

Electronic Supplementary Information

**One-step Synthesis of Hierarchical Self-supported WS₂ Film for Efficient
Electrocatalytic Hydrogen Evolution**

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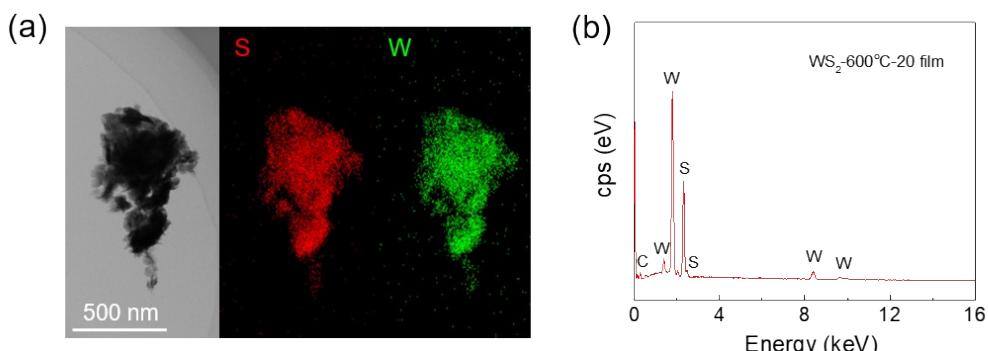


Figure S1. (a) Chemical mappings of W species and S species. (b) EDS pattern of WS₂-600°C-20 film.

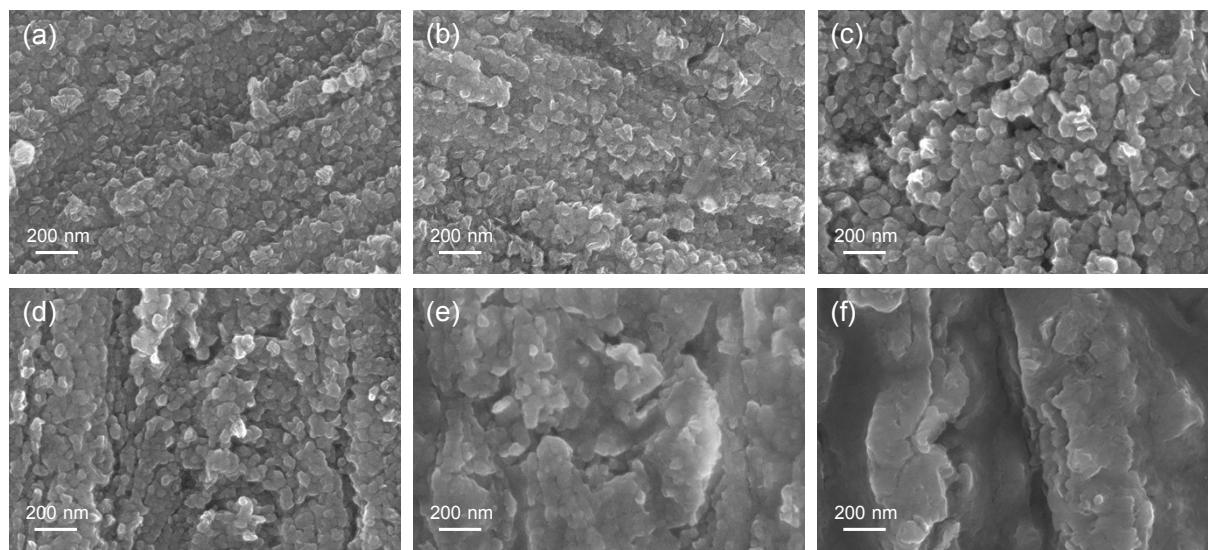


Figure S2. SEM images of (a) WS₂-500°C-20, (b) WS₂-600°C-20, (c) WS₂-700°C-20, (d) WS₂-800°C-20, (e) WS₂-900°C-20, and (f) WS₂-1000°C-20 films.

