

Supporting Information

Surface Phosphorization for Enhanced Photoelectrochemical Performance of Fe₂O₃/Si Photocathode

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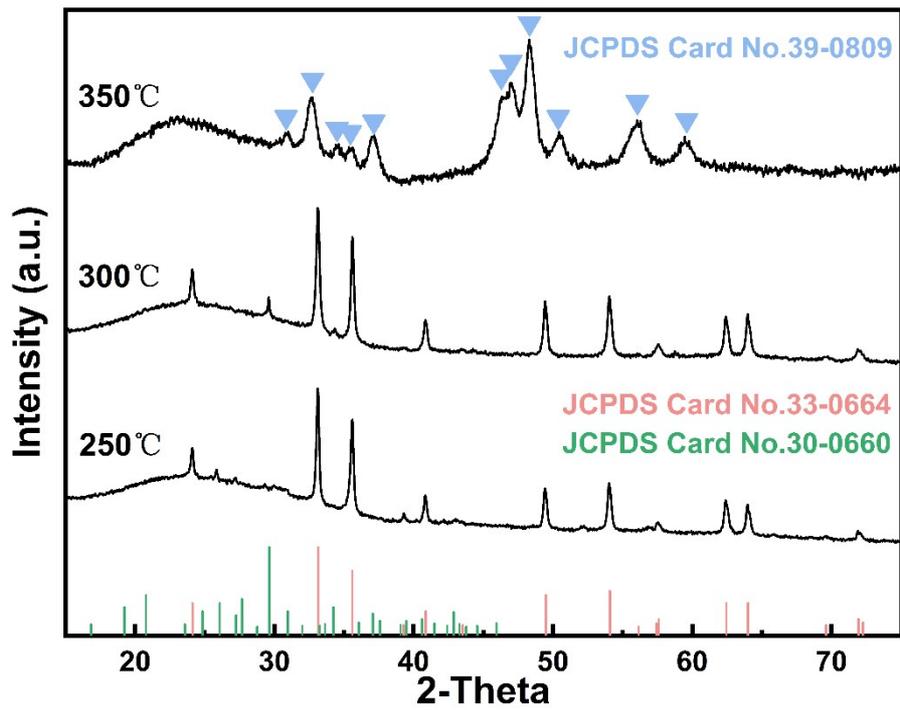


