

Supporting Information

Synthesis of vanadium based binary oxides with yolk-shell structure and its derived electrocatalysts

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Experimental details

Electrochemical measurements for HER

All the electrochemical measurements were operated with a CHI660D electrochemical workstation (CH Instruments, Inc. Shanghai) in a conventional three-electrode system consisting of a working electrode, a carbon rod counter electrode and a saturated silver chloride electrode and 0.5M H₂SO₄ was used as the electrolyte. Working electrode was fabricated by dispersing 5mg of asprepared catalyst powder in 360 μ L ethanol/40 μ L Nafion (5 wt%). After the dispersion was ultrasonicated for 30 min, 10 mL of the catalyst suspension was dropped casted onto a glassy carbon electrode with 5mm in diameter and dried in the air. All potentials presented were referenced to a reversible hydrogen electrode (RHE): $E(\text{RHE})=E(\text{Ag}/\text{AgCl}) + 0.059 \cdot \text{pH} + 0.199$ and all data referred were corrected by iR compensation. Linear sweep voltammetry (LSV) was recorded at a scan rate of 2mV·s⁻¹ to obtain the polarization curves. The long-term durability was tested by cyclic voltammetry (CV) scans from 0.1 to -0.3 V vs. RHE with a sweep rate of 100 mVs⁻¹.

Electrochemical measurements for ORR

All measurements were carried out with a CHI 660D electrochemical workstation (Chen-Hua, Shanghai, China) in a standard three-electrode cell. Working electrodes were prepared by mixing the 5mg catalyst with 180 μ L isopropanol and 20 μ L Nafion (5 wt %) by sonication 30 min to form a homogeneous ink. An amount of 4 μ L of catalyst ink was deposited onto the polished surface of a 3 mm RDE made of glassy carbon and dried in the air. A Pt foil (2 cm²) and a Hg/HgO electrode were used as the counter and reference electrode, respectively. All potentials referred to in this paper are converted to the pH-independent reversible hydrogen electrode (RHE):

$$E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.059 \cdot \text{pH} + 0.098$$

In the electrochemical measurements, all the electrodes were pretreated by cycling the potential between -0.7 and 0.3 V (vs Hg/HgO) at a sweep rate of 50 mV·s⁻¹ for 20 cycles to activate electrodes and remove the dissolved oxygen before the ORR activity tests in N₂-saturated 0.1 M KOH solution until a stable cyclic voltammogram was recorded. Then, the electrolyte was saturated with oxygen by bubbling O₂ for 30 min prior to the ORR activity tests. A flow of O₂ was maintained over the electrolyte to ensure O₂ saturation during the recording of CV. Linear-sweep voltammetry (LSV) measurements were conducted under O₂-saturated circumstance by sweeping the potential negatively from 0.3 V to -0.7 V at a scan rate of 5 mV·s⁻¹ with varying rotating speed from 2025 to 400 rpm. The stability tests of the catalysts were conducted by applying a cyclic potential sweep between -0.6 and 0 V in O₂-saturated 0.1 M KOH solution, with a scan rate of 50 mV·s⁻¹.

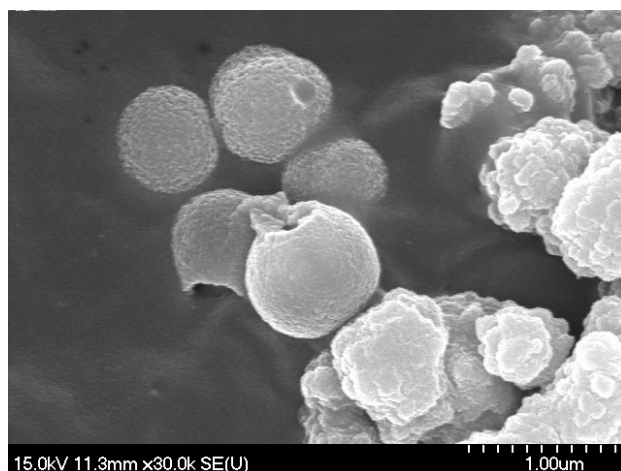


Fig. S1 the WVO_x prepared in absolute ethanol at 200 °C for 6 h.

