Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

The Effects of Exfoliation, Organic Solvents and Anodic Activation on Catalytic Hydrogen Evolution Reaction of Tungsten Disulfide

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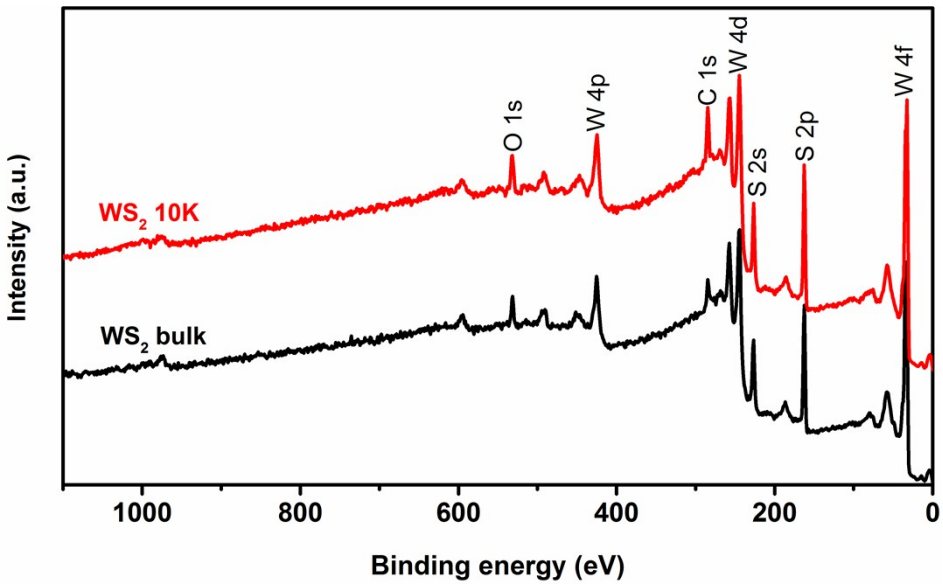

Fig. S1 XPS surveys of WS_2 bulk and WS_2 10K.

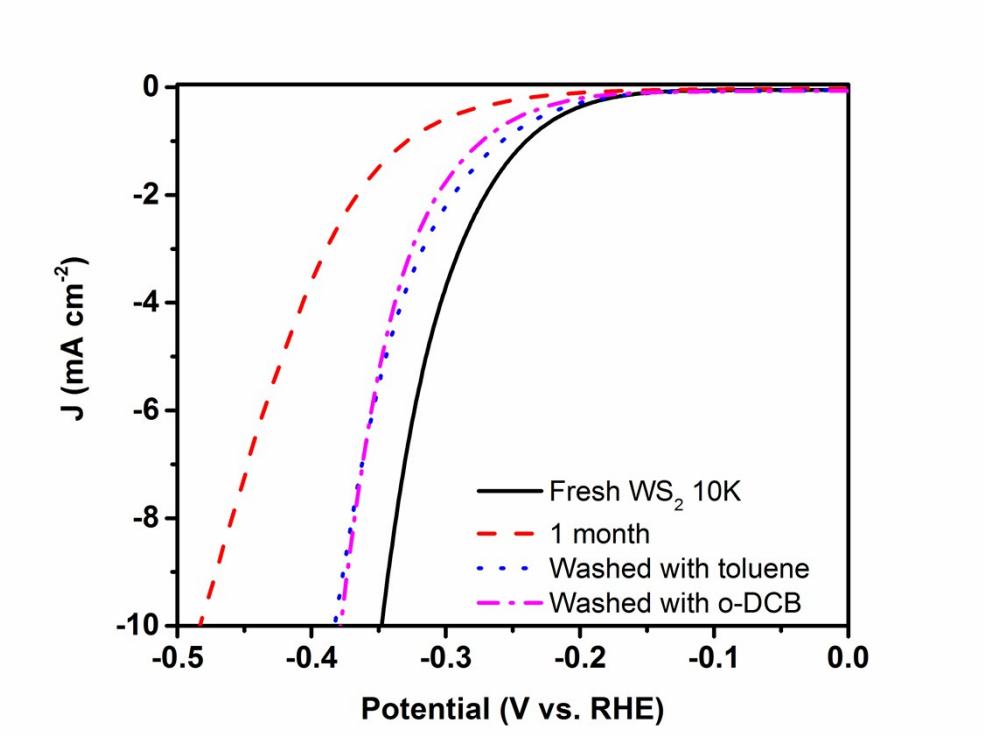

Fig. S2 Polarization curves of electrodes modified with i) freshly prepared WS_2 10K dispersion; ii) WS_2 10K dispersion 1 month old (1 month); iii) WS_2 10K dispersion 1 month old, washed with toluene and iv) WS_2 10K dispersion 1 month old, washed with o-dichlorobenzene (o-DCB).