Figure S1. XRD pattern of FePi/Fe₂O₃/p-Si-250 and FePi/Fe₂O₃/p-Si-350

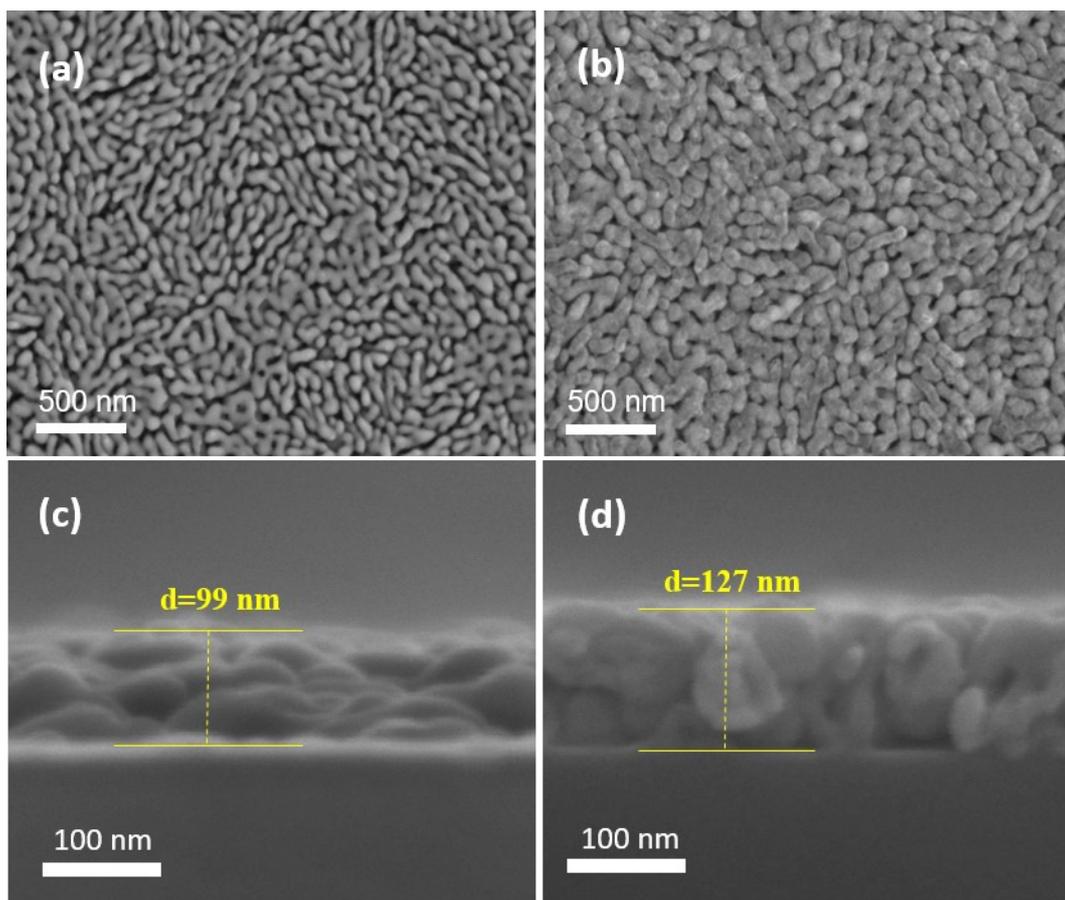


Figure S2. SEM images of (a) FePi/Fe₂O₃/p-Si-250, (b) FePi/Fe₂O₃/p-Si-350 and (c-d) corresponding cross-section images.

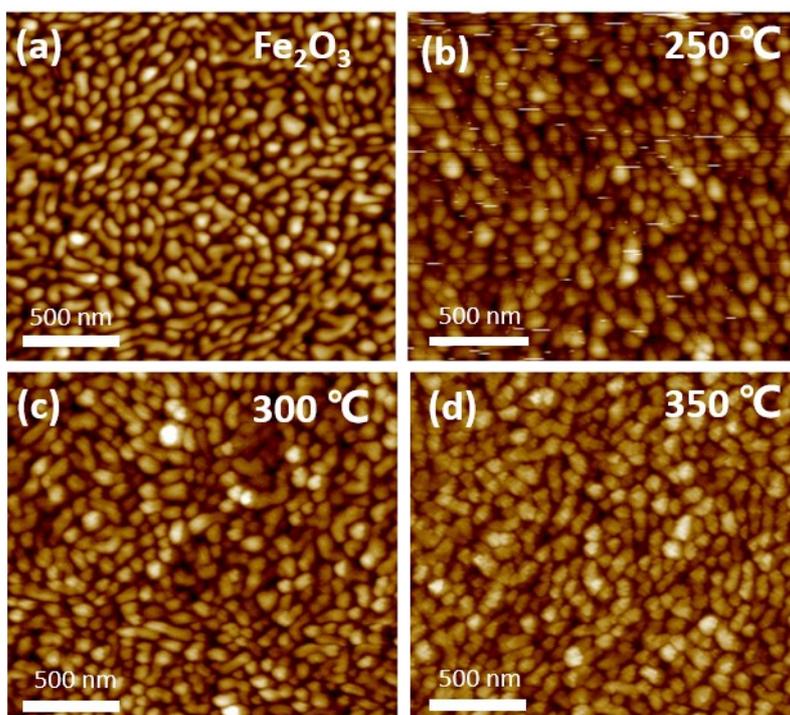


Figure S3. AFM images of (a) $\text{Fe}_2\text{O}_3/\text{p-Si}$, (b) $\text{FePi}/\text{Fe}_2\text{O}_3/\text{p-Si-250}$, (c) $\text{FePi}/\text{Fe}_2\text{O}_3/\text{p-Si}$ and (d) $\text{FePi}/\text{Fe}_2\text{O}_3/\text{p-Si-350}$.

