

Colloid Synthesis of Metallic VSe₂ Single-Layer Nanosheets as Novel Electrocatalysts for Hydrogen Evolution Reaction

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Experimental Section

I. Materials and Methods

Vanadyl acetylacetonate 99%, Selenium 99.9% metals basis, 200 mesh and Oleylamine (OM) (C₁₈, 80%–90%) were purchased from Aldrich. Hexamethylene≥99.0% were purchased from Sinopharm Chemical Reagent Co., Ltd. All electrolyte solutions were prepared with ultrapure water (GWA-UN1-F20 type Beijing Purkinje General Instrument Co., Ltd.). All other reagents were of analytical grade and used without further purification.

Synthesis of VSe₂ monolayer. 0.3mmol VO(C₅H₇O₂)₂, 0.6mmol Selenium powder and 10ml oleylamine was added to a 100mL three-necked under N₂ atmosphere. The reaction mixture was stirred moderately and was heated using a heating mantle, to remove water and other low-boiling impurities. The mixtures are evacuated for 30 minutes at 140 °C. Next the solution was purged with N₂ and heated to 330 °C. After holding the solution at 330 °C for 1.5h, the reaction was stopped and cooled down to room temperature by removing heating source. The contents of the reaction mixture were added with alcohol and transferred into centrifuge tubes, the VSe₂ nanosheets were precipitated by the centrifugation at 5000 rpm for 5 min. The

nanosheets were washed with 1:2 (v:v) cyclohexane:ethanol for several times. A part of the sample was dispersed in cyclohexane, the rest of products were dried in 60 °C in the vacuum drying oven. To demonstrate the large-scale synthesis, we performed the reaction with 40 mmol of V precursor and obtained as much as 1.36 g of VSe₂ monolayer in a single batch

Characterization. The atomistic structure information and microtopography were characterized by XRD on a Bruker D8 Advance X-ray diffractometer fitted with CuK α radiation over the 2 θ ranges from 2 θ = 10° to 70° on increments of 0.019° at the scanning speed of 4°/min, the TEM measurements on a JEOL JEM 1200 TEM microscope at an acceleration voltage of 100kV. HRTEM images were carried out on a FEI Tecnai G2 F20 field emission electron microscope with an EDS section at an acceleration voltage of 200 kV. High Angle Annular Dark Field Scanning Transmission Electron Microscope (HAADF-STEM) images and mapping section were obtained using Titan G2 60-300 TEM/STEM (FEI, America) at an acceleration voltage of 300kV. AFM on a DI Veeco Multimode SPM platform, XPS spectrum on a Kratos Amicus X-ray photo-electron spectrometer with an Al K α excitation source of 180W, Raman spectra on a LabRAM HR800 Horiba Jobin Yvon, respectively.

Electrochemical measurements. Electrochemical measurements were performed in a standard three-electrode electrochemical cell using an electrochemical workstation (CHI760E). Glassy carbon electrode, saturated calomel electrode(SCE), and platinum electrode were used as working, reference, and counter electrodes, respectively. The VSe₂ nanocrystals were washed by 1:2 (v:v) cyclohexane:ethanol for three times and precipitated by the centrifugation at 10000 rpm for 1 min. The precipitates were dispersed in ethanol. Firstly, the freestanding VSe₂ film comprised of monolayer was produced by vacuum filtering and treated by oxygen plasma exposure for 3 min. Then the VSe₂ film with OPE treatment as electrocatalysts were loading on the glassy carbon electrode with 3 μ L Nafion (0.5 wt%), drying in 60°C in the vacuum drying oven. VSe₂ was loaded onto the glassy carbon surface at 0.3 mg cm⁻². All cyclic voltammetry of the HER activity was conducted using 0.5M H₂SO₄

electrolyte under continuous purging with 99.99% N₂. Linear sweep voltammetry was performed between 0 and -0.6V with a 5mV·s⁻¹ scan rate, the Pt/C was performed using same measurements. In 0.5M H₂SO₄, E (RHE) = E (SCE) + 0.244 V. Electrochemical impedance spectroscopy was performed when the working electrode was biased at a constant -0.167V vs. RHE while sweeping the frequency from 100kHz to 10 mHz with amplitude of 2mV. The electrochemical stability of the catalyst was evaluated by cycling the electrode 100 times, each cycle started at 0V and ended at -0.6V with a scan rate of 5mV·s⁻¹.