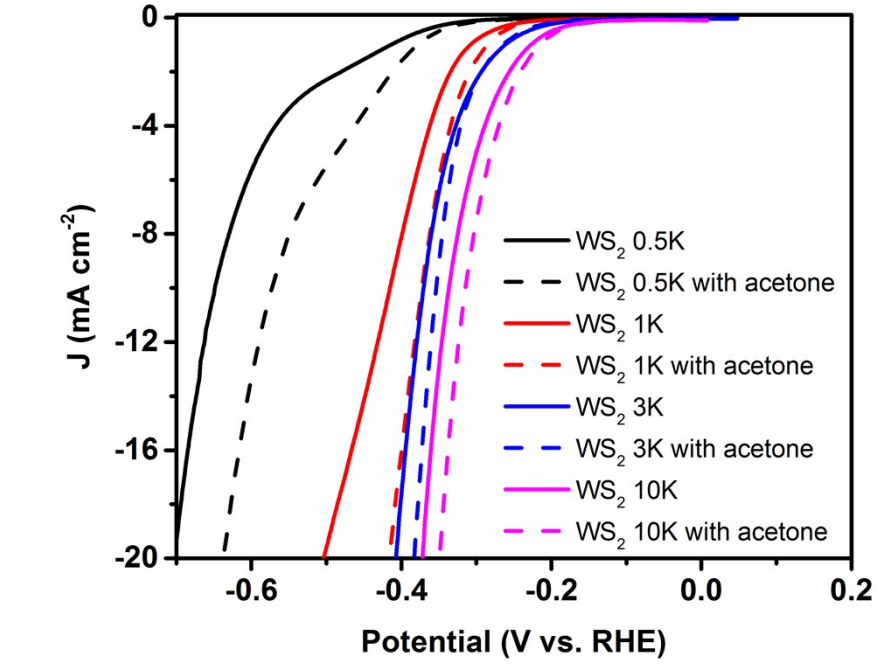

Fig. S3 Polarization curves of the electrodes modified with fresh 0.5K, 1K, 3K and 10K dispersions before (full lines) and after (dashed lines) washing with acetone.

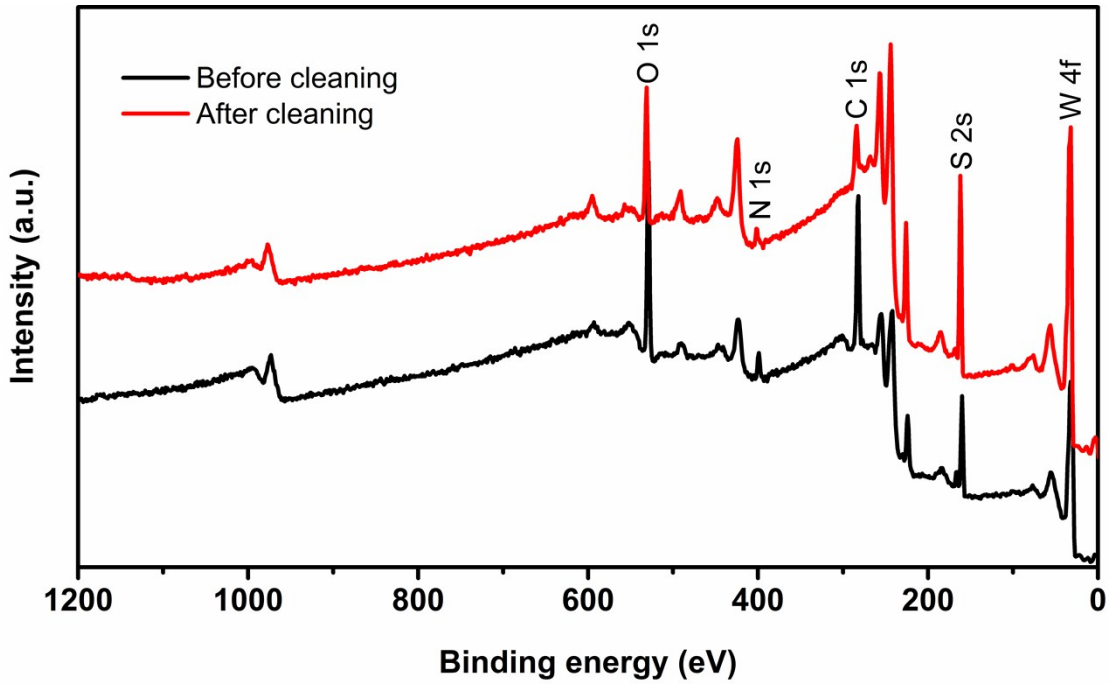

Fig. S4 XPS surveys of a GCE electrode modified with 1 month old WS_2 10K dispersion before and after cleaning with acetone.

