

Supporting information

for

Fluorine dopants in tungsten sulfides induce boosted efficiency of H₂O₂ electro-synthesis from ORR catalysis

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Experimental section

Chemicals materials: Ammonium metatungstate ($(\text{NH}_3)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$) was purchased from Kunshan Xingbang Tungsten and Molybdenum Technology Co., Ltd., Jiangsu, Ammonium Fluoride (NH_4F), ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$) and Hydrochloric Acid (HCl, Analytical pure) were obtained from China. Sinopharm Chemical Reagent Co. Ltd. All the chemicals above were used without further purification. Ultrapure water with a resistivity of 18.25Ω was used in this work.

Synthesis of Precursors: A certain amount of Ammonium metatungstate and 15ml ultrapure water were placed in a 200ml three-neck flask at room temperature to form a transparent and homogeneous solution by magnetic stirring for 10 mins. Then 17 mL of ammonium sulfide solution with a mass fraction of 8 wt % was added(W:S=1:10). At this time, the mixture above was dark green, and it was heated to 70°C . After 1 hour, the solution changed from dark green to orange. Let it cool to room temperature, slowly whisk 90 ml of 1M HCl into the solution under magnetic stir (Note: H_2S gas is produced at this step). The reddish-brown color of the solution means that the reaction is completed. Standing about 0.5 hour and then the red-brown deposit will be moved to centrifugal wash and dry.

Preparation of WS_2 and F-doped WS_2 : The dried precursor was collected and ground, followed by annealing at 450°C for 5 h with a heating rate of 5 K min^{-1} in the $10\%\text{H}_2/\text{Ar}$ for 4 hours to obtain the WS_2 . Last, the mixed solid containing 0.04g of prepared WS_2 and 0.1g of ammonium Fluoride was placed in a mortar and ground evenly, and then was thermally treated at 200°C in N_2 at a heating rate of 1 K min^{-1}

for 2 hours to obtain the F-doped WS₂.

Material Characterization

The morphological characteristics of as-prepared samples were conducted by high-resolution field emission scanning electron microscope (FEI, SU8010, JPN). The crystal structure was carried out on powder X-ray diffractometer (Bruker AXS D8 Advance, GER) with a Cu K α radiation ($\lambda = 0.15406$ nm) at a scan rate of 10° min⁻¹. The surface element composition and chemical valence were determined by X-ray photoelectron spectroscopy (ESCALAB 250Xi, USA). The micromorphology and lattice information were collected by high-resolution transmission electron microscope (FEI Talos F200x G2, USA) with energy dispersive X-ray spectroscopy. The Raman spectroscopy were recorded utilizing handheld Raman spectrometer (BWS465-532H, USA) with a 532 nm excitation laser.

Electrochemical Measurements

The ORR performance of prepared sample was carried out on an electrochemical workstation (CHI 760e) with standard three-electrode system, while a rotating ring-disk electrode (RRDE-GC1156) assembly consisting of a glassy carbon rotation disk electrode (GC: 5.61 mm inner diameter) and a Pt ring (6.25-7.92 mm) was used as work electrode which tend to be loaded with a certain amount of electrocatalyst on GC, carbon rod as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The collection efficiency (N=18%) of the RRDE was calibrated by redox reaction of [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ and all the potentials measured were corrected by the reversible hydrogen electrode ($E_{RHE} = E_{Hg/HgO} + 0.244V + 0.059 * pH$).