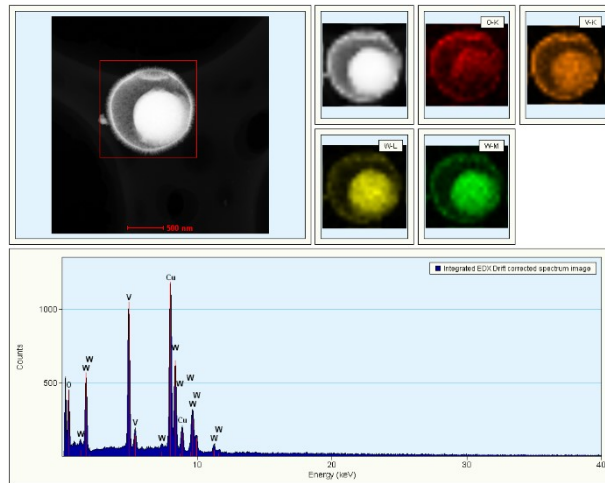


Fig. S2 the EDS spectrum of WVO_x from the selected red square region and its corresponding mapping images of this region

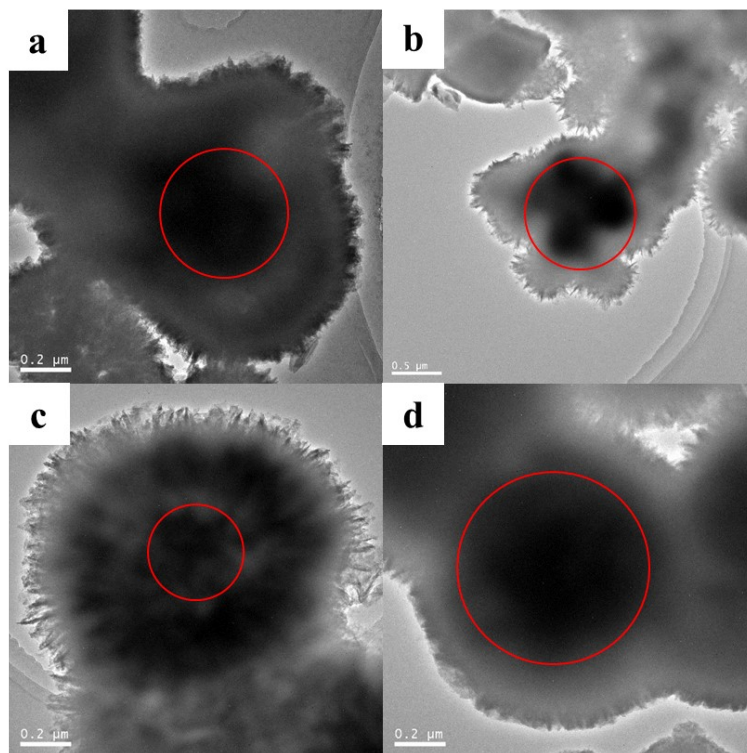


Fig. S3 TEM images of MnVO_x (a), FeVO_x (b), CoVO_x (c), and ZnVO_x (d) prepared in absolute ethanol.