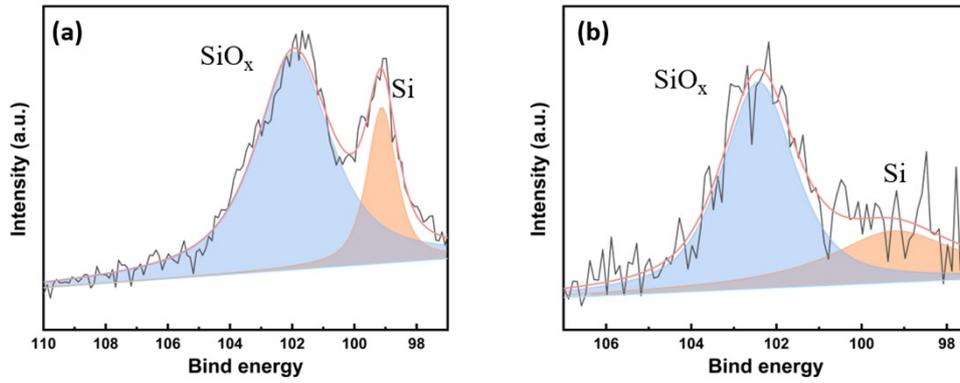


Figure S4. Si 2p spectra obtained from the surface (a) of $\text{Fe}_2\text{O}_3/\text{p-Si}$ and (b) $\text{FePi}/\text{Fe}_2\text{O}_3/\text{p-Si}$.

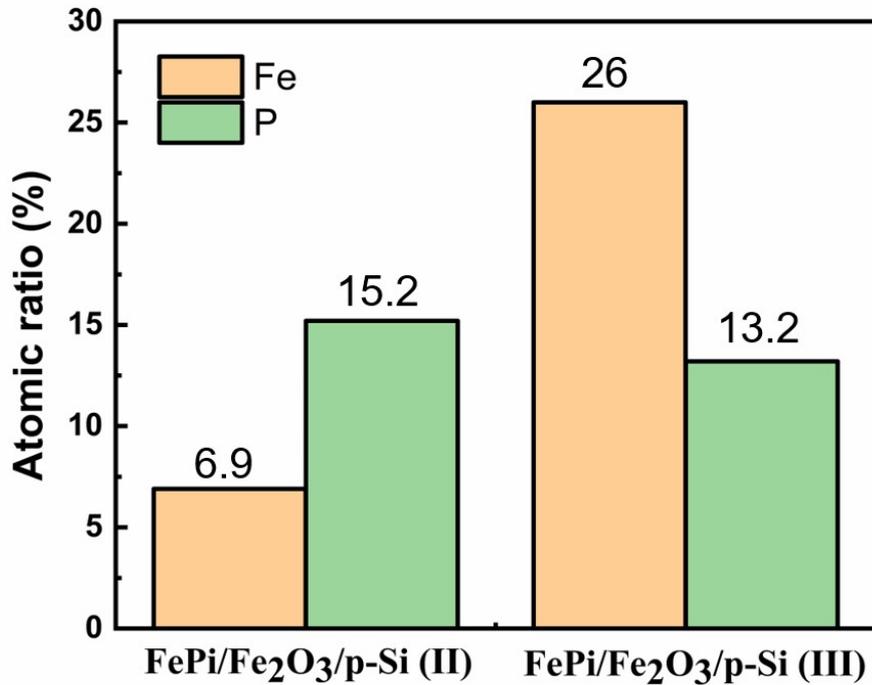


Figure S5. The atomic ratio of Fe and P obtained from XPS surface (II) and depth profiling measurement (III) of $\text{FePi}/\text{Fe}_2\text{O}_3/\text{p-Si}$