The 0.1 M KOH with 13.0 of pH value as electrolyte used for the measurement. In order to uniformly load the catalyst, traditionally, 2 mg of as-prepared catalyst was mixed with 1 ml liquids containing 15 μ l of 5 wt % Nafion solution, 205 μ l ethanol and 780 μ l ultrapure water, and sonicated for at least 30 mins to gain a homogeneously dispersed catalyst ink, which be pipetted onto glassy carbon disk to achieve 0.1mg/cm² of catalyst load. The electrolyte was saturated with oxygen by constantly bubbling high-purity O₂ for 30 mins before each electrochemical test and the O₂ was maintained over the electrolyte during the recording process. The precycling steps was conducted by cyclic voltammetry from 0 to 1.2V (vs. RHE) at a scan rate of 50 mV s⁻¹ at 1600 r.p.m for activating surface of the electrode, in which coincident cyclic curves were obtained. Then, the productivity of H₂O₂ was investigated by Linear sweep voltammetry, which was conducted by scanning from 0 to 1.2V (vs. RHE) at a scan rate of 5 mV s⁻¹ with 1600 rpm, while the Pt ring potential was kept at 0.5V (vs. RHE). The stability of catalysts was tested by chronoamperometry at 0.6 V (vs. RHE) with a 1600 rpm rotating speed in O₂-saturated electrolyte.

The peroxide yield (HO_2^- %) and the corresponding electron transfer number (n) were calculated based on the following formula:

$$HO_2^- = 200 \times \frac{(I_r/N)}{I_d + (I_r/N)} \%$$

$$n = 4 \times \frac{I_d}{I_d + (I_r/N)}$$

Where the I_r and I_d denote the ring current and ring current, respectively. The N is the

collection efficiency of the Pt ring electrode (N=18% in this work).

The selectivity of the prepared-catalyst for the electrosynthesis of hydrogen peroxide was observed by comparing the CV curves recorded in a N₂-saturated electrolyte with those in an O₂-saturated electrolyte.

The electron transfer number (n) of the obtained-catalyst was further investigated via linear sweeping voltammetry with scanning rate of 5 mV s⁻¹ at various rotating speeds (425,625,1200,1600 and 2025 r.p.m.). The Koutecky-Levich equation was taken to calculate the number of electrons transferred during the ORR by plotting the inverse of i_{dl}^{-1} (diffusion limiting current), which as a function of $\omega^{-1/2}$ (rotating speed, rad s⁻¹):

$$i^{-1} = i_k^{-1} + i_{dl}^{-1} + i_k^{-1} + \frac{1}{0.62nFAC_{O_2}D_{O_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}}$$

And then the n can be derived from B on the basis of Koutecky-Levich equation:

$$B = (n0.62FAC_{O_2}D_{O_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}})^{-1}$$

Where D_{O_2} (1.9×10^{-5} cm² s⁻¹), C_{O_2} (1.2×10^{-6} mol cm⁻³), ν (0.01 cm² s⁻¹) denote the diffusion coefficient of O₂, the concentration of the dissolved O₂ and the kinematic viscosity in 0.1M KOH, respectively. The F (95485 C mol⁻¹) is the Faraday constant, A (0.2475 cm²) is the geometric area of glassy carbon rotation disk electrode, and ω is the rotational speed of the work electrode.

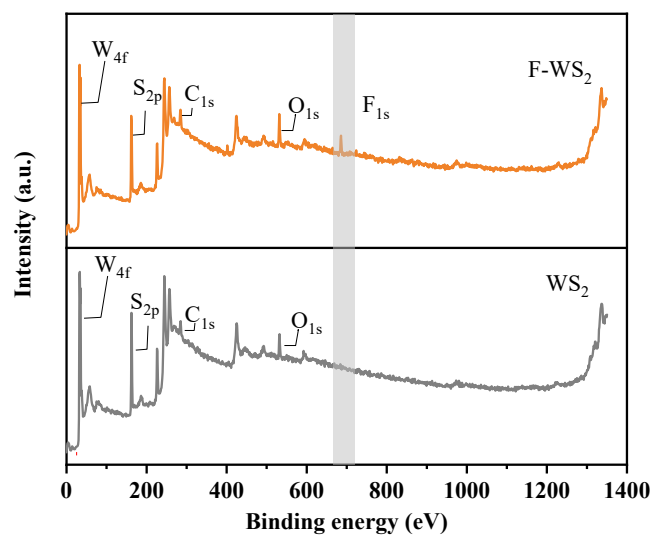


Figure S1 XPS survey scan of WS₂ and F-WS₂ electrocatalysts.

