Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Amine-assisted Exfoliation and Electrical Conductivity Modulation toward Few-Layer $FePS_3$ Nanosheets for Efficient Hydrogen Evolution

Zhi Yu[1], Jing Peng[1], Yuhua Liu[1], Wenxiu Liu[1], Haifeng Liu[2], Yuqiao Guo[1]*

[1]Hefei National Laboratory for Physical Sciences at the Microscale, and School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

E-mail: guoyq@ustc.edu.cn

[2]Analytical and Testing Center, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, P. R. China

Table of Contents

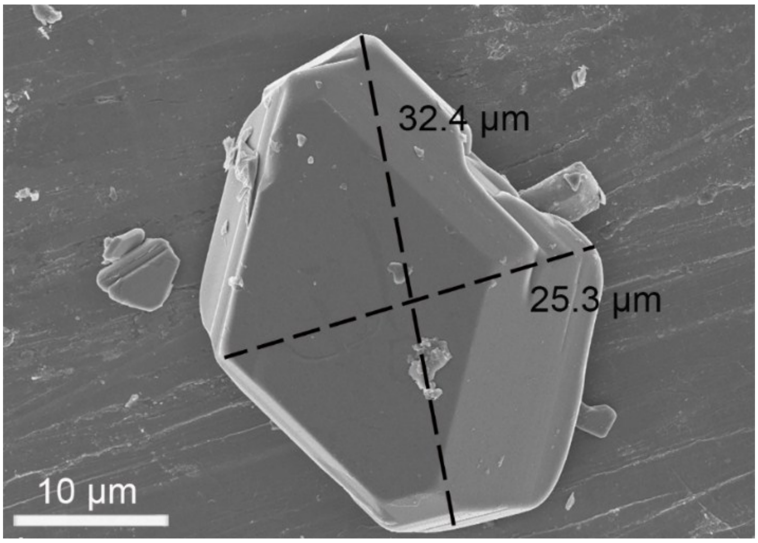

Figure S1. SEM image of the bulk $FePS_3$.

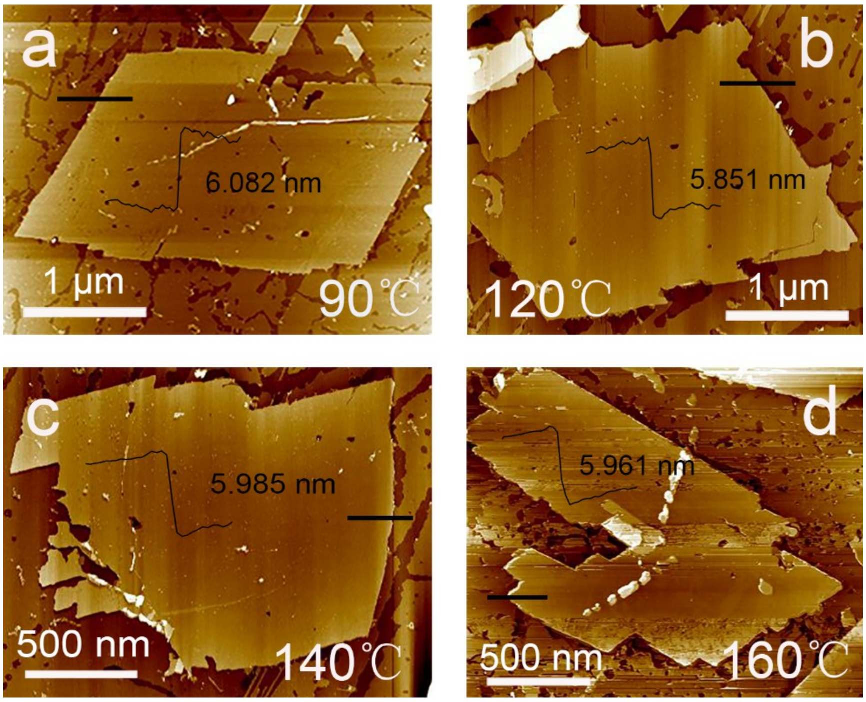

Figure S2. AFM images of nanosheets for (a) $FePS_3$-90, (b) $FePS_3$-120, (c) $FePS_3$-140 and (d) $FePS_3$-160.