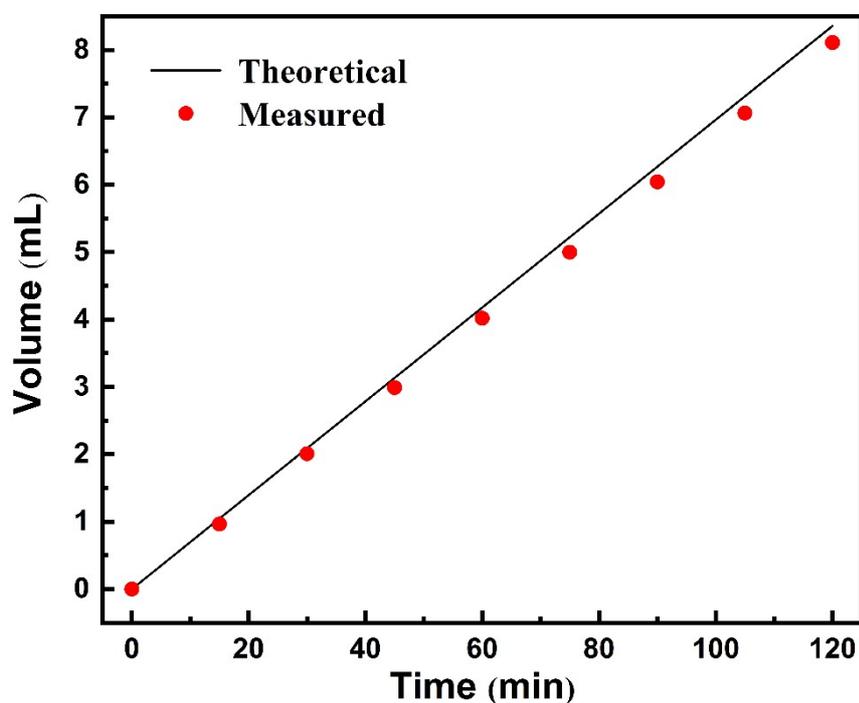


Figure S6. Faradic efficiency of FePi/Fe₂O₃/p-Si measured by the volume of H₂ produced at constant current density of -10 mA cm⁻² in 2 hours.

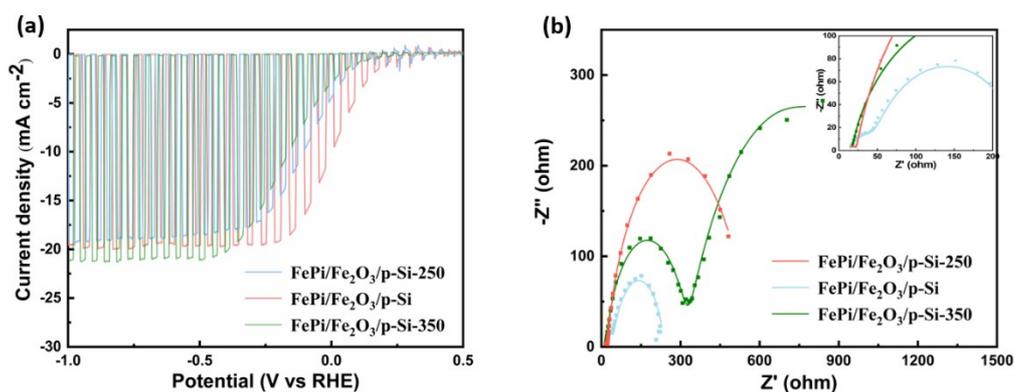


Figure S7. (a) Chopped LSVs of FePi/Fe₂O₃/p-Si-250, FePi/Fe₂O₃/p-Si and FePi/Fe₂O₃/p-Si-350 in 1M KOH under illumination; (b) Nyquist plots of FePi/Fe₂O₃/p-Si-250, FePi/Fe₂O₃/p-Si and FePi/Fe₂O₃/p-Si-350 at 200 mV_{RHE} in 1M KOH, the inset is the enlarged view of curves at high frequency;