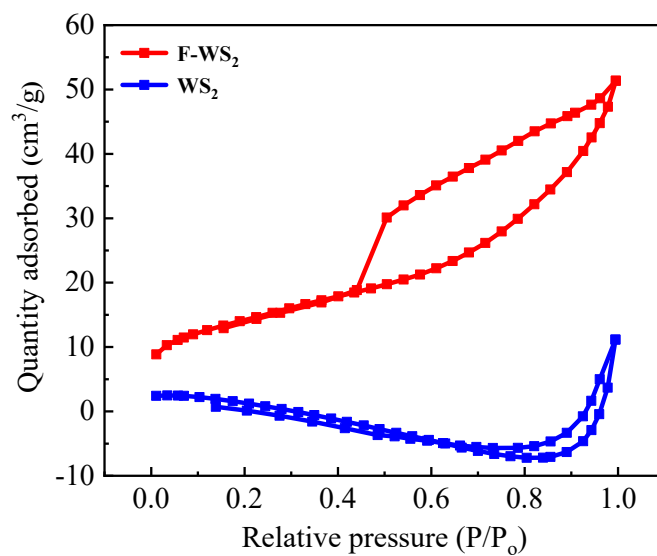


Figure S2 N₂ isothermal adsorption/desorption curves of F-WS₂ and WS₂.

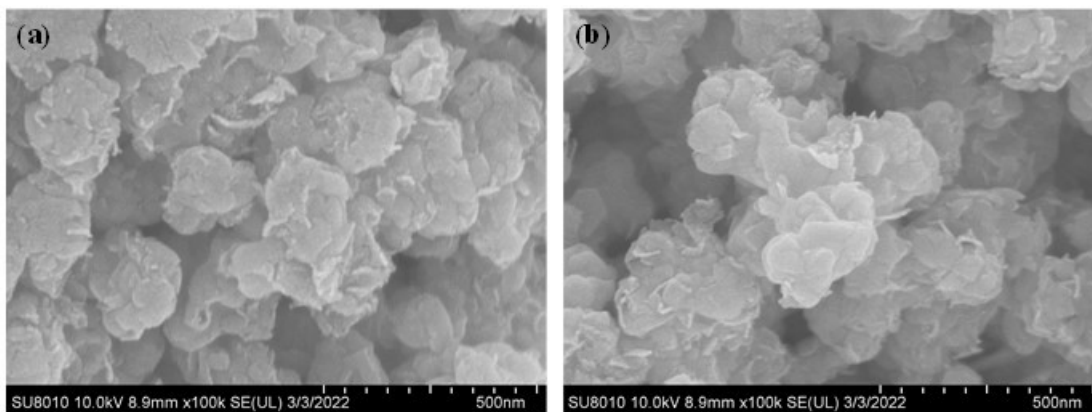


Figure S3 SEM images of WS₂ (a) and F-WS₂ (b) electrocatalysts.

