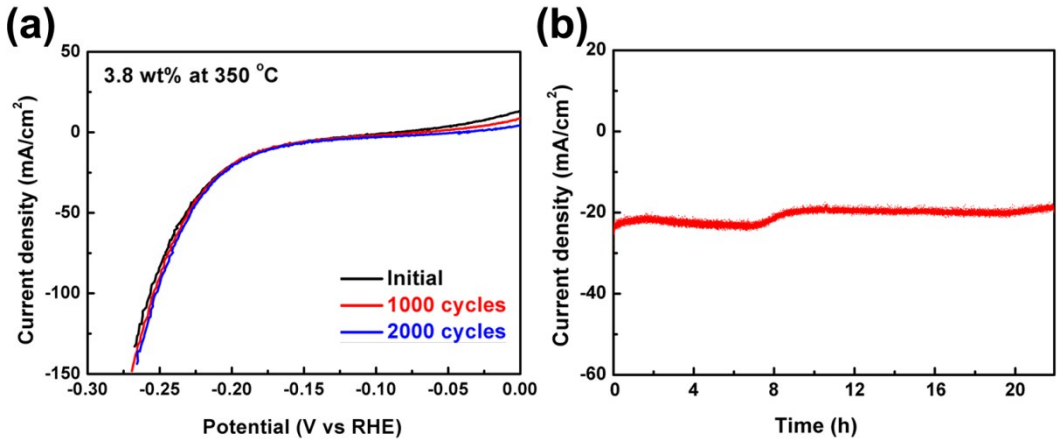

Figure S4. The stability test of WS_2 catalysts grown on three-dimensional graphene/Ni foam at 350 °C with the precursor concentration of 3.8 wt% in DMF. (a) Cyclability test with a scanning rate of 80 mV/s. (b) Time dependence of cathodic current density during electrolysis under a static overpotential of 200 mV for this sample.

8. The comparison of our catalysts and other kinds of electrocatalysts available from literature

Table S2. Comparison of different cheap and earth-abundant electrocatalysts available from literatures.

Catalyst	Current *j*	η	Tafel slope	Electrolyte	Source
WS_2/graphene/Ni foam	77 mA/cm^2	200 mV	43 mV/dec	0.5 M H_2SO_4	This work
Metallic WS_2 nanosheets	30 mA/cm^2	200 mV	70 mV/dec	0.5 M H_2SO_4	Ref. 14
WS_2 nanoflakes	30 mA/cm^2	200 mV	48 mV/dec	0.5 M H_2SO_4	Ref. 15
WS_2 nanotubes	10 mA/cm^2	325 mV	113 mV/dec	1 M H_2SO_4	Ref. 16
WS_2 nanosheets/carbon cloth	17 mA/cm^2	250 mV	105 mV/dec	0.5 M H_2SO_4	Ref.21
WS_2/reduced graphene oxide	23 mA/cm^2	300 mV	58 mV/dec	0.5 M H_2SO_4	Ref. 13
ExfoliatedWS_2 nanosheets	5 mA/cm^2	200 mV	60 mV/dec	0.5 M H_2SO_4	Ref. 12
Tungsten carbide particles	10 mA/cm^2	250 mV	NA	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.* **2014**, *53*, 5131
WN/reduced graphene oxide	20 mA/cm^2	300 mV	118 mV/dec	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.* **2015**, *54*, 6325
WP_2 submicroparticles	30 mA/cm^2	200 mV	57 mV/dec	0.5 M H_2SO_4	*ACS Catal.* **2015**, *5*, 145
MoP nanoparticles	10 mA/cm^2	125 mV	54 mV/dec	0.5 M H_2SO_4	*Adv. Mater.* **2014**, *26*, 5702
Ni_5P_4-Ni_2P nanosheet	100 mA/cm^2	200 mV	79 mV/dec	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.* **2015**, *54*, 8188
CoP nanocrystals/CNT	32 mA/cm^2	200 mV	54 mV/dec	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.* **2014**, *53*, 6710
CoP nanowire arrays/CC	90 mA/cm^2	200 mV	51 mV/dec	0.5 M H_2SO_4	*J. Am. Chem. Soc.* **2014**, *136*, 7587
Ni_2P nanoparticles	100 mA/cm^2	200 mV	46 mV/dec	0.5 M H_2SO_4	*J. Am. Chem. Soc.* **2013**, *135*, 9267
CoS_2/RGO-CNT	10 mA/cm^2	142 mV	51 mV/dec	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.* **2014**, *126*, 12802
$CoSe_2$/carbon fiber	10 mA/cm^2	139 mV	42 mV/dec	0.5 M H_2SO_4	*J. Am. Chem. Soc.* **2014**, *136*, 4897
MoS_x/N-doped CNT forest	10 mA/cm^2	110 mV	40 mV/dec	0.5 M H_2SO_4	*Nano Lett.* **2014**, *14*, 1228
MoS_2/graphene	100 mA/cm^2	200 mV	42 mV/dec	0.5 M H_2SO_4	*Adv. Funct. Mater.* **2013**, *23*, 5326