Supporting Figures

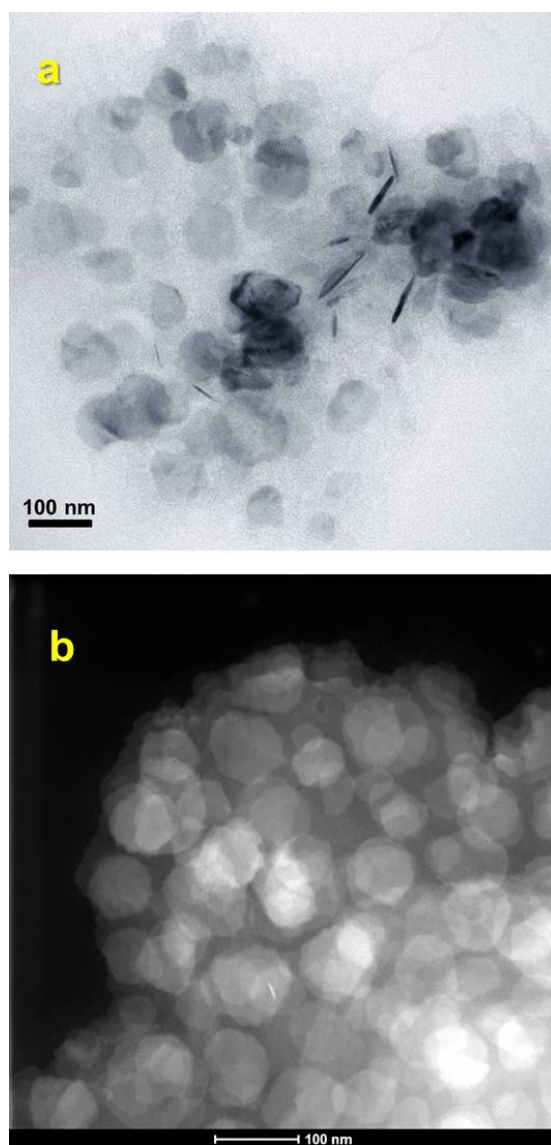


Figure S1 (a) Typical TEM image and (b) enlarged HAADF-STEM image of VSe₂ monolayer.



Figure S2 Gram-scale production of VSe₂ single-layer nanosheets.

Table S1. The experiment conditions for synthesis of high-quality VSe₂ monolayer

Sample	Reaction temperature (°C)	Reaction time	Solvent and capping ligand	Selenium source	Product
1	235	1.5h	OM	Se	VO _x , VSe ₂ , Se, SeO _x
2	260	1.5h	OM	Se	VO _x , VSe ₂ , Se, SeO _x
3	280	1.5h	OM	Se	VSe ₂ , Se, SeO _x
4	300	1.5h	OM	Se	VSe ₂ , Se
5	235	1.5h	ODA	Se	VSe ₂ , Se
6	291	1.5h	TDA	Se	VSe ₂ , Se
7	330	1.5h	OLA	Se	Impurity, Se
8	235	1.5h	ODA	SeO ₂	VSe ₂ bulk, Se, SeO ₂
9	330	1.5h	OM	SeO ₂	VSe ₂ , Se
10	330	1min	OM	Se	VSe ₂ , Se
11	330	20min	OM	Se	VSe ₂ , Se
12	330	40min	OM	Se	VSe ₂ , Se
13	330	1h	OM	Se	VSe ₂ monolayer
14	330	1.5h	OM	Se	VSe ₂ monolayer