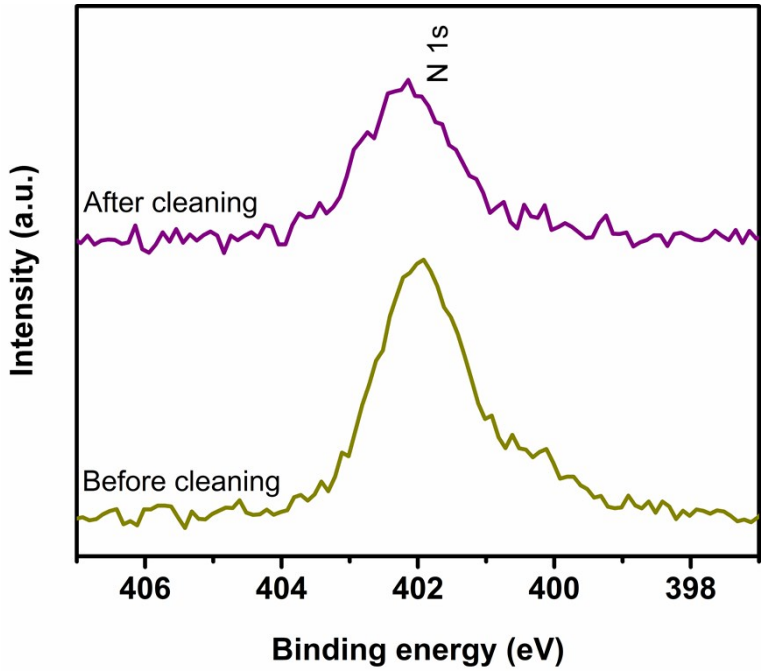

Fig. S5 High-resolution N1s core level XPS spectra from a GCE electrode modified with 1 month old WS_2 10K dispersion before and after cleaning in acetone.

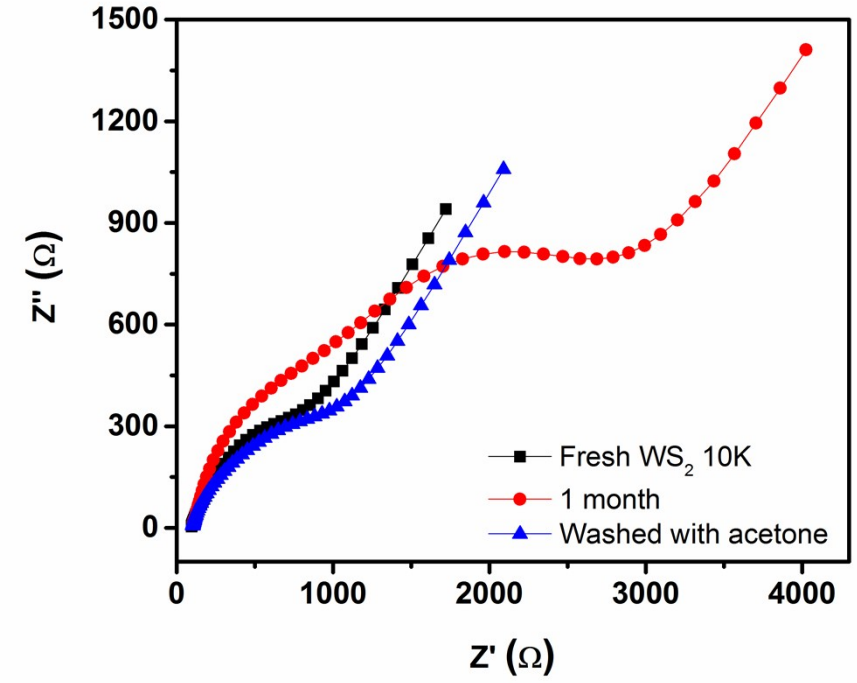

Fig. S6 Electrochemical impedance spectra of the electrodes modified with i) freshly prepared WS_2 10K dispersion; ii) WS_2 10K dispersion 1 month old and iii) WS_2 10K dispersion 1 month old, washed with acetone. The measurements were conducted in 0.1 M KCl-0.01 M phosphate buffer solution (pH = 7.4) containing 5 mM $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ (1:1).