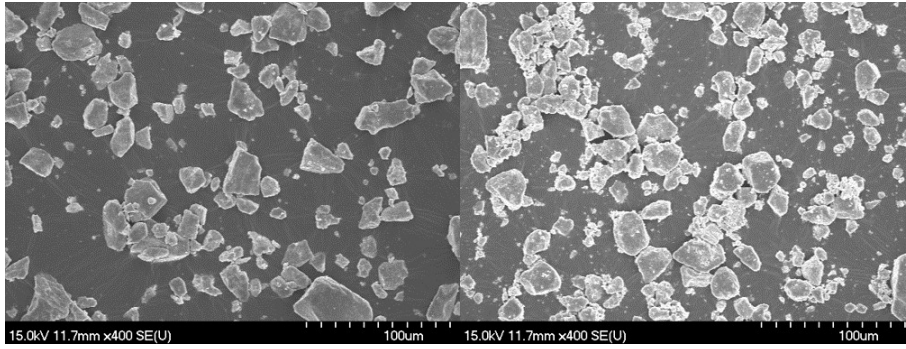


Fig. S4 SEM images of NiVO_x prepared in absolute ethanol.

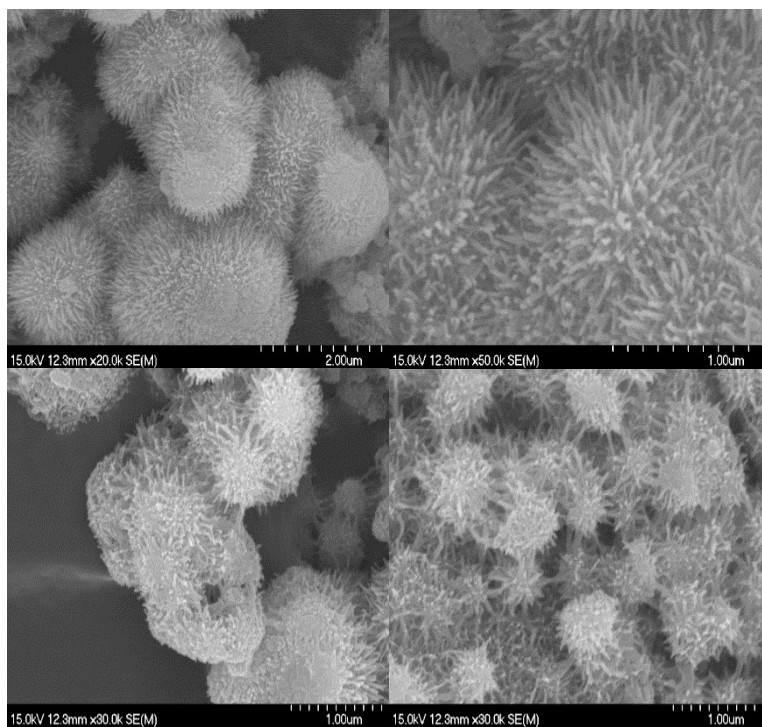


Fig. S5 SEM images of WVO_x prepared in $CH_3CH_2OH+H_2O$ ($CH_3CH_2OH:H_2O=1:1$)