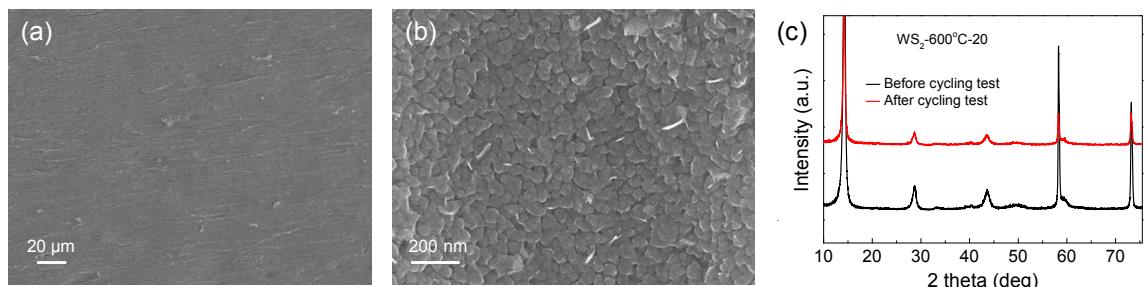


Figure S3. (a) Low- and (b) high-magnification SEM images of WS₂-600°C-20 film after cycling test. (c) Comparison of XRD patterns of WS₂-600°C-20 film before and after cycling test.

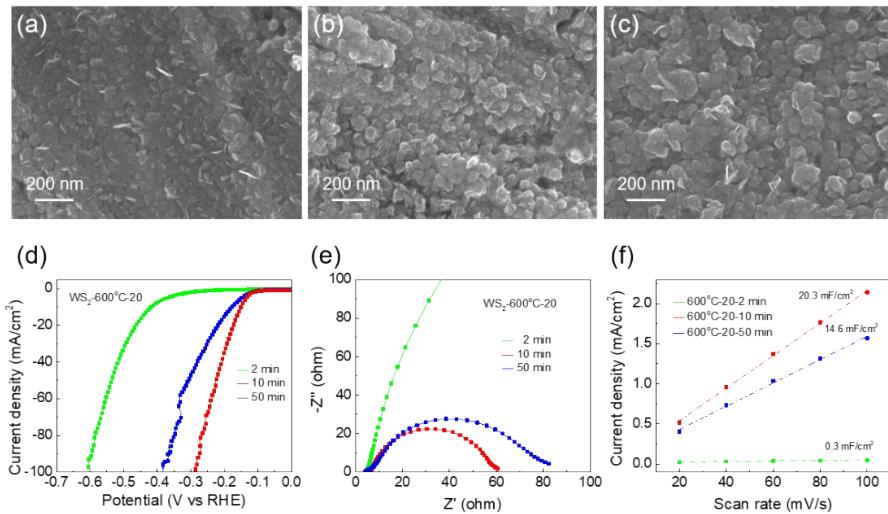


Fig S4. SEM images of (a) WS₂-600°C-20-2min, (b) WS₂-600°C-20-10min, (c) WS₂-600°C-20-50min. (d) Polarization curves, (e) electrochemical impedance spectra and (f) linear fittings of the capacitive current densities at different scan rates of WS₂-600°C-20 films with different reaction times.

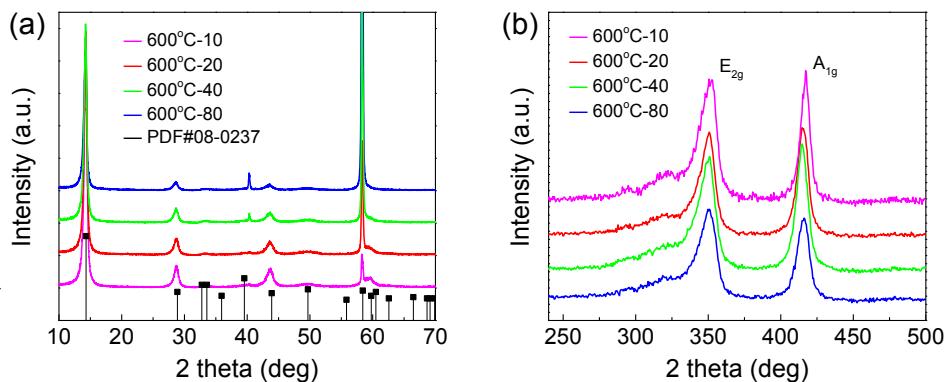


Figure S5. (a) XRD patterns, (b) Raman spectra of WS₂-600°C films with different molar ratios of W/S.