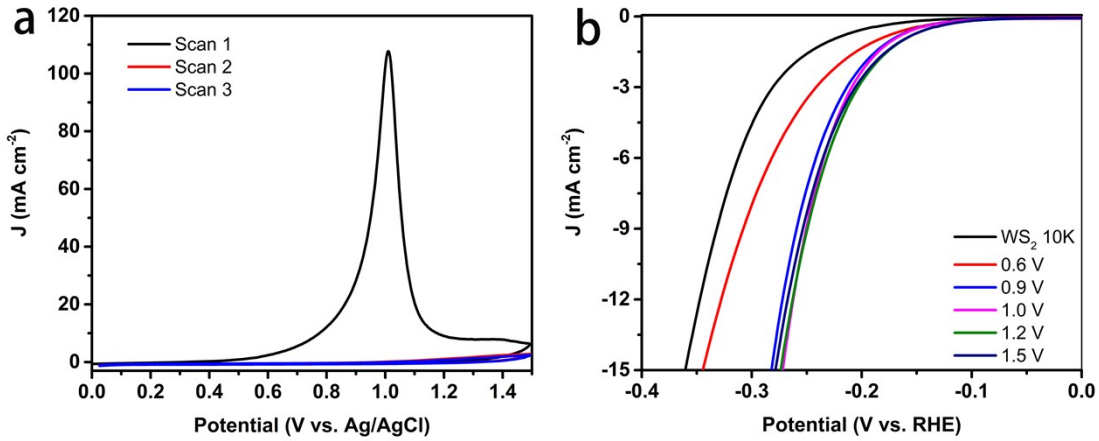

Fig. S7 a) Cyclic voltammetry scans of a WS_2 10K modified electrode performed between 0 and 1.5 V (vs. Ag/AgCl) in 0.5 M H_2SO_4. b) Polarization curves of WS_2 10K modified electrodes before and after activation at different potentials in 0.5 M H_2SO_4.

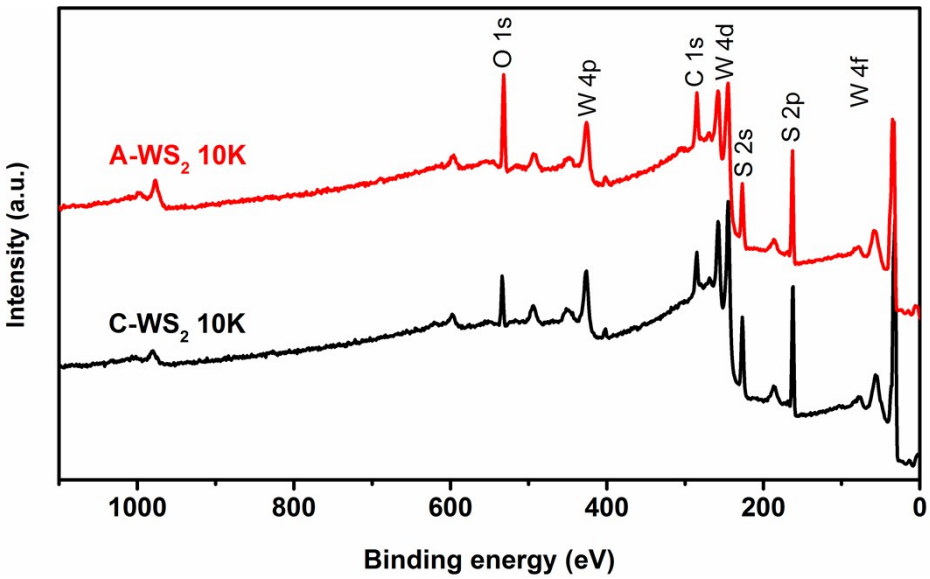

Fig. S8 XPS surveys of WS_2 10K before (C-WS_2 10K) and after (A-WS_2 10K) activation.

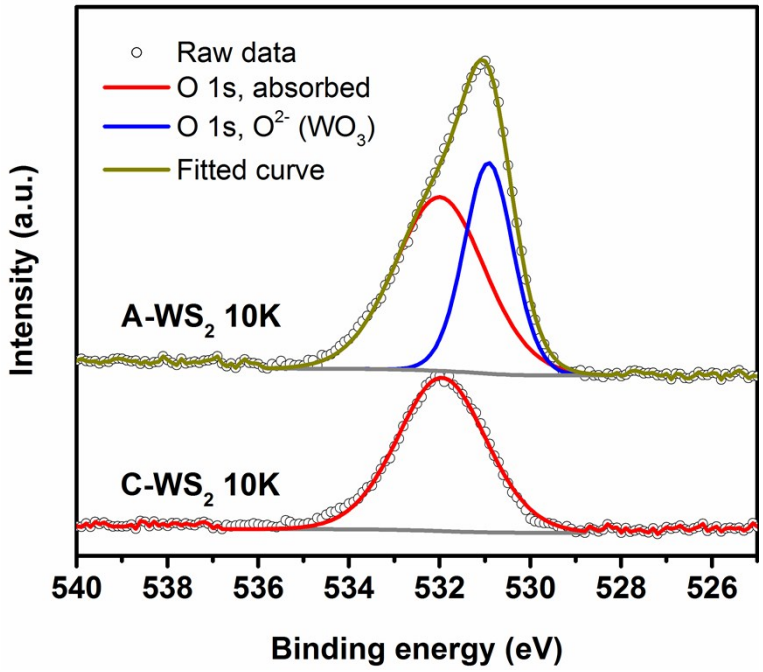

Fig. S9 High resolution O 1s core level XPS spectra of WS_2 10K before (C-WS_2 10K) and after (A-WS_2 10K) activation.