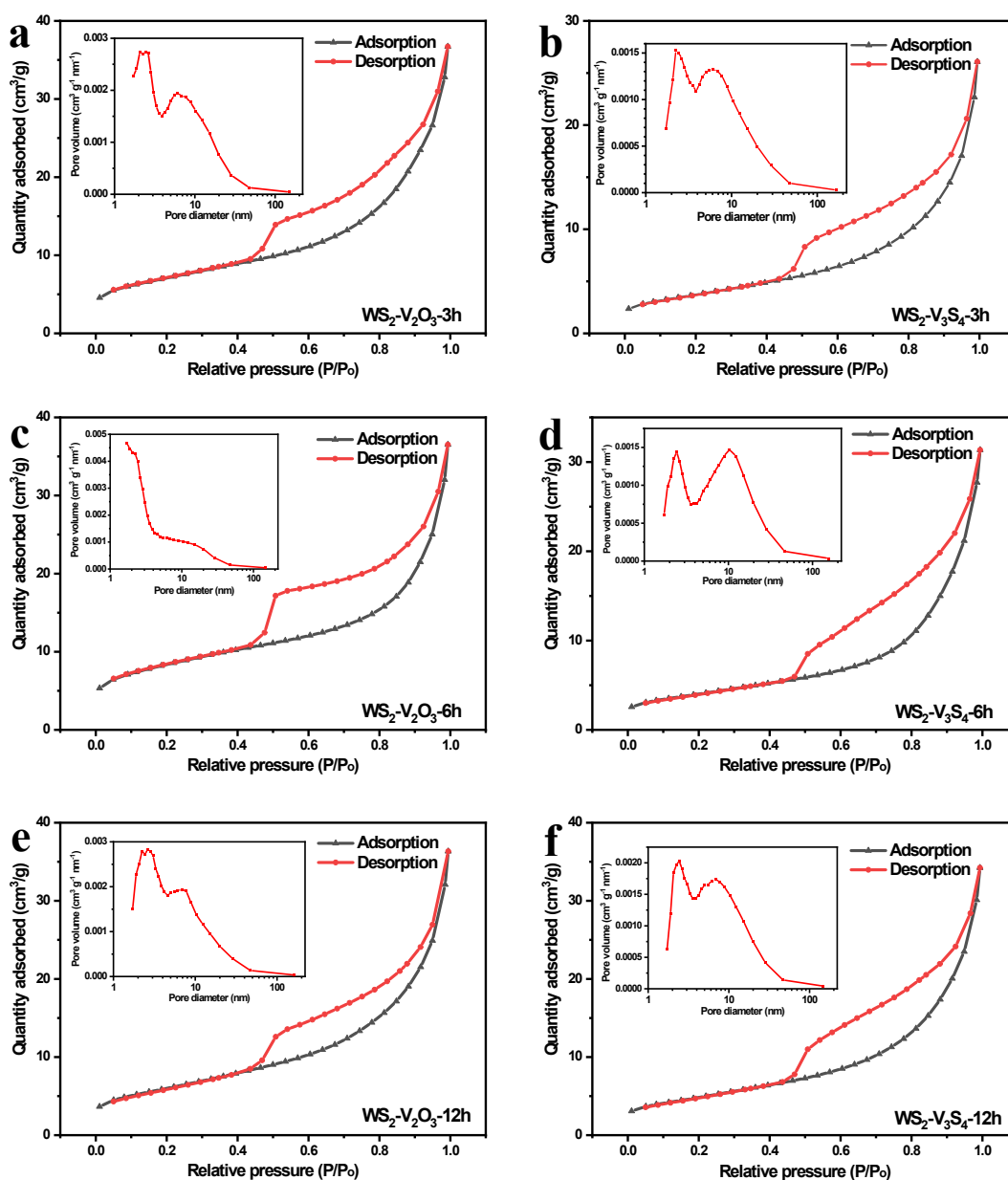


Fig. S6 N_2 adsorption-desorption, and pore size distribution plots of the synthesized catalysts. (a, c, e) $WS_2-V_2O_3-3h$, $WS_2-V_2O_3-6h$, $WS_2-V_2O_3-12h$; (b, d, f) $WS_2-V_3S_4-3h$, $WS_2-V_3S_4-6h$, $WS_2-V_3S_4-12h$