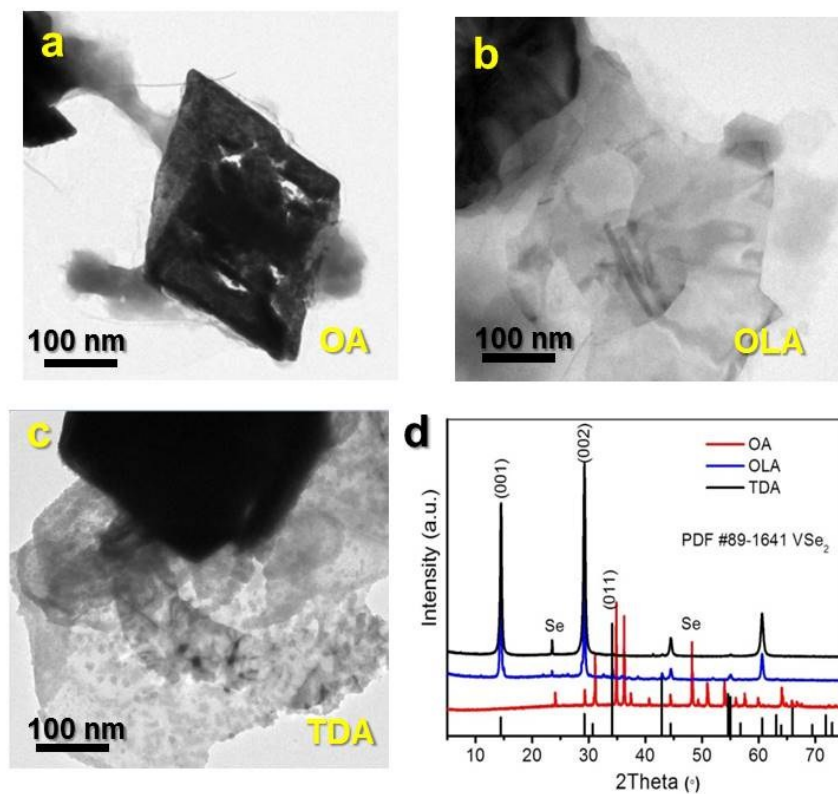


Figure S3. Capping ligand-dependent experiment. TEM images of VSe₂ nanosheets prepared with OA (a), OLA (b) and TDA (c) as capping ligand. (d) Corresponding XRD patterns.

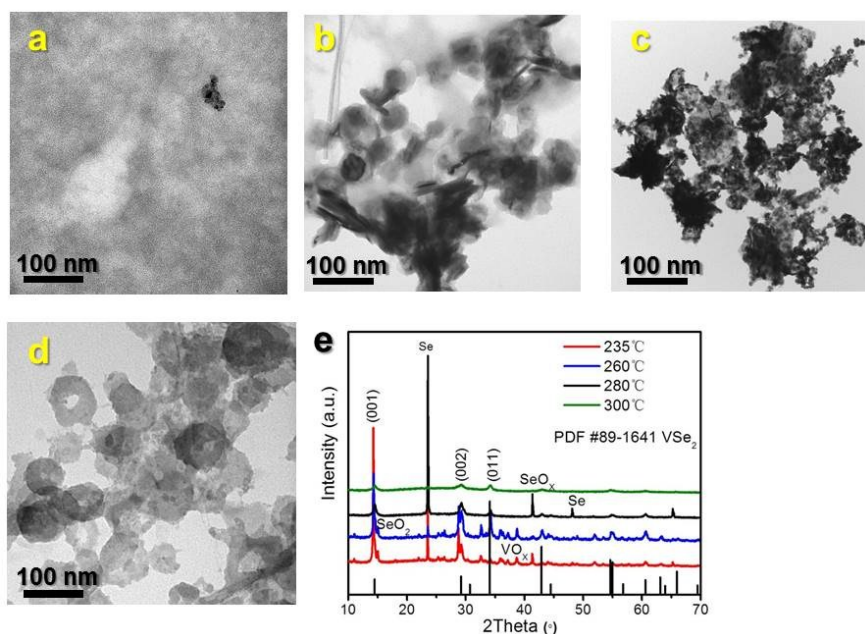


Figure S4. Reaction temperature-dependent experiment. TEM images of VSe₂ nanosheets prepared at different temperature 230 °C (a), 260 °C (b), 280 °C and 3000 °C. (e) Corresponding XRD patterns.

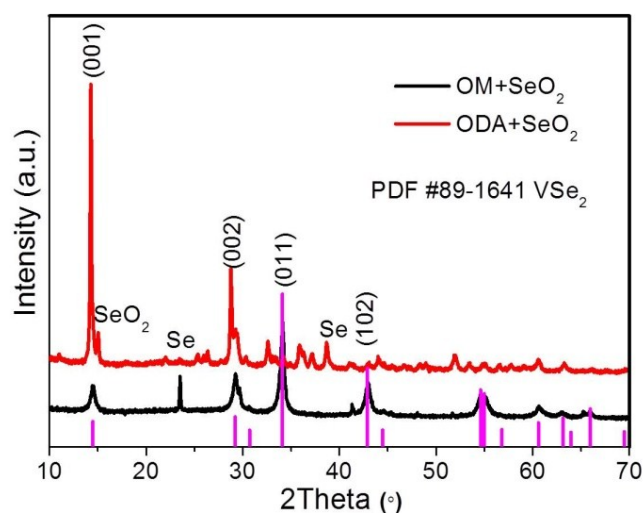


Figure S5. Se precursor -dependent experiment. XRD patterns of samples prepared with SeO_2