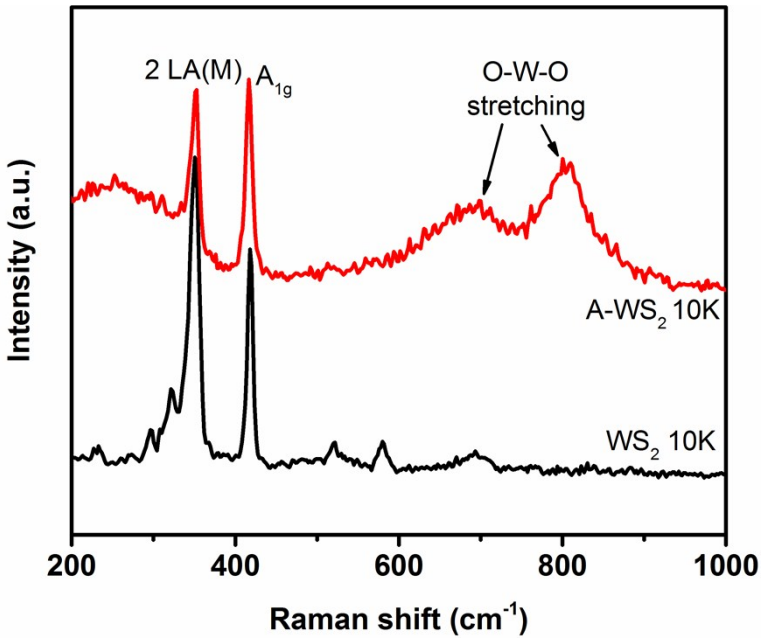

Fig. S10 Raman spectra of WS_2 10K before (WS_2 10K) and after (A-WS_2 10K) activation.

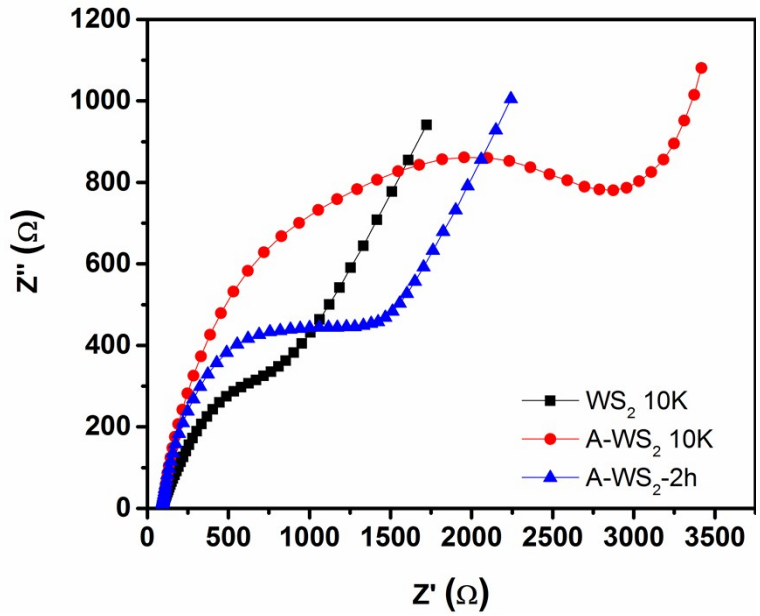

Fig. S11 Electrochemical impedance spectra of a WS_2 10K electrode: i) before activation (WS_2 10K); ii) after activation (A-WS_2 10K) and iii) after activation and 2 hours HER test (A-WS_2-2h). EIS was conducted in 0.1 M KCl-0.01 M phosphate buffer solution (pH = 7.4) containing 5 mM $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ (1:1).

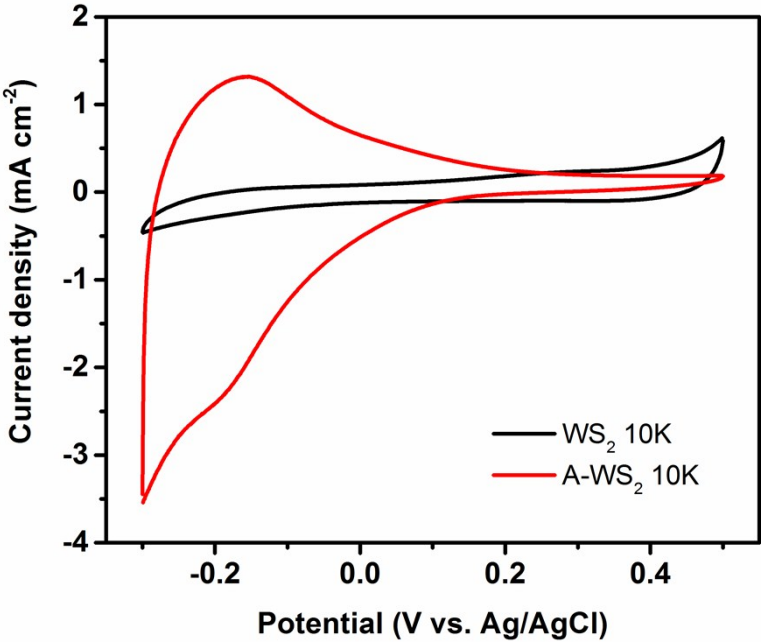

Fig. S12 Cyclic voltammograms performed between 0.5 and -0.3V (vs. Ag/AgCl) with a scan rate of 100 mV s^{-1} in 0.5 M H_2SO_4 for i) WS_2 10K and ii) activated WS_2 10K (A-WS_2 10K), respectively.