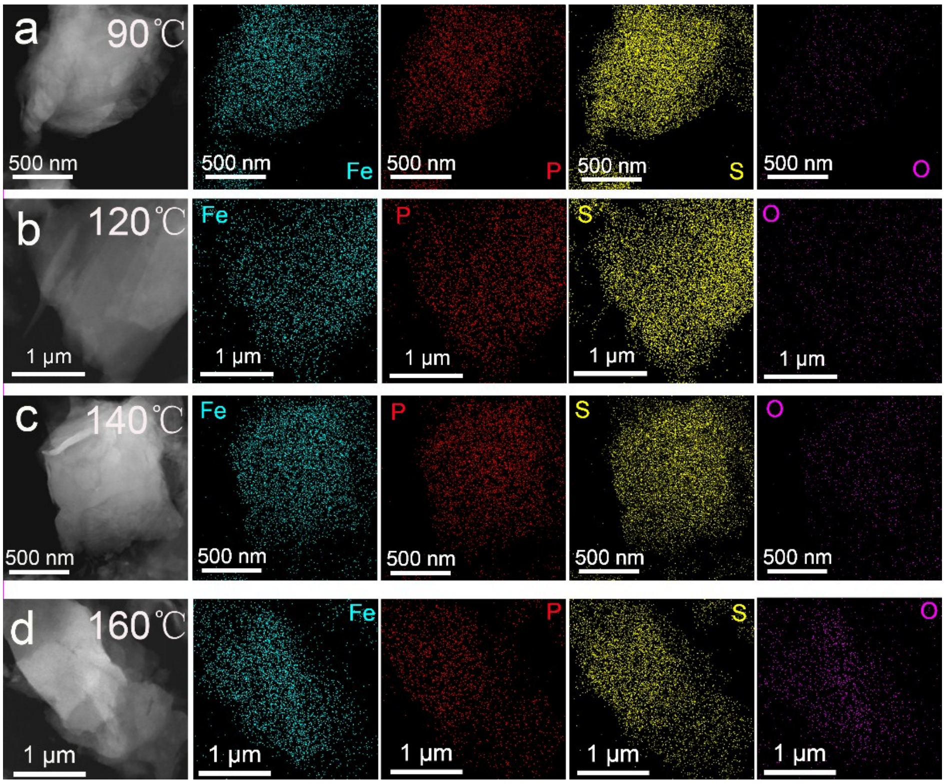

Figure S3. Dark field image and the corresponding EDS mapping of elements images of the $FePS_3$ nanosheets for (a) $FePS_3$-90, (b) $FePS_3$-120, (c) $FePS_3$-140 and (d) $FePS_3$-160.