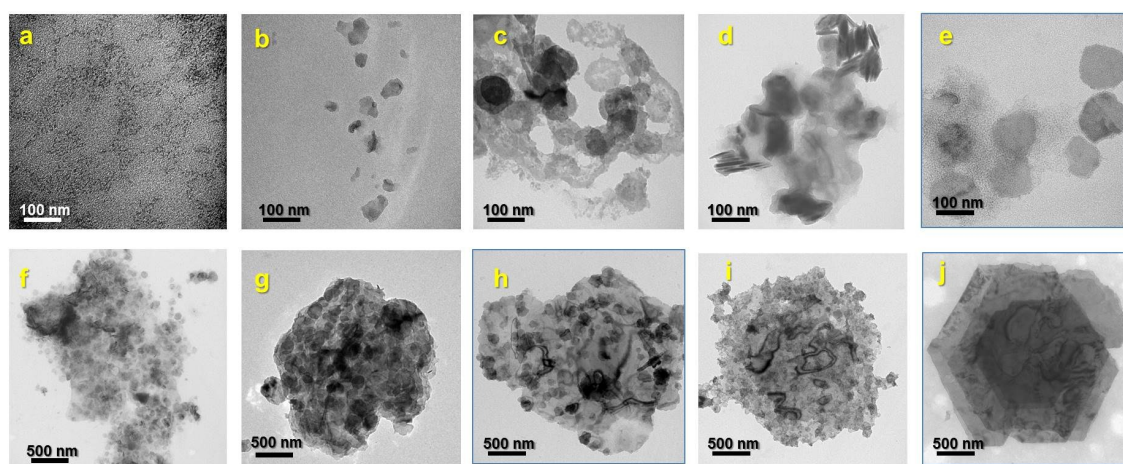


Figure S6. Reaction time-dependent experiment

The formation mechanism of the VSe_2 nanosheet. TEM images of aliquots taken during the formation of the VSe_2 nanosheet, highlighting initial nucleation (a-b), agglomeration (c-d), and coalescence of nanoparticle seeds into monolayer (e). Further growth involves lateral and vertical growth. Firstly, the monolayers show a clear tendency to self-assemble into large 2D sheets driven by the oriented attachment (f-g). Interestingly, once lateral growth has defined the large 2D nanosheet (h-i), we see evidence of vertical growth that generally maintains the lateral dimensions while increasing the thickness. Obviously, the initial large 2D nanosheet acts as a template for the growth of subsequent layers, which suggests that the nanosheets “grow out” laterally and then “grow up” vertically^{1,2}.

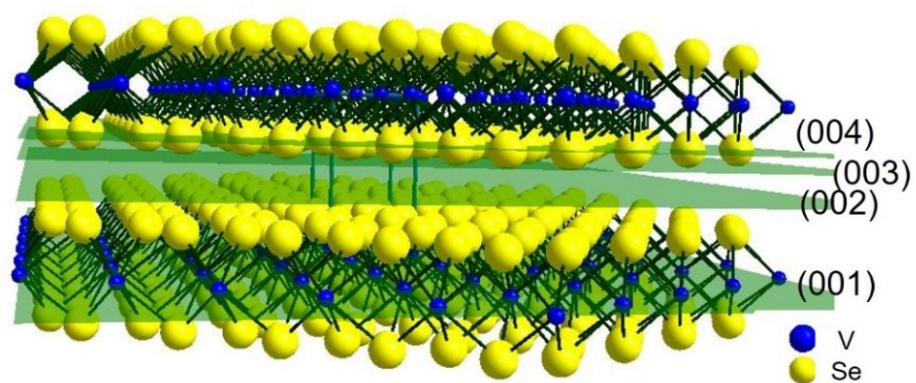


Figure S7 Crystal structure model of VSe₂ multiple-layer.