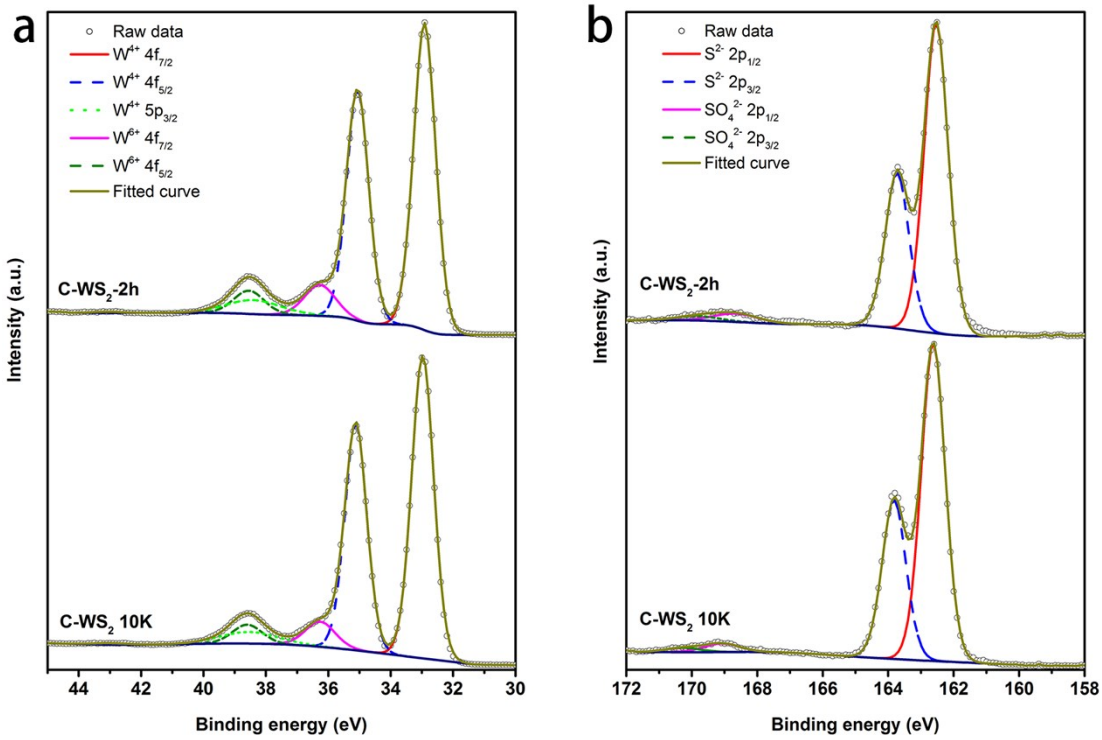

Fig. S13 High resolution (a) W 4f and 5p and (b) S 2p core level XPS spectra of controlled WS_2 10K before (C-WS_2 10K) and after (C-WS_2-2h) 2h HER test.

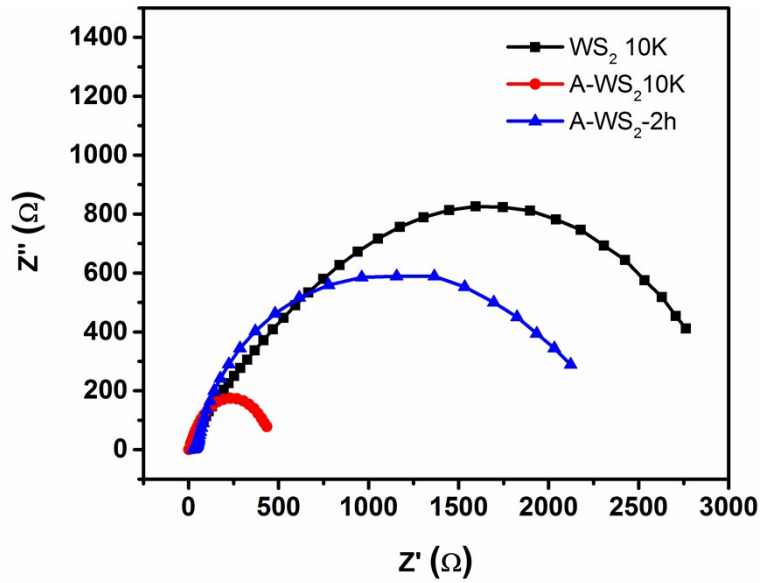

Fig. S14 Electrochemical impedance spectra of i) WS_2 10K; ii) activated WS_2 10K (A-WS_2 10K) and iii) activated WS_2 10K subjected to 2 hours HER test (A-WS_2-2h) in 0.5 M H_2SO_4.

