Supporting Information for

Van der Waals 3D Heterostructure via Spontaneous Self-Restacked Assembling for Enhanced Water Oxidation

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Methods

Materials

Nickel powder (Aladdin, 99.9%), iron powder (Aladdin, 99.95%), manganese powder (Aladdin, 99.95%), zinc powder (Aladdin, 99.9%), cobalt powder (Aladdin, 99.9%), cadmium powder (Aladdin, 99.98%), Phosphorus Red (Aladdin, lump, 99.999%) and Sulfur powder (Aladdin, 99.99%) were used as-purchased without further purification for the synthesis of the compound. The demonized (DI) water was obtained from a Millipore Autopure system (18.2 M Ω , Millipore Ltd., USA). All the other materials for electrochemical measurements were of analytical grade and without further purification.

Fabrication of MPS₃ (M=Mn, Fe, Co, Ni, and Zn) Powders, and Ni_{0.8}M_{0.2}PS₃ (M=Mn, Fe, Co and Zn) Powders

The MPS₃ and Ni_{0.8}M_{0.2}PS₃ powders were synthesized by the solid-state reaction.¹ The mixture with stoichiometric amounts of nickel, iron, phosphorus, and sulfur was ground uniformly in a mortar to ensure the reaction happens sufficiently and sealed in quartz ampoules with an internal pressure to 10^{-5} Torr. Then the sealed quartz ampoules were heated to 750°C in muffle furnace and maintained at this temperature for 7 days. After cooling down to room temperature, the sample was collected and stored in an Ar-filled glove box for further use.

Preparation of MPS₃ (M=Mn, Fe, Co, Ni and Zn) nanosheets

The MPS₃ nanosheets were prepared by the ultrasonic exfoliation.² Firstly, the glass bottle with 500 mg of MPS₃ powders and 200 mL of formamide was blew with argon gas for 30 minutes. After carefully sealing, the glass bottle was sonicated by ultrasonic cleaner for 6 hours. With intactly standing overnight, the mixture was obtained by centrifuging the suspension in the upper two-thirds of the glass bottle at 1080*g* for 40 minutes to remove bulky crystals. Finally, the nanosheets were collected by centrifuging upper two-thirds of the mixture at 17300*g* for 1 hour, washed using ethanol, dried in a vacuum oven, and stored in an Ar-filled glove box for further use.

Construction of Restacked NiPS₃/MPS₃ (M=Mn, Fe, Co and Zn) nanosheets

The restacked NiPS₃/MPS₃ nanosheets were constructed by a simple air pump filtration. Firstly, the mixture was prepared by mixing stoichiometric amounts of NiPS₃ nanosheets and MPS₃ nanosheets. Then, the uniform dispersion suspension was obtained by dispersing the mixture in formamide through ultrasonication for 2h. Finally, through simple air pump filtration, the restacked NiPS₃/MPS₃ nanosheets were obtained and stored in an Ar-filled glove box for further use.

Preparation of NiFe-LDH

In a typical procedure, 3 mmol of Ni(NO₃)₂·6H₂O and 0.75 mmol of Fe(NO₃)₃·9H₂O were dissolved in 50 mL of deionized water under continuous magnetic stirring. The mixture was then slowly added into 50 mL of aqueous NaOH solution (0.15 M) to initiate precipitation. The collected precipitates were re-dispersed in deionized water and transferred into a Teflon-lined autoclave for hydrothermal treatment at 120°C for 24 h. Finally, the NiFe-LDH product was recovered by centrifugation, rinsed with water, and dried at 60°C under vacuum.