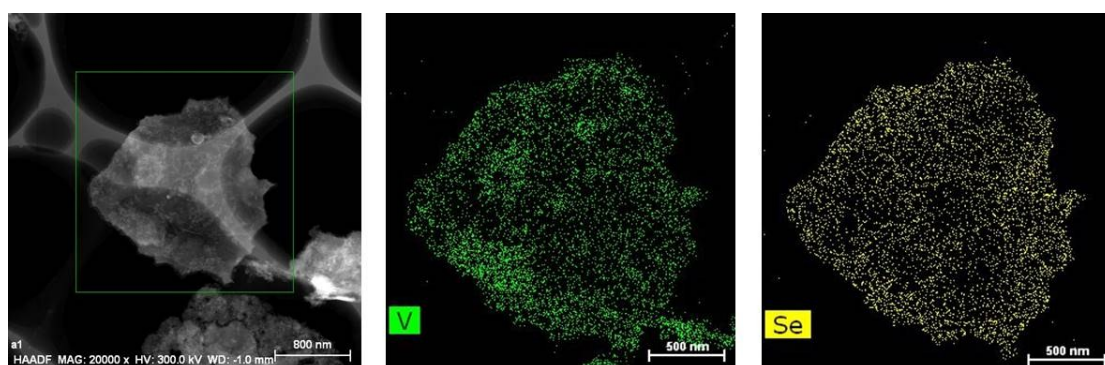


Figure S8 HAADF-STEM and EDS mapping of VSe₂ multiple-layer

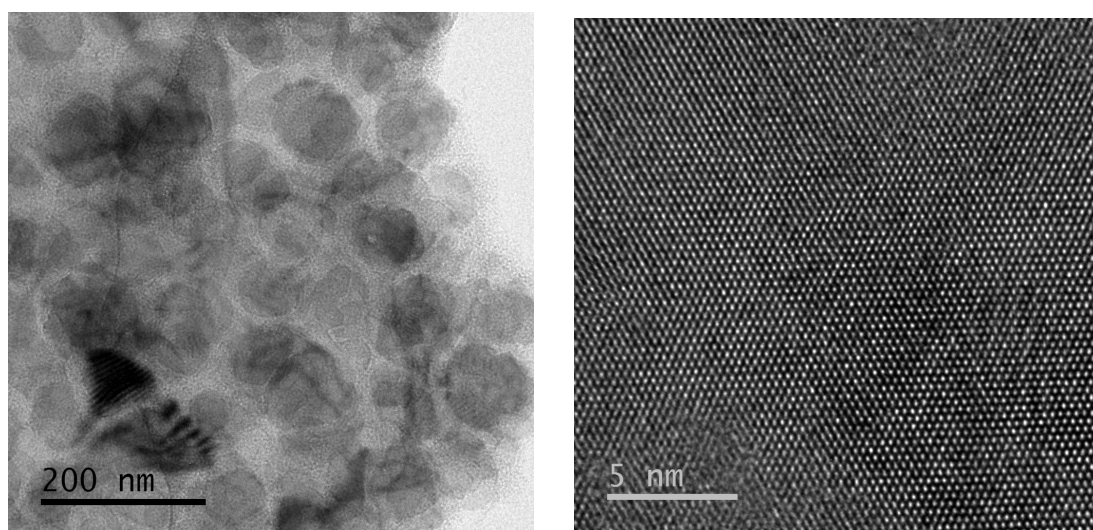


Figure S9 TEM and HRTEM images of the VSe₂ monolayer after OPE

After OPE, there are no obvious defects and changes observed in the morphology and crystal structure of VSe₂ monolayer.

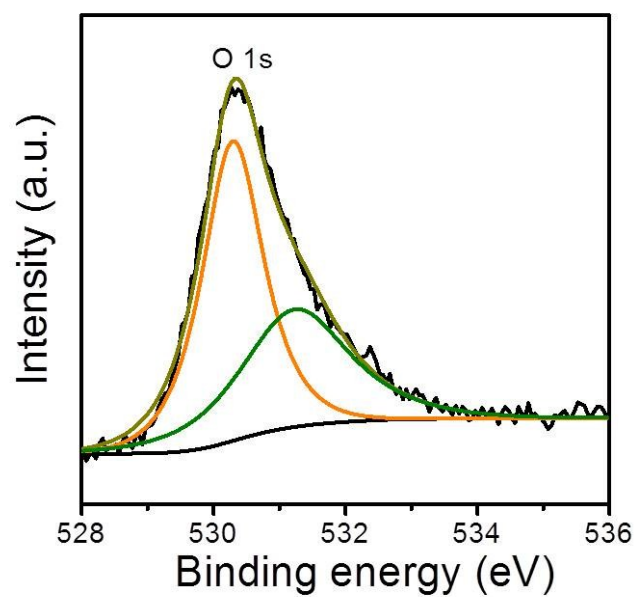


Figure S10. XPS spectra of VSe₂ single-layer nanosheets before and after OPE.