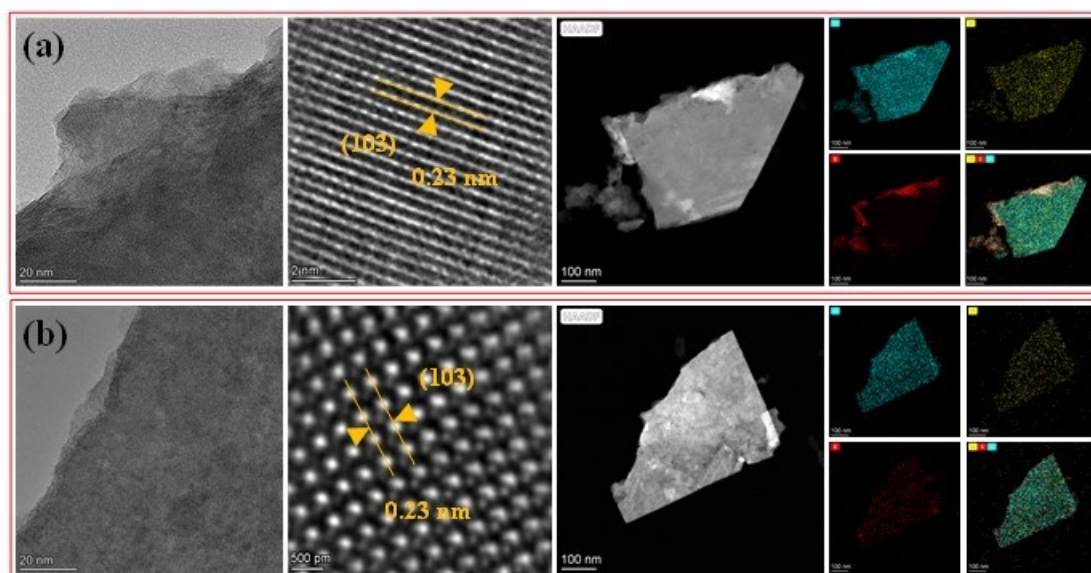


Figure S4 TEM image of F-WS₂ at edge sites (a) and in-plane (b).

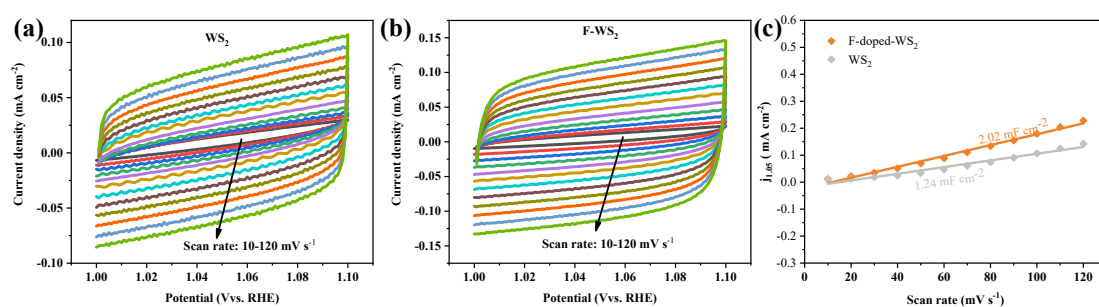


Figure S5 Cyclic voltammograms of WS₂ (a) and F-WS₂ (b). (c) Double layer capacitances of WS₂ and F-WS₂.

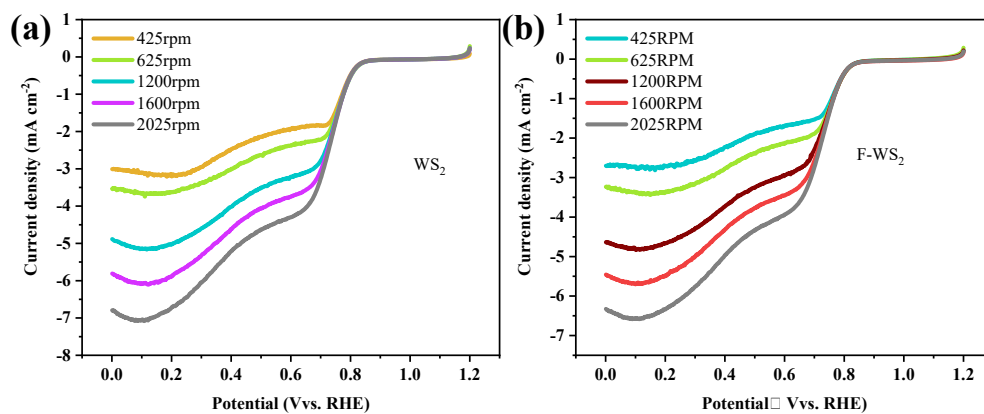


Figure S6 LSV curves of WS₂ and F-WS₂ with different rotation speeds.