Material characterization

X-ray diffraction (XRD) measurements were recorded on Rigaku MiniFlex 600 diffractometer with Cu K α radiation (λ =0.1542 nm) from 10° to 70° under a constant voltage of 40 kV and a current of 15 mA. Morphology and EDX mapping were analyzed by HITACHI SU8600 cold field emission scanning electron microscope (CFESEM). All samples were coated with a thin layer of gold prior to CFESEM observations. Transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HR-TEM) images were obtained on a Tecnai G2 F30 filed emission transmission electron microscopy. Atomic-scale STEM images were recorded on a probe aberration-corrected STEM (Cubed Titan G2 60-300, FEI, USA) operated at 300 kV. The surface morphology and topography of the samples were characterized using atomic force microscopy (AFM) on Asylum Research Cypher ES. Inductively coupled plasma optical emission spectrometry (ICP-OES) analyses were performed on a Plasma Quant PQ9000 ICP spectrometer. Wettability measurements were tested via a contact angle meter (Sindin, SDC-100) and the liquid used to measure the contact angle is the demonized (DI) water. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) analysis was made with Thermo Scientific Nexsa G2. All XPS spectra were corrected using C_{1s} line at 284.8 eV. Raman spectroscopy measurements were carried out on a Labram HR Evolution spectrophotometer with 532 nm wavenumber of the excitation light source (HORIBA SCIENTIFIC, maximum power: 30W). Zeta potential was collected by Brookhaven's NanoBrook 90Plus PALS. UV-vis diffuse reflectance spectrum measurements were carried out on a Shimadzu UV-2600 spectrometer. Synchrotron radiation X-ray absorption fine structure (XAFS) spectroscopy of Ni K-edge was collected in transmission mode using a Si (111) double crystal monochromator at the 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF).

Electrocatalytic OER Measurement

Most electrochemical measurements were performed using a Pt plate as counter electrode (area: 10*10 mm²), a Hg/HgO as reference electrode, and the prepared glassy carbon electrode (diameter: 3 mm) as working electrode in 1 M KOH via adopting a three-electrode test system under room temperature. For electrode preparation, 8 mg of catalyst, 1.6 mg

carbon black and 25 µL Nafion perfluorinated resin solution in lower aliphatic alcohols and water (5 wt%) were dispersed in 2 mL N, N-Dimethylformamide (DMF) by sonication for over 30 minutes. Subsequently, 3.6 µL of the prepared suspension was drop-cast onto a glassy carbon electrode with a loading of 0.2 mg cm⁻² and left to dry under ambient conditions. Linear sweep voltammetry (LSV) was carried out at a scan rate of 5 mV s⁻¹ with 80% iR compensation correction on CHI760E electrochemistry workstation. Operando electrochemical impedance spectroscopy (EIS) tests were performed at different applied potentials in the frequency range of 0.01-100000 Hz on a Bio-Logic (SP-150). Cyclic voltammetry (CV) measurements were performed without *iR* correction at a scan rate of 5.0 mV s⁻¹ on a Bio-Logic (SP-150). The double-layer capacitance (C_{dl}) was determined by analyzing the capacitive current associated with double-layer charging using CV at varying scan rates. CV measurements were conducted around the open-circuit potential at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹. The C_{dl} was calculated by plotting the difference in current densities ($\Delta j = j_a - j_c$), where j_c and j_a represent the cathodic and anodic current densities, respectively, against the scan rate. The slope of this plot corresponds to twice the value of C_{dl}. All the potentials were calibrated with respect to the reversible hydrogen electrode (RHE) scale according to the equation: $E_{RHE} = E_{Hg/HgO} + 0.059$ × pH + 0.098 V. The Tafel slope was calculated by the equation below: $\eta = a + b \times log j$. Where η stands for the overpotential, b stands for the Tafel slope, j stands for the current density. The electrochemical active surface area (ECSA) of catalyst was calculated by the equation: ECSA = C_{dl}/C_s . Where C_s is the specific capacitance of planar surface with an atomically smooth under identical electrolyte conditions. We use the general value of 40 μ F cm⁻².³

In situ Raman spectroscopy

In situ Raman spectroscopy was performed using a Labram HR Evolution spectrophotometer equipped with a 532 nm excitation light source. The custom Teflon electrolytic cell was assembled with the prepared catalyst as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode (saturated KCl solution) as the reference electrode.

Theoretical Calculation

All the spin polarized calculations were performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package.^{4,5} The nuclei-electron and the electron exchange correlation interactions were described by the projector augmented wave (PAW) potentials with the Perdew-Burke Ernzerh of (PBE) functional, respectively.⁶ The cutoff energy for plane-wave basis functions was set to 450 eV with the energy change convergence criterion of 1×10^{-5} eV. Atomic positions were allowed to relax until the sum of the absolute forces reached down to 0.02 eV Å⁻¹. A vacuum layer of 15 Å is added perpendicular to the sheet to avoid artificial interaction between periodic images. The Monkhorst-Pack mesh of $3 \times 3 \times 1$ was used in K-sampling.