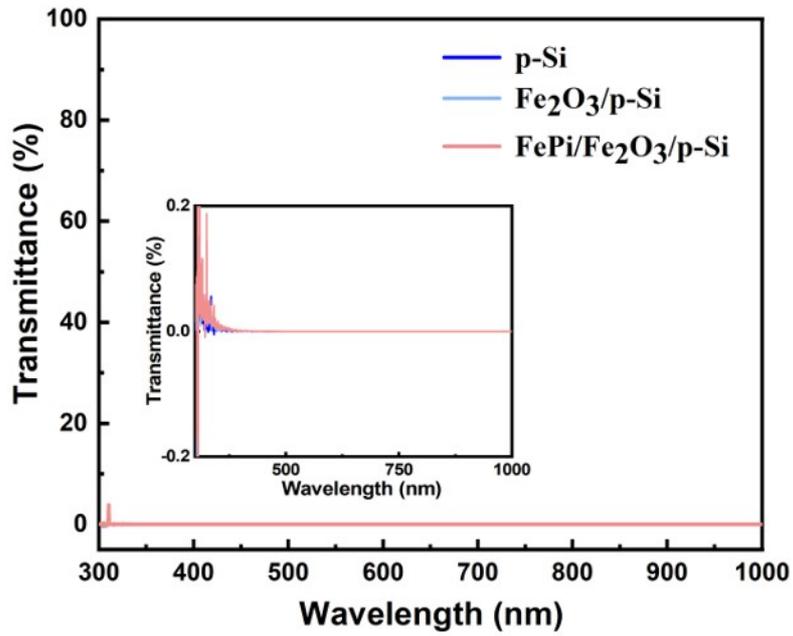


Figure S8. Transmittance of p-Si, Fe₂O₃/p-Si and FePi/Fe₂O₃/p-Si in the range from 300 to 1000 nm

Table S1. A survey on the PEC performance based on recent reports of Si-based photocathode

Photocathode	Substrate	Electrolyte	Onset potential (mV _{RHE})	j_0 (at 0 V _{RHE}) (mA cm ⁻²)	Saturated current density (mA cm ⁻²)	Ref.
FePi/Fe ₂ O ₃ /p-Si	Planar Si	1 M KOH	390	-11.9	-20	This work
Fe ₂ O ₃ /p-Si	Planar Si	1 M KOH	189	-1.3	-26.5	This work
Fe ₂ O ₃ /p-Si	Planar Si	1M NaOH	250	-0.75	-34	1
SiMP/Fe ₂ O ₃	p-type Si micropillar	0.5M NaSO ₄	200	-0.02	-0.65	2
Ni/p-Si	Planar Si	0.5 M H ₂ SO ₄	110	5.57	-30	3
Si/TiO ₂ /Co	Planar Si	0.5 M Na ₂ SO ₄	320	-0.7	-	4
Si/C _N /TiO ₂ /NiCo P	Etched Si	1 M KOH	420	-19.87	-22.5	5
Si _{PN} /CN/MoS _x	Micro-pyramid Si	0.5 M H ₂ SO ₄	230	-10	-	6
MoO _x /p-Si	Planar Si	0.5 M H ₂ SO ₄	-	0	-30	7
Si-NiS	Si NW array	1 M KOH	200	-12	-25	8

Table S2. The resistance values and CPE obtained from the deconvolution of the EIS Spectra

	Rs/Ohm	CPE1*E-6/F s^(a-1)	Rct1/Ohm	CPE2*E-6/F s^(a-1)	Rct2/Ohm
p-Si	16.88	2.85 (n=0.96)	6853	-	-
Fe ₂ O ₃ /p-Si	12.38	9.28 (n=0.78)	3459	-	-
FePi/ Fe ₂ O ₃ /p-Si- 250	11.92	0.12 (n=0.85)	528.2	13.19 (n=0.71)	10.96
FePi/ Fe ₂ O ₃ /p-Si	13.42	67.58 (n=0.67)	188.3	31.38 (n=0.84)	35.57
FePi/ Fe ₂ O ₃ /p-Si- 350	16.51	6.34 (n=0.83)	306.4	1499 (n=0.72)	833.9

Table S3. The calculated Gibbs free energy of the adsorption energies of H* on several different sites of the (001) surface for Fe₂O₃-FePi hereto-structure surfaces.

H location sites	H-Fe	H-O1	H-O2	H-P
$\Delta G_{H^*}/\text{eV}$	0.126	0.457	1.510	0.458

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