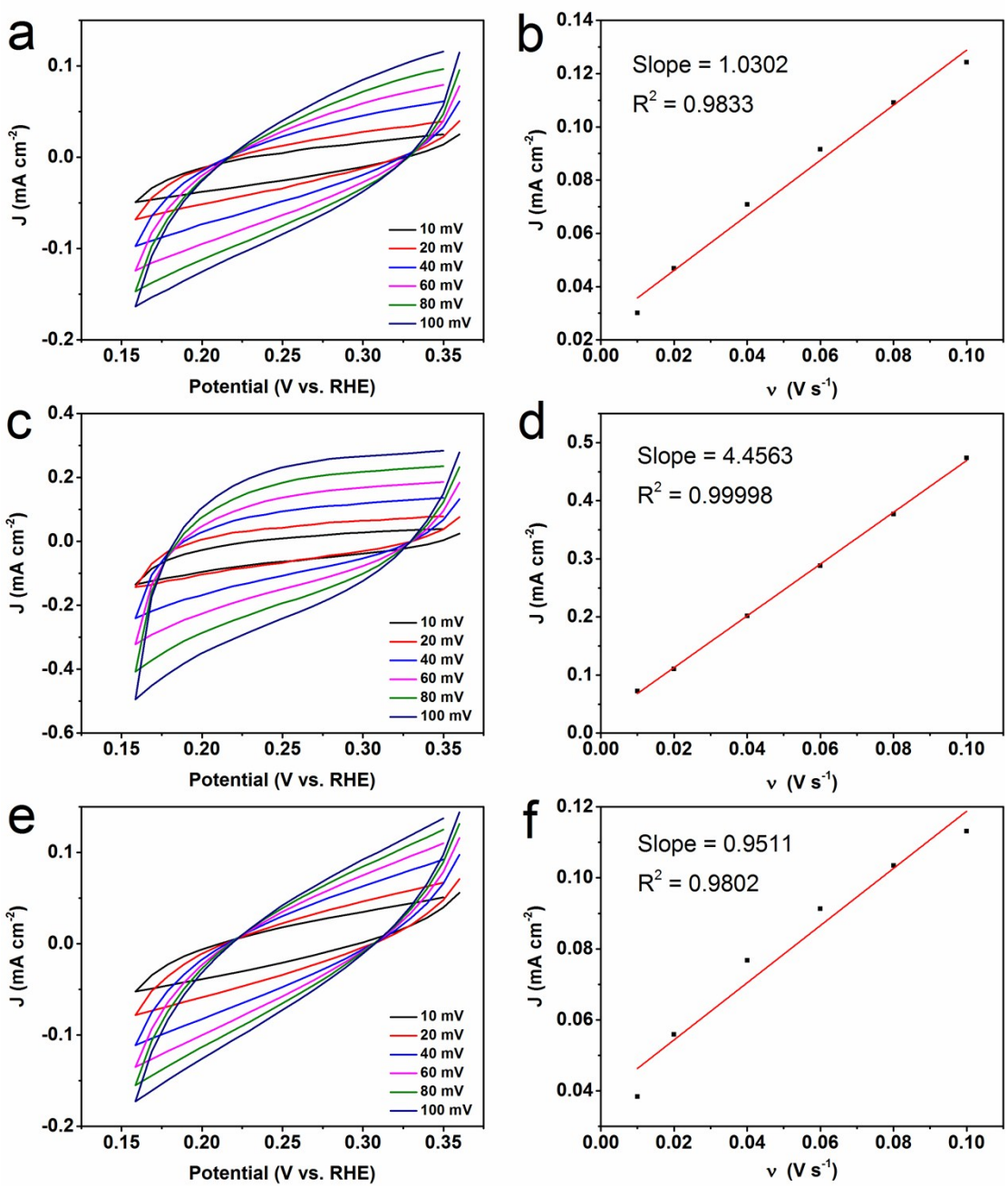

Fig. S15. Cyclic voltammogram scans of (a) WS_2 10K, (c) a-WS_2 10K and (e) a-WS_2-2h at different scan rates (0.1, 0.08, 0.06, 0.04, 0.02 and 0.01 V s^{-1}) and the corresponding capacitive current density measured at 0.25 V (vs. RHE) plotted as a function of scan rate (b, d, f). The average value of the slope was determined as the double-layer capacitance (C_{dl}) of each catalyst. The calculated C_{dl} of WS_2 10K, A-WS_2 10K and A-WS_2-2h are 1.03, 4.46 and 0.95 mF cm^{-2}, respectively.