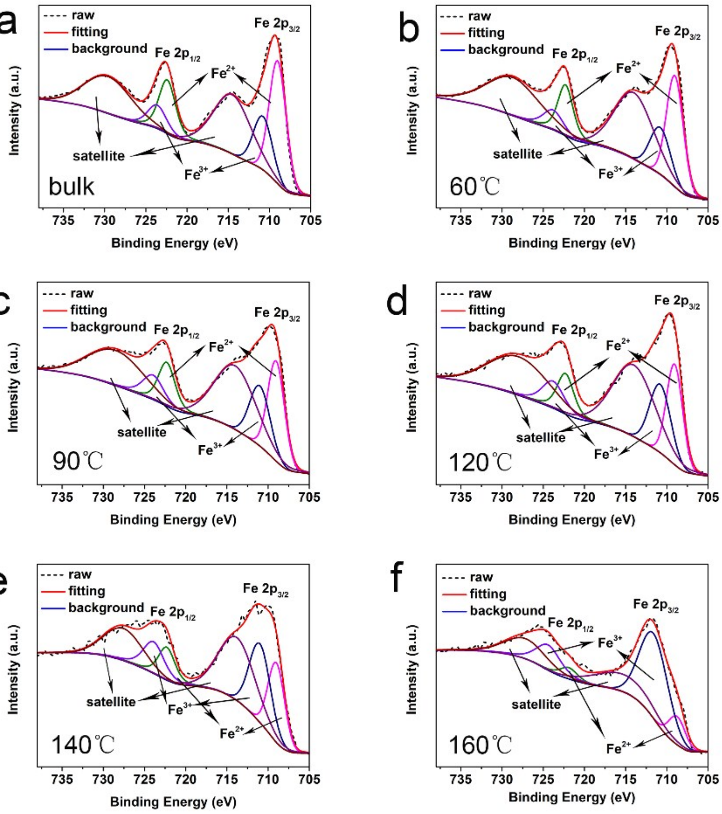

Figure S4. High-resolution XPS spectra of Fe 2p for different samples. (a) bulk, (b) $FePS_3$-60, (c) $FePS_3$-90, (d) $FePS_3$-120, (e) $FePS_3$-140 and (f) $FePS_3$-160.

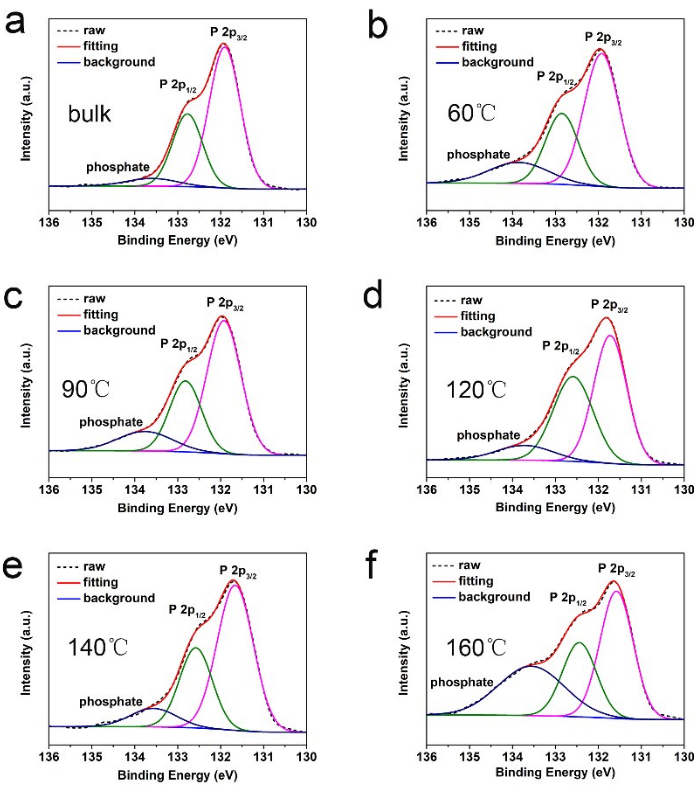

Figure S5. High-resolution XPS spectra of P 2p for different samples. (a) bulk, (b) $FePS_3$-60, (c)

$FePS_3$-90, (d) $FePS_3$-120, (e) $FePS_3$-140 and (f) $FePS_3$-160.