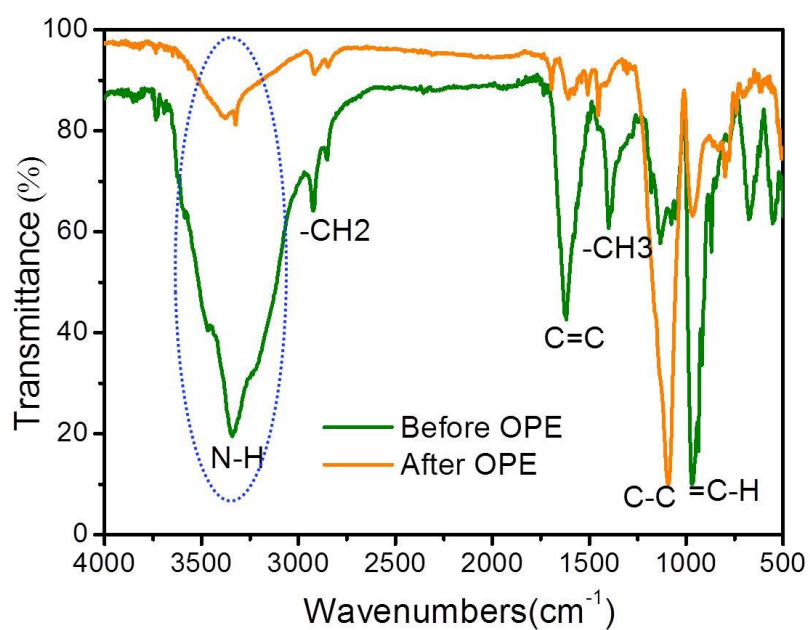


Figure S11. FTIR spectrum of VSe₂ single-layer nanosheets for O1s after OPE.

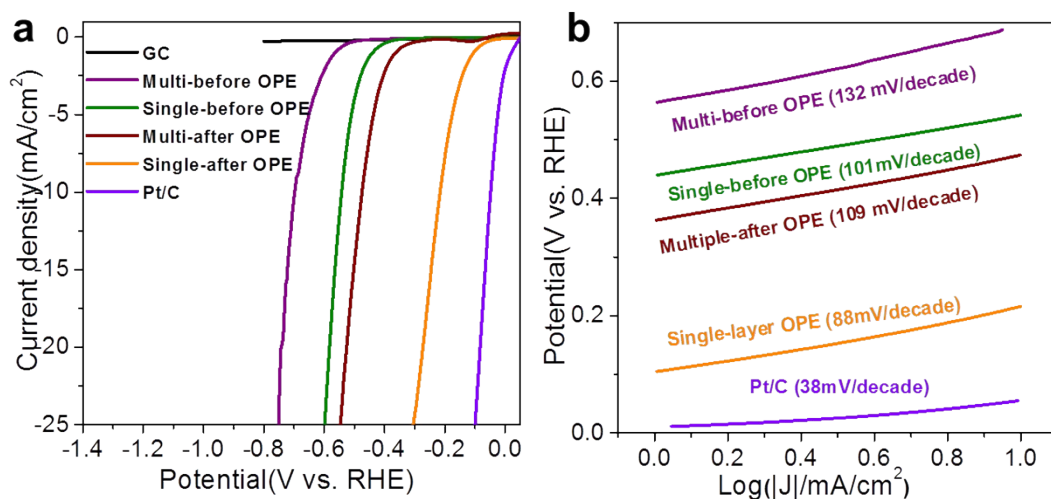


Figure S12. Electrocatalytic performance of VSe₂ single-layer and multiple-layer nanosheets before and after OPE. (a) Polarization curves. (b) Corresponding Tafel plots.

REFERENCES

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