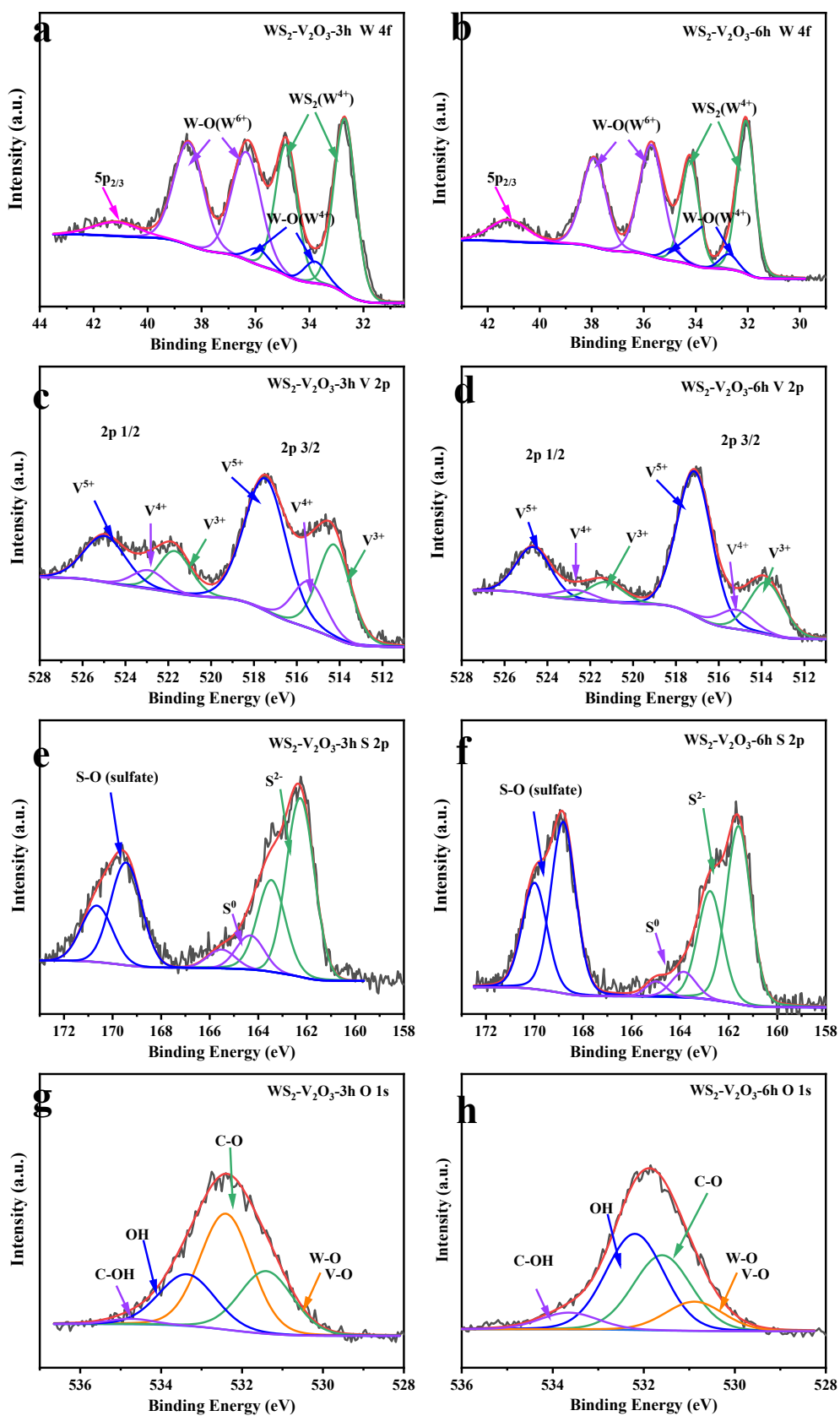


Fig. S7 XPS spectra of $\text{WS}_2\text{-V}_2\text{O}_5\text{-3h}$: (a) W 4f, (c) V 2p, (e) S 2p, (g) O 1s. and $\text{WS}_2\text{-V}_2\text{O}_5\text{-6h}$: (b) W 4f, (d) V 2p, (f) S 2p, (h) O 1s.