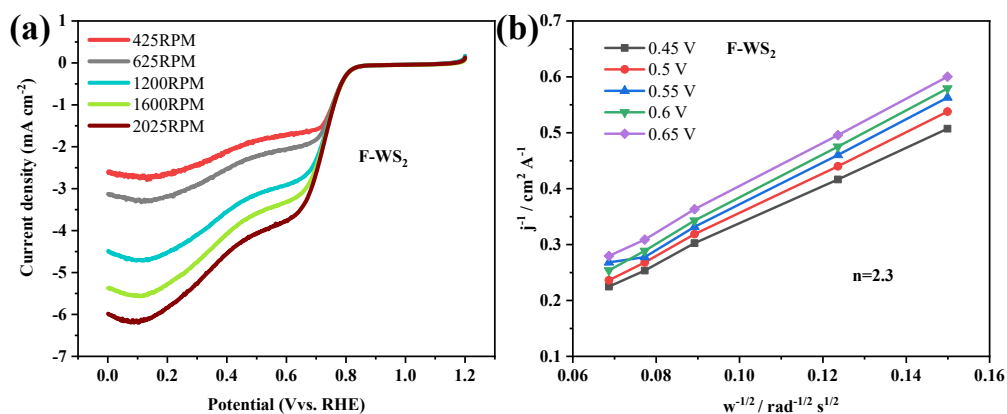


Figure S7 LSV curves of F-WS₂ and related numbers of transferred electrons after 1000 cycles.

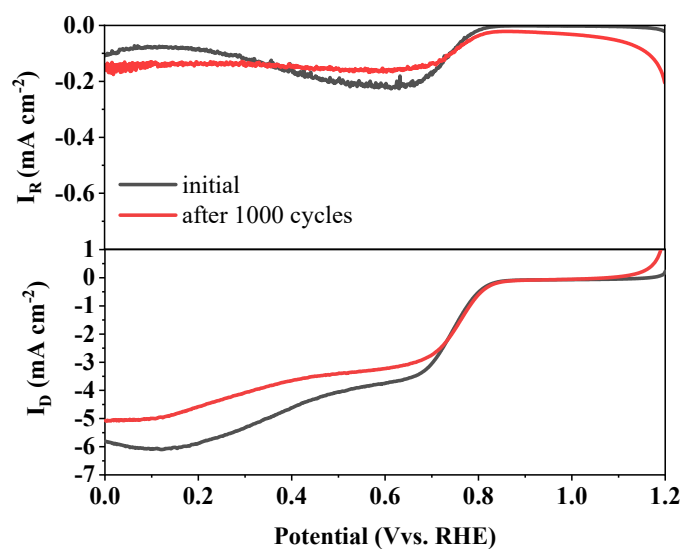


Figure S8 Disk- and ring- current densities of WS₂ before and after 1000 cycles.

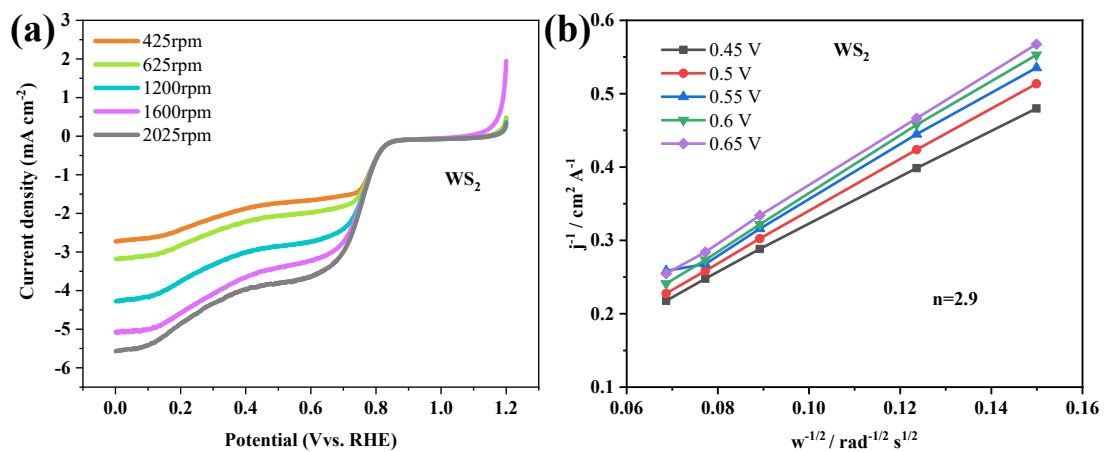


Figure S9 LSV curves and related numbers of transferred electrons of WS_2 after 1000 cycles.