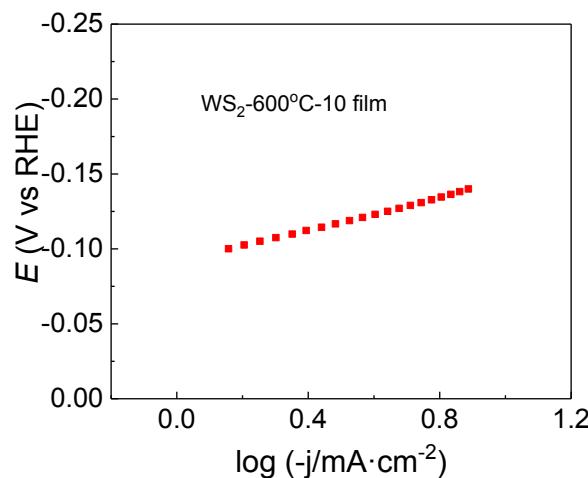


Figure S6. Tafel plot of WS_2 -600°C-10 film.

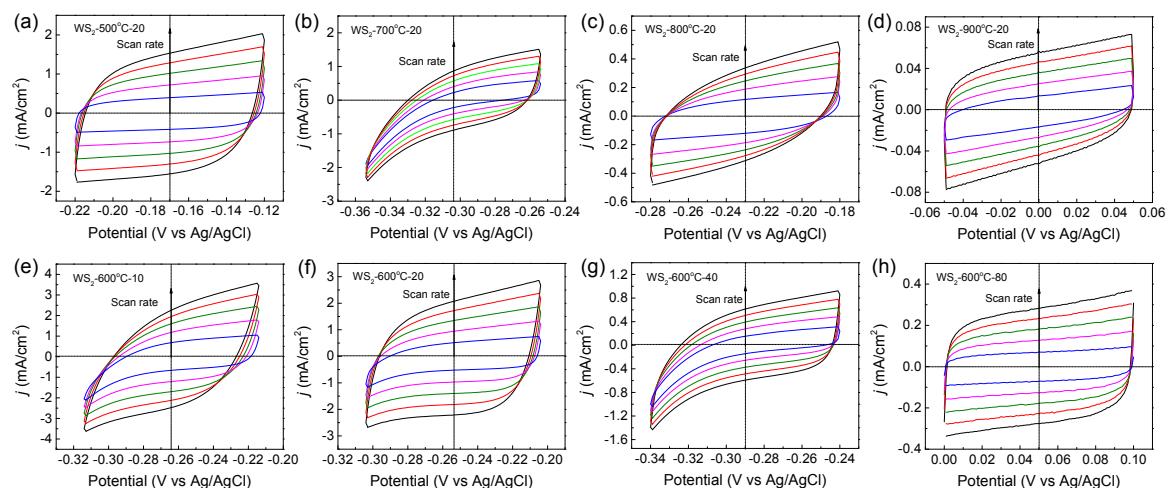


Figure S7. Electrochemical double-layer capacitance measurements of WS_2 films at different scan rates (20, 40, 60, 80, and 100 mV s⁻¹). (a) WS_2 -500°C-20, (b) WS_2 -700°C-20, (c) WS_2 -800°C-20, (d) WS_2 -900°C-20, (e) WS_2 -600°C-10, (f) WS_2 -600°C-20, (g) WS_2 -600°C-40, and (h) WS_2 -600°C-80.

Table S1. Comparison of the electrocatalytic activities of WS₂ film with reported WS₂ structures for HER.

Catalyst	Substrate	Method	Overpotential η mV/10 mA cm ⁻²	Tafel slope [mV dec ⁻¹]	Stability
2H-WS ₂ (this work)	W foil	SACVT	137	54	200 h
WS ₂ nanoflakes ¹	ITO	exfoliation	~350	200	N/A
WS ₂ nanosheets ²	o-carbon fiber	hydrothermal	278	99	1000 cycles
WS ₂ nanosheets ³	Au foil	CVD	~320	100	1000 cycles
1T' WS ₂ nanoparticles ⁴	glassy carbon	colloidal	200	50.4	46 days
2H-WS ₂ nanoplates ⁵	glassy carbon	thermal treatment	280	60	8 h
2H-WS ₂ nanosheets ⁶	glassy carbon	exfoliation	205	70	500 cycles
1T-WS ₂ nanodots ⁷	graphite disks	exfoliation	151	70	500 cycles
WS ₂ nanoribbons ⁸	glassy carbon	solvothermal	225	68	1000 cycles
WS ₂ nanoflakes ⁹	glassy carbon	solvothermal	100	48	10000 cycles
1T' WS ₂ nanosheets ¹⁰	glassy carbon	exfoliation	~220	60	10000 cycles
WS ₂ film ¹¹	carbon cloth	thermal treatment	~210	68	3 h

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