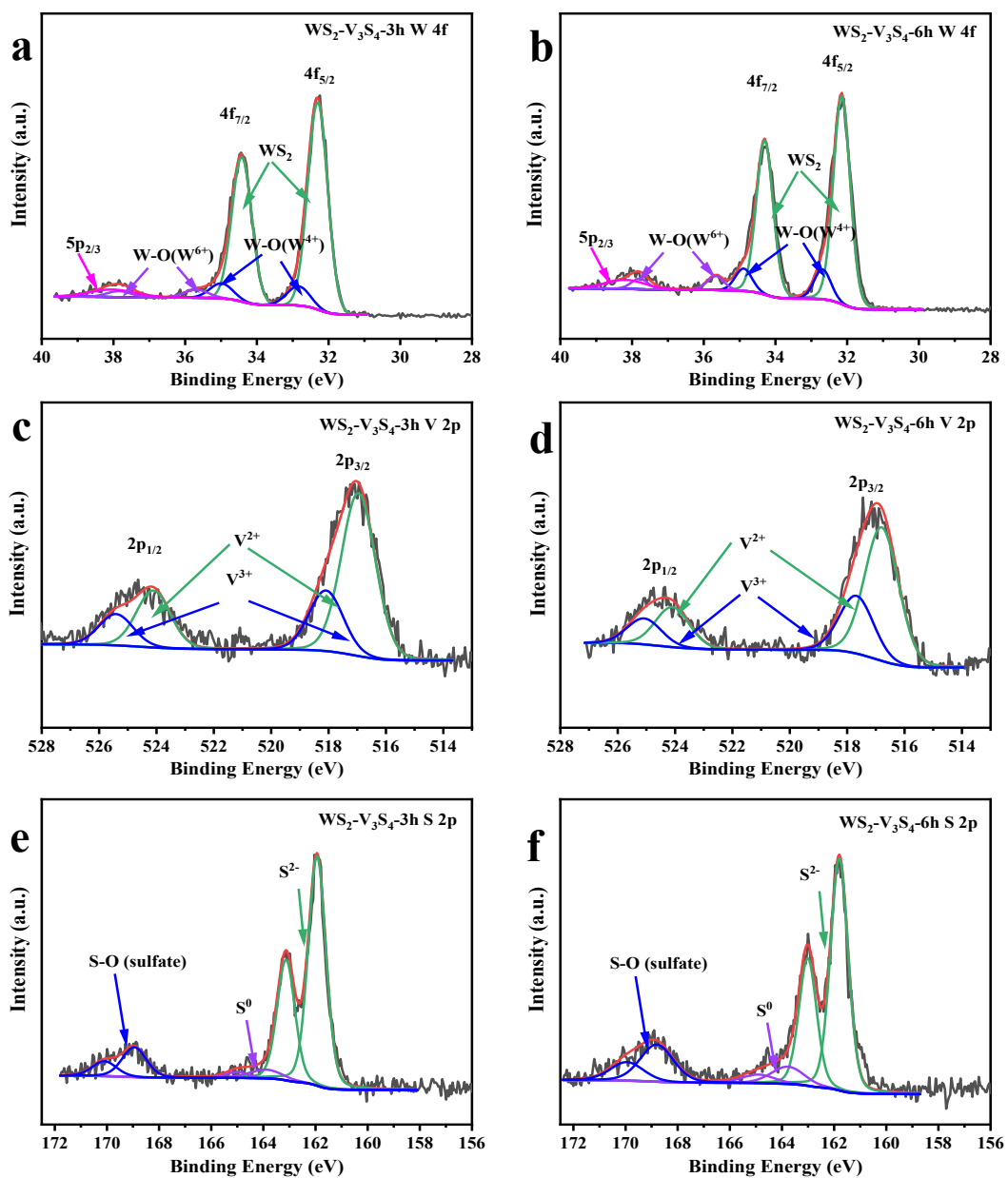


Fig. S8 XPS spectra of WS₂-V₃S₄-3h: (a) W 4f, (c) V 2p, (e) S 2p, and WS₂-V₃S₄-6h: (b) W 4f, (d) V 2p, (f) S 2p.