Table S1 XPS data of composition of WS_2 bulk and 500, 1K, 3K and 10K centrifugation products.

	WS_2 bulk	WS_2 0.5K	WS_2 1K	WS_2 3K	WS_2 10K

S (%At conc)	65.5	65.2	65.2	65.4	66.0
W (%At conc)	34.5	34.1	34.8	34.6	34.0
Ratio of S to W	1.9 : 1	1.9 : 1	1.9 : 1	1.9 : 1	1.9 : 1

Table S2 The atomic ratios of S to W and W(VI) to W(IV) of controlled WS_2 10K (C-WS_2 10K), activated WS_2 10K (A-WS_2 10K), activated WS_2 10K subjected to 0.5 and 2 hours HER test (A-WS_2-0.5h and A-WS_2-2h) and controlled WS_2 10K subjected to 2 hours HER test (C-WS_2-2h).

	C-WS_2 10K	A-WS_2 10K	A-WS_2-0.5h	A-WS_2-2h	C-WS_2-2h
Ratio of S to W	1.9 : 1	1.6 : 1	1.7 : 1	1.8 : 1	1.9 : 1
Ratio of W(VI) to W(IV)	0.1 : 1	0.4 : 1	0.3 : 1	0.2 : 1	0.1 : 1

Table S3 Comparison of the electrocatalytic activity of WS_2 nanosheets/nanodots (WS_2 NSDs) and activated WS_2 NSDs *versus* the WS_2-based catalysts on GCE (two catalysts on carbon fiber paper and carbon cloth have been pointed out) reported recently for HER in 0.5 M H_2SO_4 .

Catalysts	Mass loading (mg cm^{-2})	Overpotential (mV) for j=10 mA cm^{-2}	Tafel Slope ($mV\ dec^{-1}$)	Reference
WS_2 NSDs	0.283	337	80	This work
Activated WS_2 NSDs	0.283	255	73	This work
WS_2 nanoflakes	1	~358	~200	1
BuLi exfoliated WS_2 nanosheets (~80% 1T- WS_2)	0.001-0.0065	240 (1T) 440 (2H)	55(1T) 110(2H)	2
BuLi exfoliated WS_2	0.0707	~690	~110	3
$WS_{2(1-x)}Se_{2x}$ nanotubes on CFP	0.21	~270	105	4
WS_2 on carbon cloth	-	225	105	5
WS_2 nanosheets	0.0566	~380	~95	6
WS_2 nanosheets/quantum dots	0.0354	~340 (DMF)	70 (DMF)	7

		~355 (NMP)	75 (NMP)	
Aromatic-exfoliated WS_2	0.0142	~520	~70	8
WS_{3-x} Films	-	494	43.7	9
Ta-doped WS_2	0.0707	~720	~170	10

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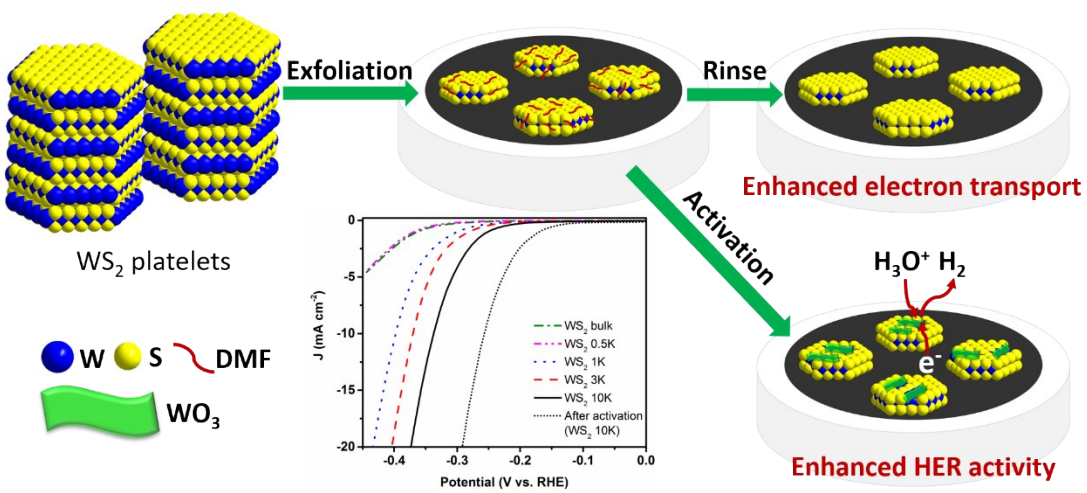
Exfoliation
Rinse
Enhanced electron transport
Activation
WS2 platelets
W
S
DMF
WO3
J (mA cm-2)
Potential (V vs. RHE)
WS2 bulk
WS2 0.5K
WS2 1K
WS2 3K
WS2 10K
After activation (WS2 10K)
H3O+ H2
e-
Enhanced HER activity