For $Ni_xFe_{1-x}PS_3$, we constructed two models for doping and stacking. The binding energy of the stacking was calculated due to the following equation:

 $\Delta E_{ab} = E_{ab} - E_a - E_b$

Hubbard-U correction method was applied to improve the description of localized Fe and Ni d-electrons in the $Ni_xFe_yPS_3$ with U = 3.10, U = 4.20, respectively.⁷

The d band center was calculated due on the following equation:

Ep(d) = ∫ρEdE/∫ρdE

where ρ is the projected electron density of states (DOS) at the energy level of E. $\!\!^{8}$



Figure S1. Schematic of structures of TMDs and Cu-intercalated TMDs. (a) NPS, (b) FPS, (c) restacked NPS and FPS (mole ratio=1:1), (d) restacked NPS and FPS (mole ratio=2:1), (e) restacked NPS and FPS (mole ratio=3:1), (f) restacked NPS and FPS (mole ratio=4:1, RNFPS), (g) restacked NPS and FPS (mole ratio=5:1). (h) DNFPS.



Figure S2. (a) Tyndall effect seen for NPS NSs in formamide, (b) Transmission electron microscopy (TEM) image of NPS NSs, (c) Atomic force microscope (AFM) of NPS NSs, (d) Tyndall effect seen for FPS NSs in formamide, (e) TEM image of FPS NSs, (f) AFM image of FPS NSs.



Figure S3. (a) and (b) are SEM images of NPS in different scale bars, the ring-shaped graph shows the mole content of each element, (c) the EDS elemental mapping images of (b).



Figure S4. (a) and (b) are SEM images of FPS in different scale bars, the ring-shaped graph shows the mole content of each element, (c) the EDS elemental mapping images of (b).



Figure S5. (a) and (b) are SEM images of DNFPS in different scale bars, the ring-shaped graph shows the mole content of each element, (c) the EDS elemental mapping images of (b).



Figure S6. (a), (b) and (c) are SEM images of RNFPS in different scale bars, the ring-shaped graph shows the mole content of each element, (d) the EDS elemental mapping images of (c).



Figure S7. (a) TEM and (b) STEM of RNFPS, (c) the EDS elemental mapping images of (b).



Fig. S8. Wettability measurements of (a) RNFPS, (b) DNFPS, (c) NPS and (d) FPS.



Figure S9. UV-vis diffuse reflectance absorption spectra of (a) RNFPS, (b) DNFPS, (c) NPS and

(d) FPS. The estimated band gaps of (e) RNFPS, (f) DNFPS, (g) NPS and (h) FPS. (i) The band gap of catalysts.



Figure S10. The XPS wide survey scan spectra of RNFPS, DNFPS, NPS and FPS.



Figure S11. XPS spectra of (a) P 2p and (b) S 2p of RNFPS, DNFPS, NPS and FPS.



Figure S12. Secondary electron cut-off edge, Fermi edge of (a) RNFPS, (b) DNFPS, (c) NPS and (d) FPS and (e) work function acquired by UPS measurements.



Figure S13. XANES for the Ni K-edge of RNFPS, DNFPS and NPS compared to Ni foil as reference sample.



Figure S14. Ni K-edge EXAFS spectra of RNFPS, DNFPS and NPS.



Figure S15. Tafel plots of RNFPS, DNFPS, MNFPS, NiFe-LDH, NPS and FPS.



Figure S16. The double-layer capacitance of (a) RNFPS, (b) DNFPS, (c) MNFPS, (d) NiFe-LDH, (e) NPS, and (f) FPS.



Figure S17. C_{dl} of RNFPS, DNFPS, MNFPS, NiFe-LDH, NPS and FPS.



Figure S18. ECSA normalized LSV curves.



Figure S19. Chronopotentiometry stability tests of DNFPS and NPS at 100 mA cm⁻² in 1 M KOH.



Figure S20. The CV tests of (a) RNFPS, (b) DNFPS, (c) NiFe-LDH, (d) NPS, and (e) FPS. (f) Currents density as a function of multiple parallel CV curves.



Figure S21. (a) EIS of different samples at a positive potential of 1.58 V versus RHE. The ball represents the original data and the dotted line represents the fitted data. (b) The equivalent circuit model. Q: Constant phase element. R: Resistor.



Figure S22. Bode phase plots of the in situ electrochemical impedance spectroscopy on (a) FPS and (b) NiFe-LDH.