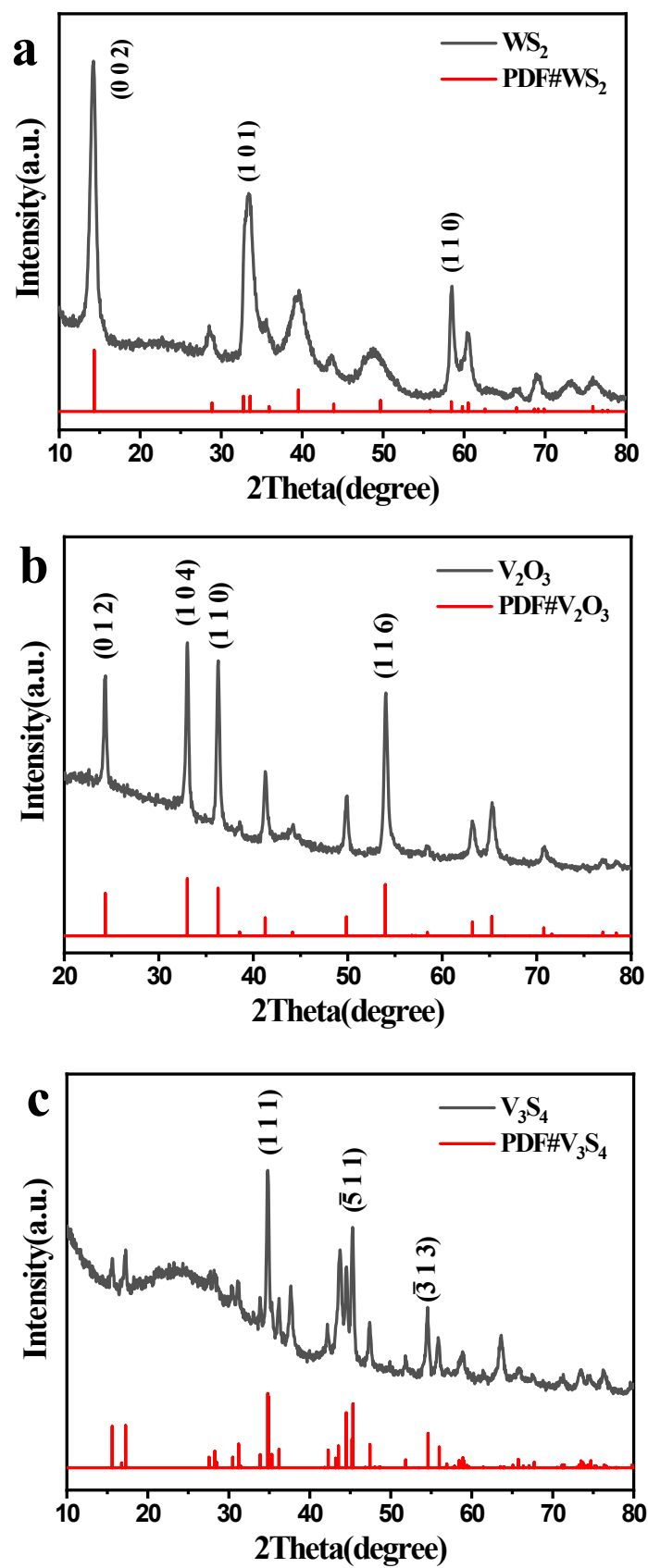


Fig. S9 XRD patterns of (a) WS_2 , (b) V_2O_3 and (c) V_3S_4 .

