Supporting Information for

Exfoliation of ultrathin FePS₃ layers as promising electrocatalyst for

oxygen evolution reaction

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Material's characterizations. JEM-2100F field emission transmission electron microscopy (TEM) with an acceleration voltage of 200 kV was used to collect high-resolution TEM images. Raman spectra were detected by a Renishaw RM3000 Micro-Raman system with a 514.5 nm Ar laser. Atomic force microscopy (AFM, Veeco Multimode V) was performed at room temperature. X-ray diffraction (XRD) was recorded by a Philips X'Pert Pro Super diffractometer equipped with Cu Ka radiation ($\lambda = 1.54178$ Å). X-ray photoelectron spectroscopic (XPS) measurements were carried out in the Photoemission Endstation at the BL10B beamline in the National Synchrotron Radiation Laboratory (NSRL). Fe K-edge XAFS measurements were made at the beamline 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The X-ray was monochromatized by a double-crystal Si (111) monochromator for BSRF. The energy was calibrated using an iron metal foil for the Fe K-edge. The monochromator was detuned to reject higher harmonics. The acquired EXAFS data were processed according to the standard procedures using the WinXAS3.1 program¹. Theoretical amplitudes and phase-shift functions were calculated with the FEFF8.2 code² using the crystal structural parameters of the FePS₃. Nitrogen sorption-desorption isotherms were recorded in the TriStar 3020 V 1.03 (V 1.03) system to confirm the pore diameter distributions and Brunauer-Emmett-Teller (BET) surface area.

Electrochemical measurements. All the catalytic tests were measured in alkaline

solution in 1 M KOH using a typical three-electrode cell setup (CHI 660E). A 5 mm glassy carbon rotating disk electrode covered with different samples as working electrode. Carbon rod was used as the counter electrode and the Ag/AgCl (3M KCl-filled) electrode was used as reference electrode. The catalytic ink was obtained by adding 2 mg catalyst into 250 μ L of isopropyl alcohol, 750 μ L of water and 30 μ L of Nafion (5 wt.%) solution and sonicating for 1 h. After this, 15 μ L of the ink was dropped onto the glassy carbon electrode and dried at room temperature. The linear sweeping voltammetry (LSV) curve was recorded at a scan rate of 5 mV/s and electrode rotation speed at 2000 rpm. The Tafel equation η =b*log(-j) + a was used to linear fit the Tafel slope plots, where b=2.3RT(α F)⁻¹ represents the Tafel slop and j represents the exchange current density. As for the stability testing, the carbon paper is used as the electrode, which is helpful for the post-cycling characterizations.

Theoretical modeling and calculations. We used first-principles Vienna ab initio (VASP) simulations package for energy and band structure calculations using density functional theory $(DFT)^{3-4}$ to check the incite of atomic and electronic structure variation on OER performance. We used structure models from X-ray absorption fine structure spectroscopy (XAFS). A spin polarized plane-wave were used for calculation using first principle density functional theory treated through projector augmented wave (PAW) technique⁵ with Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional⁶. A bulk and few layers systems were used for these calculations from model of XAFS. The distance between two adjacent adatoms is set 12 Å. The vacuum size was set 15 Å between two adjacent layers to avoid the interaction between these layers. The cut-off energy of 500 eV was chosen for electronic structure calculations. The Brillouin zone integrations were used to perform within the Monkhorst Pack (MP) scheme using special k point meshes⁷. The k-points grid of $8 \times 8 \times 1$ were used to optimize the structure and for static electronic structure calculations 15×15×1 k-point mesh were used respectively with a Γ -center scheme. The structures were relaxed by force and energy convergence criterion using conjugated gradient method until the Hellmann-Feynman force and energy on each atom was less than 0.01 eVÅ⁻¹ and 10^{-5} eV, respectively.



Figure S1. a) The SEM image of the as-synthesized bulk FePS₃ sample. b) The Raman spectra of the as-synthesized bulk FePS₃ sample.



Figure S2. X-ray photoelectron spectroscope (XPS) of FePS₃ before ball milling. a) Survey XPS spectrum of FePS₃. b) XPS spectrum of P 2p core level of FePS₃. c) XPS spectrum of S 2p core level of FePS₃.



Figure S3. X-ray photoelectron spectroscope (XPS) of FePS₃ after ball milling. a) Survey XPS spectrum of FePS₃. b) XPS spectrum of P 2p core level of FePS₃. c) XPS spectrum of S 2p core level of FePS₃.



Figure S4. X-ray photoelectron spectroscope (XPS) of O 1s in FePS₃.



Figure S5. XANES spectra for FePS₃ before (black) and after (red) ball milling.



Figure S6. Fitting curves for EXAFS data at the Fe K-edge XANES spectra for FePS₃ before a) and after b) ball milling.

Table S1. Structural parameters of the Fe-S, Fe-Fe and Fe-O shells at the FePS₃ before and after ball milling. (N, coordination number; R, bond distance; σ^2 , Debye-Waller factor; Error bounds (accuracies) were estimated as N, ±5%; R, ±1%; σ^2 , ±5%)

Sample	Bond	Ν	Bond length	σ²(10 ⁻³ Ų)
Before milling	Fe-S	6	2.53	11.0
	Fe-Fe	3	3.44	7.9
After milling	Fe-O	0.9	1.96	4.1
	Fe-S	3.5	2.53	11.3
	Fe-Fe	1.9	3.43	8.3

Table S2. The fitting results of EIS spctra.

	IrO ₂	FePS ₃ after balling	FePS ₃ before balling
$\mathbf{R}_{\mathbf{S}}(\mathbf{\Omega})$	13.5	7.615	8.617
$\mathbf{R}_{\mathbf{C}}(\mathbf{\Omega})$	754.3	2266	14868



Figure S7. The amperometric i-t curve for $FePS_3$ after ball milling in 1 M KOH medium at the potential of 1.7 V.



Figure S8. The comparison of XRD of FePS₃ before and after OER cycling.



Figure S9. The XPS of Fe 2p core level of FePS₃ before ball milling, after ball milling and after OER cycling. It can be observed that the FePS₃ nanosheets upshift to higher energy after ball milling at Fe $2p_{1/2}$ compare to the pristine FePS₃, which can be attributed to the slight oxidation of FePS₃ in the ball milling process. Meanwhile, the XPS spectra of FePS₃ nanosheets also upshift to higher energy after OER cycling due to the forming of FeOOH on the surface.



Figure S10. TEM elemental mapping of FePS₃ after cycling.



Figure S11. (a) The density of state calculation for bulk FePS₃ crystals. (b) The density of state calculation for few layer FePS₃ structure. (c) The electron states of bulk FePS₃ crystals. (d) The electron states of few layer FePS₃ structure.

In contrast to bulk FePS3, the spin-up states of the few layes FePS3 structure around the Fermi level can cross the band gap, and the electrons are excited as the metallic confinement within the band gap. The transformation of bulk FePS₃ to few layers structure in Fig.S8 c and d suggest that the surface distortion can break the double degeneracy of FePS₃ layers. And it can generate the Fe ions with 3d electrons population of the occupied anti-bonding eg orbital as well as with that of t_{2g} orbital of un-occupied sates which can form $t_{2g}{}^3e_{g}{}^2$ electronic configuration. It is noting from Fig.S8 d that the holes are increased in t_{2g} orbital state of Fe_{1-x}, which can enhance the electro-elation of the oxygen absorbed atoms. This will assist the absorption of catalytically active group to form absorbent variety, which may resulting in the improvement of the OER performance for the few layes FePS₃ structure.

Reference:

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