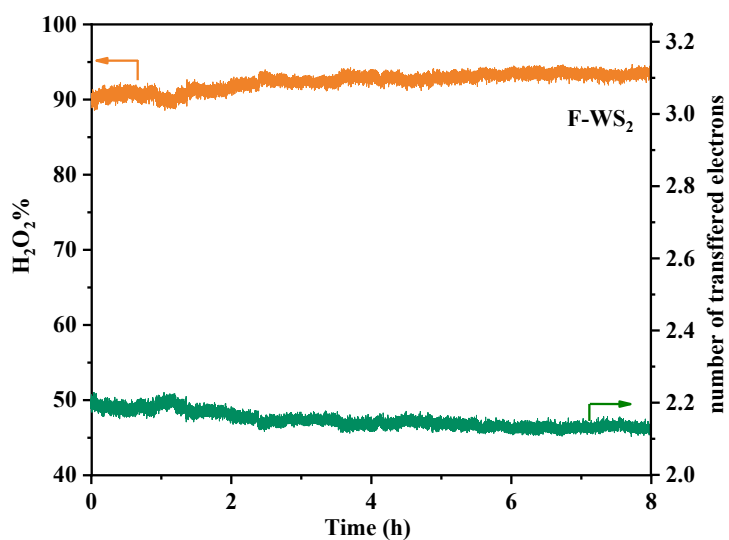


Figure S10 H_2O_2 generation and numbers of transferred electrons of F-WS_2 during i-t test.

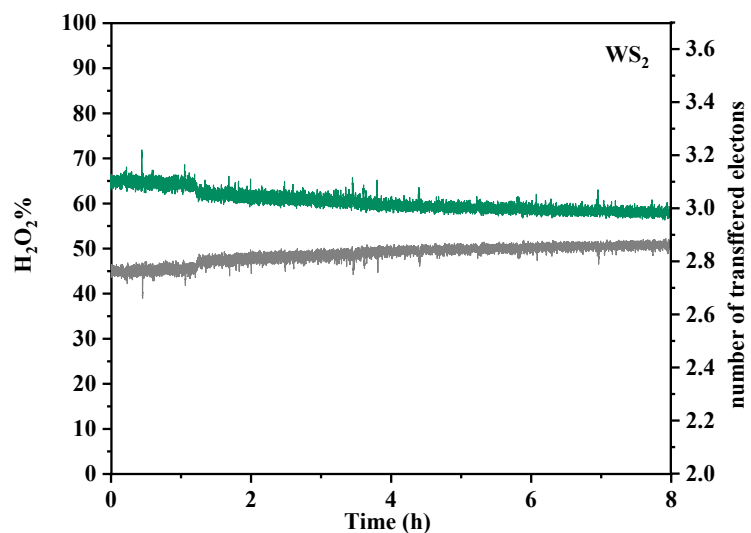


Figure S11 H₂O₂ generation and numbers of transferred electrons of WS₂ during i-t test.

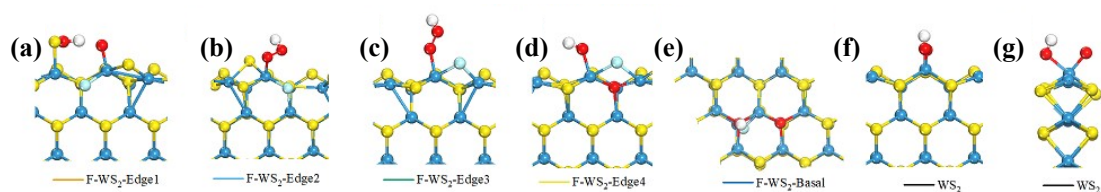


Figure S12 Chemical structures of OOH species on various F-WS₂ and WS₂.