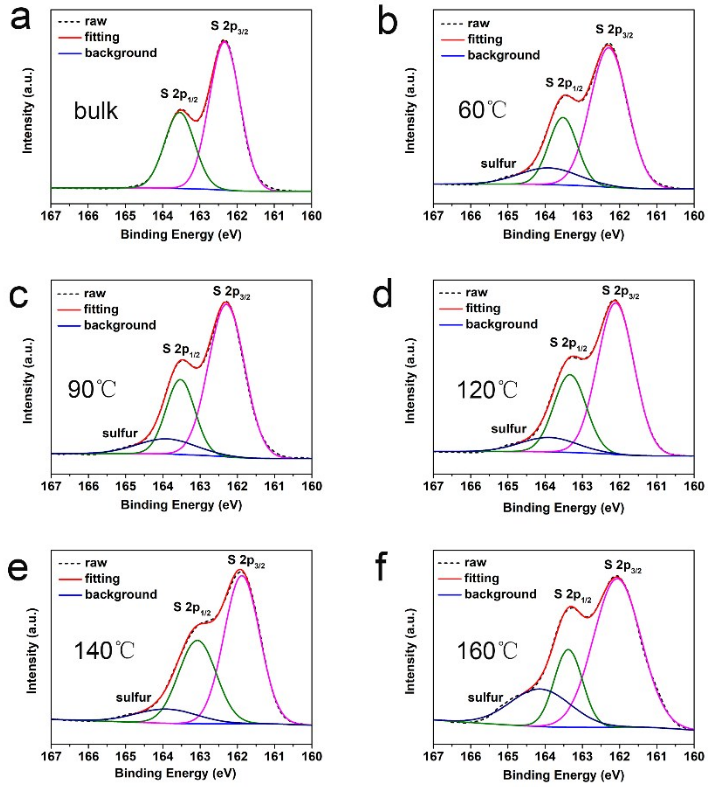

Figure S6. High-resolution XPS spectra of S 2p for different samples. (a) bulk, (b) $FePS_3$-60, (c) $FePS_3$-90, (d) $FePS_3$-120, (e) $FePS_3$-140 and (f) $FePS_3$-160.

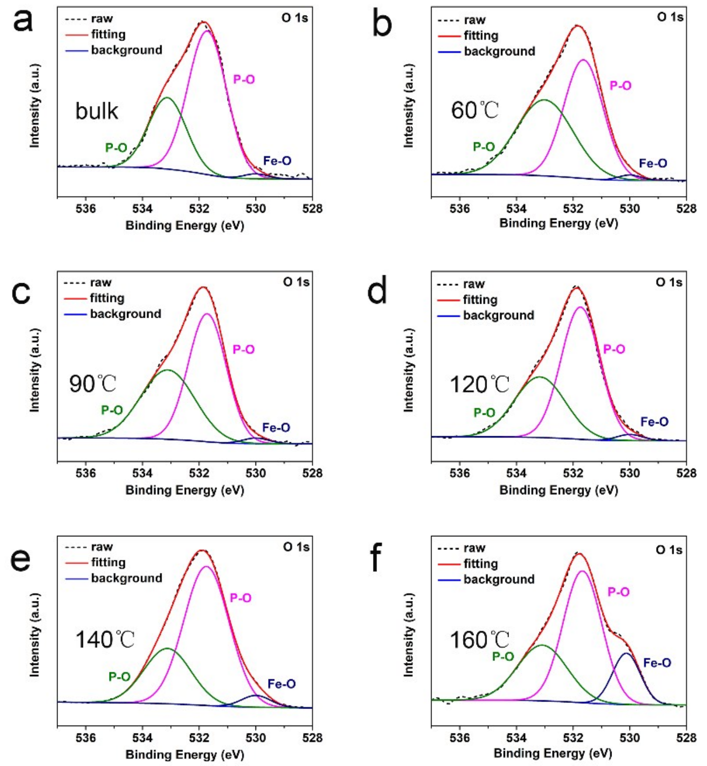

Figure S7. High-resolution XPS spectra of O 1s for different samples. (a) bulk, (b) $FePS_3$-60, (c)

$FePS_3$-90, (d) $FePS_3$-120, (e) $FePS_3$-140 and (f) $FePS_3$-160.

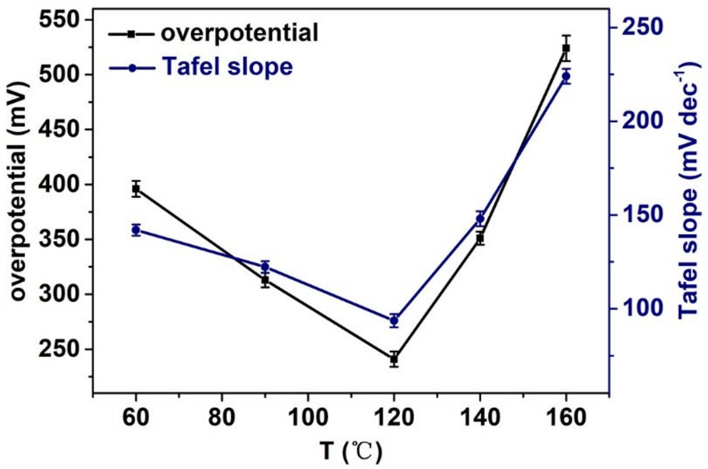

Figure S8. Valley-shaped behavior in temperature dependence of HER catalytic activity.