Figure S23. Potential-dependent in situ Raman spectra of (a) RNFPS, (b) DNFPS and (c) NPS.



Figure S24. Part of in situ Raman spectra of RNFPS and DNFPS.



Figure S25. The XRD pattern of TRNFPS and TDNFPS.



Figure S26. Raman spectra of TRNFPS and TDNFPS.



Figure S27. XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) P 2p, (d) S 2p and (e) O 1s of TRNFPS and TDNFPS.



Figure S28. (a)XANES for the Ni K-edge and (b) Ni K-edge FT-EXAFS spectra in R space of TRNFPS and TDNFPS.



Figure S29. HAADF-STEM images of (a), (b) TRNFPS and (c), (d) TDNFPS.



Figure S30. HAADF-STEM mapping images of TRNFPS.



Figure S31. HAADF-STEM mapping images of TDNFPS.



Figure S32. The EDS elemental of (a) TRNFPS and (b) TDNFPS.



Figure S33. XRD patterns for MnPS₃, CoPS₃, and ZnPS₃.



Figure S34. Tyndall effects seen for MnPS₃ NSs, CoPS₃ NSs, and ZnPS₃ NSs.



Figure S35. Raman spectra of DNMPS, DNCPS, and DNZPS.



Figure S36. TEM, STEM, and the EDS elemental mapping images of (a) RNMPS, (b) RNCPS, and (c) RNZPS. The scale bars are 500 nm, 1 μ m and 1 μ m for (a), (b) and (c).



Figure S37. LSV curves of RNMPS, RNCPS, RNZPS, DNMPS, DNCPS, and DNZPS. The DNMPS, DNCPS, and DNZPS are short for doped Ni_{0.8}Mn_{0.2}PS₃, doped Ni_{0.8}Co_{0.2}PS₃ and doped Ni_{0.8}Zn_{0.2}PS₃

Table S1. ICP-OES measurements for catalysts.

| Catalysts | Ni wt% (mg L ⁻¹) | Fe wt% (mg L ⁻¹) | Ni:Fe (mole ratio) |
|-----------|------------------------------|------------------------------|--------------------|
| RNFPS | 1.323 | 0.3733 | 3.682 |
| DNFPS | 2.347 | 0.5921 | 4.162 |

Table S2. Zeta potential measurements for catalysts.

| Catalysts | Zeta potential (mV): | Zeta potential (mV): | Zeta potential (mV): | Average zeta potential (mV): |
|-----------|-------------------------|-------------------------|-------------------------|---------------------------------|
| RNFPS | -20.12 | -22.82 | -21.39 | -21.44 |
| DNFPS | 5.87 | 2.27 | -0.82 | 2.44 |
| NPS | 29.31 | 26.19 | 26.14 | 27.21 |
| FPS | -22.37 | -20.70 | -23.79 | 22.29 |

Table S3. Comparison of the OER performance compared to previously reported catalysts inalkaline electrolyte.

| Catalysts | η at j = 20 mA cm ⁻² (mV) | Tafel slope (mV dec ⁻¹) | Electrolyte | Ref. |
|--|---|---|-------------|-----------|
| RNFPS | 257 | 49 | 1.0 M KOH | This work |
| $Ni_{0.8}Fe_{0.2}PS_3$ | 278 | 52 | 1.0 M KOH | 28 |
| MoS ₂ /NiPS ₃ | 330 | 86 | 1.0 M KOH | 45 |
| $V_{Ni,S}$ -NiPS ₃ | 327 | 78 | 1.0 M KOH | 46 |
| NiS ₂ /NiSe ₂ | 290 | 119 | 1.0 M KOH | 47 |
| NiPS ₃ /Ni ₂ P | 260 | 78 | 1.0 M KOH | 48 |
| $Ni_{0.9}Fe_{0.1}PS_3$ | 329 | 69 | 1.0 M KOH | 49 |
| NiPS _{2.7} Se _{0.3} | 277 | 76 | 1.0 M KOH | 50 |
| CoPS₃ | 377 | 94 | 1.0 M KOH | 51 |
| NiCo ₂ S ₄ @NiFe-LDH | 313 | 86 | 1.0 M KOH | 52 |
| Fe(III)/NiS | 287 | 76 | 1.0 M KOH | 53 |

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