Supporting Information

N-doped WS₂ nanosheets: a High-Performance Electrocatalyst for the Hydrogen Evolution Reaction

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EXPERIMENT SECTION

Synthesis of the N doped WS₂ nanosheets. N doped WS₂ nanosheets were synthesized using one step sintering method using molybdenum chloride (WCl₆, J&K, 99.9 %) and thiourea (J&K, 99 %) as W, S and N sources. In briefly, 0.5 g WCl₆ and different mass ratio of thiourea (1:1, 1:2 and 1:4) were mixed in a beaker and then the ethanol was added slowly into the beaker under stirring, creating a brown solution. Then, the precursor powders were formed after drying the solution. Further, the precursor powders were heated in a tube furnace for 2 h under argon flow at 550 °C.

Calculations. The N doped and pristine WS₂ systems were calculated at the level of density functional theory 1 by using the Vienna *ab* initio Simulation Package (VASP).² The studied model consists $3 \times 3 \times 1$ unit cell for N doped and pristine WS₂, where the vacuum space of 15 Å were applied to the two layers in nearest-neighbor unit cells. The generalized gradient approximation (GGA) was used to account for exchange and correlation in the Perdew–Burke–Ernzerhof form³, where the plane wave basis set with kinetic energy cutoff of 500 eV was employed. The Brillouin zone was done using a 9 \times 9 \times 1 k-points for the supercells.

Characterzation. The samples' morphology were obtained by the scanning electron

microscope (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, TecnaiTM G2 F30, FEI, USA). X-ray diffraction (XRD, X' Pert PRO PHILIPS with Cu Kα radiation) was employed to study the crystal structure of the samples. The bonding characteristics of the samples were captured by the X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra). Raman spectra was obtained by using the Jobin-Yvon LabRam HR80 spectrometer (Horiba Jobin Yvon, Inc.) with a 532 nm line of Torus 50 mW diode-pumped solid-state laser under backscattering geometry. The Brunauer–Emmett–Teller (BET) nitrogen physisorption experiments were carried out on a Micromeritics ASAP 2010 system.

Electrochemical characterization. To fabricate the electrochemical testing electrode, 10 mg of samples and 10 mg of carbon black (Vulcan XC72) were added in to 50 mL Petroleum ether with the sonicate of 2 hrs and then dried at 40 °C Further, the mixture of 3 mg of this catalyst, 1470 µL N, N-Dimethyl Formamide and 30 µL Nafion-117 solution were added into a 5 mL container to disperse the catalysts in the ink. Finally, 12 μ L of the fresh catalyst ink was dropped onto a glassy carbon electrode (0.071 cm² geometrical area, Pine Research Instrument) and dried at room temperature where the loading amount was estimated to be 0.32 mg cm⁻² for the samples. Electrochemical measurements were carried out with the electrochemical workstation (CHI 660E, USA) in a standard three-electrode cell, where the glassy carbon (GC) coated with various samples was the working electrode (WE), Ag/AgCl and the Pt/C electrods were the reference and counter electrode, respectively. Linear sweep voltammetry (LSV) was performed with the scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄ at the room temperature, where the electrolyte was first purged by high purity N_2 gas. The cyclic voltammetry (CV) measurements were carried out at the scan rate of 100 mV s⁻¹ to reveal the stability performance of the catalysts. During the electrochemical testing, all the electrochemical measurements were *iR*-corrected by the equation of E(RHE)=E(Ag/AgCl) + 197 mV. The Nyquist plots were tested at overpotential of 260 mV with frequencies changing from 100 kHz to 0.1 Hz, where the impedance datas were fitted to a simplified Randles circuit to obtain the series and charge-transfer resistances.

Active Sites Calculation: The number of active sites (*n*) is examined using CVs with pH=7 phosphate buffer at a scan rate of 50 mV s⁻¹. When the number of voltammetric charges (*Q*) is obtained after deduction of the blank value, *n* (mol) can be calculated with the equation of n=Q/2F, where *F* is Faraday constant (96485 C mol⁻¹). TOF (S⁻¹) is calculated with the equation of TOF=I/(2Fn) where *I* (A) is the current of the

polarization curve obtained from the LSV measurements.^{4,5}

Capacitance measurements and relative comparison of active surface area

To estimate the differences in electrochemically active surface areas of various catalysts, the cyclic voltammetry (CV) method was employed to measure the electrochemical double-layer capacitance (EDLC), C_{dl} .⁶ The C_{dl} is respected to be linearly proportional to effective active surface area relatively. And this is an appropriate strategy because the number of active sites often scales with the catalyst surface area. Cyclic voltammetry curves were obtained at various scan rates (20, 40, 60, etc. mV/s) at -0.2~0 V vs the RHE region. The halves of the positive and negative current density differences $\Delta j/2$ ($\Delta j=j_a-j_c$) at the center of the scanning potential ranges are plotted vs the voltage scan rate.

- 1 G. Kresse and D. Joubert; Phys. Rev. B, 1999, 59, 3.
- 2 G. Y. Sun, J. Kurtia, P. Rajczy, M. Kertesza, J. Hafner, and G. Kresse; J. Molecular Structure (Theochem) 2003, 624, 37.
- 3 J. P. Perdew, K. Burke, M. Ernzerhof; Phys. Rev. Lett., 1996, 77, 18.
- 4. J. Yin, P. Zhou, L. An, L. Huang, C. Shao, J. Wang, H. Liu, P. Xi, Nanoscale. 2016, 1390, 8.
- 5. W. Cui, Q. Liu, N. Cheng, X. Sun, Chem. Commun. 2014, 9340, 50.
- J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F. Jaramillo, ACS Catal. 2014, 4, 3957.

Catalyst	Onset potential [mV vs.RHE]	η at $J = 100$ mA/cm ² [mV]	Tafel slope (mV/dec)	Exchange current density (mA/cm ²)	Potential at the TOF of 0.725 s ⁻¹ (mV)
N-WS ₂ -Ar	-120	-226	82.55	0.124	124
N-WS ₂ -H ₂	-86	-197	69.69	0.174	108
Pt/C (20%)	0	-97	30.60	0.710	0

Table 1 Electro-catalytic parameters for samples of N doped WS₂ nanosheets.



concentration and (b) N-WS₂-Ar sample annealing at different H_2 flows.



Figure S2. N 1s spectrum for sample N-WS₂-H_{2.}



Figure S3. XRD and Raman results for sample N-WS₂-Ar after its 5000 CV cycles.



Figure S4. The CVs at various scan rates obtained during the determination of C_{dl} for sample (a) N-WS₂-Ar and (b) N-WS₂-H₂.