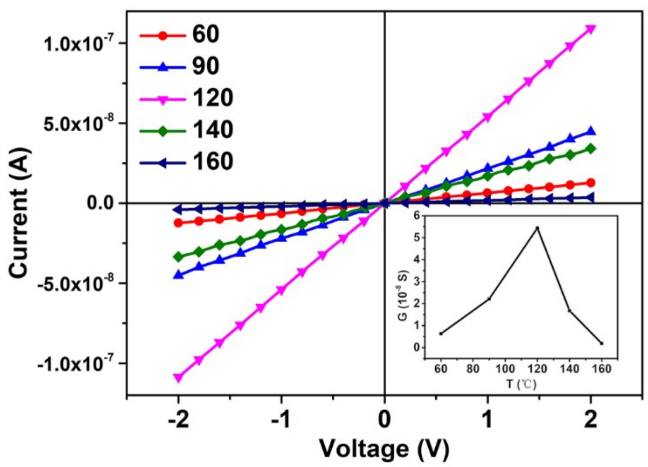

Figure S9. Current-voltage (I-V) characteristic curves for different $FePS_3$ samples in the sweeping voltage from -2 to 2 V and conductance versus temperature plot (inset).

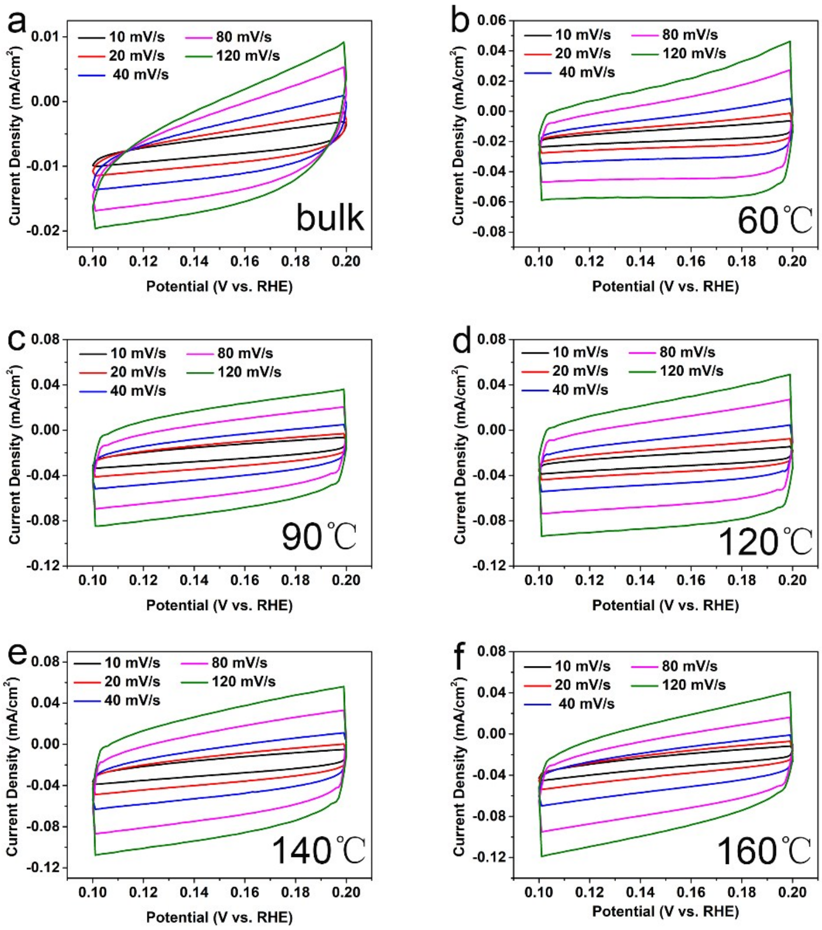

Figure S10. Electrochemical double layer capacitance (C_{dl}) measurements. Cyclic voltammetry (CV) measurements from 0.1 V to 0.2 V (vs. RHE) of (a) bulk and nanosheets for (b) $FePS_3$-60, (c) $FePS_3$-90, (d) $FePS_3$-120, (e) $FePS_3$-140 and (f) $FePS_3$-160.