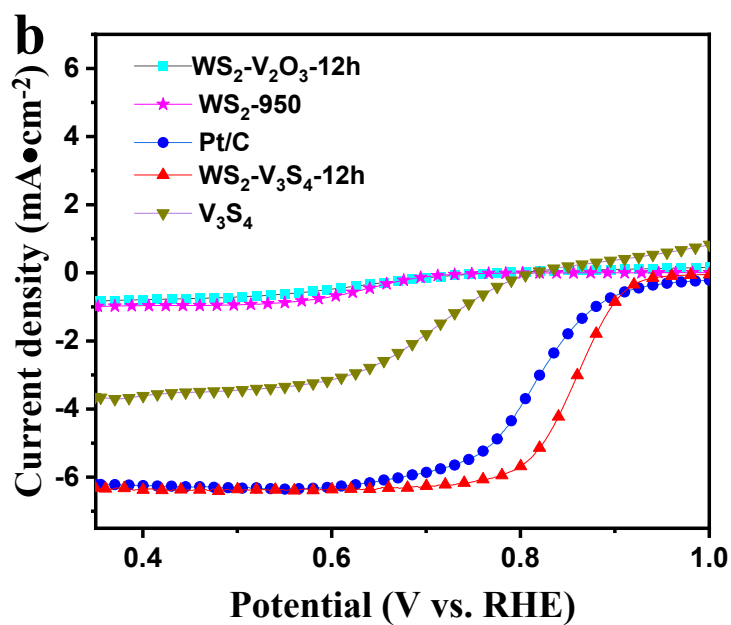
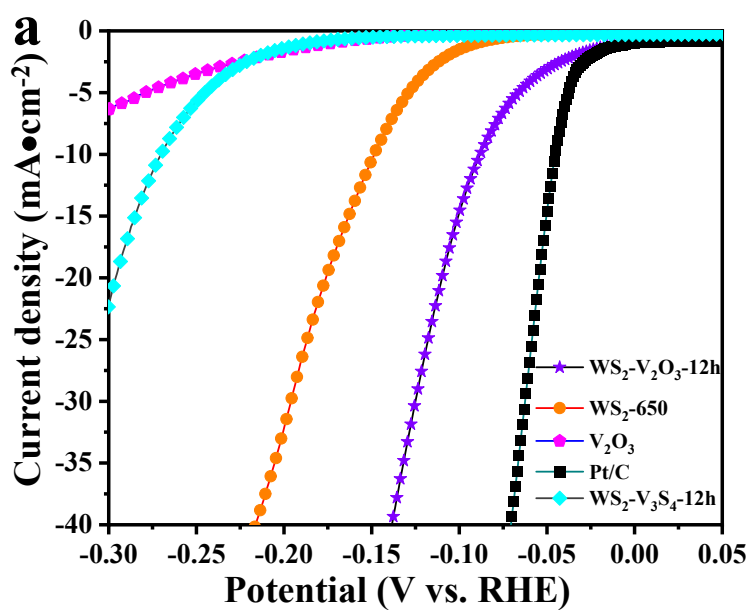


Fig. S10 (a) Polarization curves obtained from WS₂-V₂O₃-12h, WS₂-650, V₃S₄, WS₂-V₃S₄-12h and 20% Pt/C in 0.5 M H₂SO₄ at a scanning rate of 2 mV s⁻¹; All polarization curves are corrected for iR losses except for Pt. (b) Polarization curves of WS₂-V₂O₃-12h, WS₂-950, V₃S₄, WS₂-V₃S₄-12h and 20% Pt/C in O₂-saturated 0.1 M KOH solution with scan rate of 5 mV·s⁻¹.

Table S1. Structural Parameters from Nitrogen Sorption Isotherms of the WS₂-V₂O₃ and WS₂-V₃S₄ samples which were obtained at different hydrothermal times (3h, 6h and 12h)

sample	BJH pore size (nm)	pore volume (cm³/g)	BET surface area (m²/g)
WS₂-V₂O₃-3h	10.45	0.054	25.02
WS₂-V₂O₃-6h	9.71	0.052	29.69
WS₂-V₂O₃-12h	10.55	0.055	21.69
WS₂-V₃S₄-3h	12.23	0.040	13.37
WS₂-V₂S₄-6h	13.93	0.048	14.39
WS₂-V₃S₄-12h	11.98	0.053	17.46