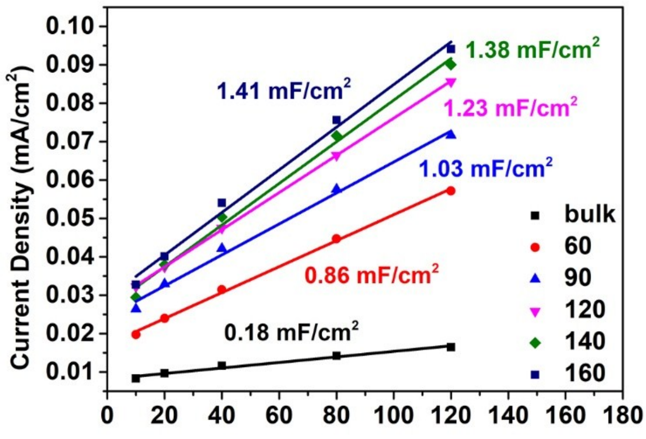

Figure S11. The plots showing the extraction of the C_{dl} for different $FePS_3$ samples.

Table S1. Atomic percentage extracted from EDS analysis

	60 ℃	90 ℃	120 ℃	140 ℃	160℃
Fe %	16.53	18.22	18.02	19.32	20.83
P %	17.16	19.58	19.01	19.72	19.09
S %	51.76	52.78	48.69	49.64	33.21

Table S2. Peak area ratio of Fe^{3+}/Fe^{2+} from Fe 2p XPS spectra

	bulk	60℃	90℃	120℃	140℃	160℃
$S(Fe^{3+})/S(Fe^{2+})$	0.49	0.54	0.73	0.89	1.25	5.09

Table S3. Atomic percentage extracted from XPS analysis

	bulk	60 ℃	90 ℃	120 ℃	140 ℃	160℃
Fe %	13.43	9.10	9.22	9.14	9.19	8.18
P %	14.50	9.74	9.50	9.78	9.93	7.85
S %	41.63	28.03	25.26	23.76	22.52	12.27
O %	5.83	13.65	13.92	14.38	14.85	39.71

Table S4. The average valence of Fe, P and S and calculated chemical component of different samples.

	average valence of Fe	average valence of P	average valence of S	calculated chemical component
bulk	+2.33	+4.08	-2.00	$FeP_{1.08}S_{3.10}O_{0.27}$
$FePS_3$-60	+2.35	+4.15	-1.75	$FeP_{1.07}S_{3.08}O_{0.70}$
$FePS_3$-90	+2.42	+4.16	-1.79	$FeP_{1.03}S_{2.74}O_{0.90}$
$FePS_3$-120	+2.47	+4.12	-1.82	$FeP_{1.07}S_{2.60}O_{1.07}$
$FePS_3$-140	+2.56	+4.15	-1.82	$FeP_{1.08}S_{2.45}O_{1.29}$
$FePS_3$-160	+2.84	+4.32	-1.61	$FeP_{0.96}S_{1.50}O_{2.29}$

Table S5. The charge transfer resistance (R_{ct}) from EIS.

	bulk	60℃	90℃	120℃	140℃	160℃
R_{ct} (Ω)	1185	266	212	113	222	432

Table S6. Comparison on HER catalytic performance of recently reported $FePS_3$.

Sample	η (mV)	Tafel Slope (mV/dec)	Electrolyte	Synthetic Methods	Reference
$FePS_3$-120 nanosheets	**241±7**	**93.7±3.5**	**0.5M H_2SO_4**	**Amine-assisted exfoliation**	**This work**
sonicated $FePS_3$ crystal	>950	~200	0.5M H_2SO_4	Liquid sonication in deionized water	*ACS applied materials & interfaces*, 2017, **9**, 12563-12573.
$FePS_3$ nanosheets	>350	109	1M KOH	Liquid sonication in DMF	*ACS Catalysis*, 2017, **7**, 8549-8557.
$FePS_3$@rGO	108	54	0.5M H_2SO_4	Liquid sonication and hydrothermal method	*ACS Energy Letters*, 2016, **1**, 367-372.