

Hollow Fe₄C/FeP Nanoboxes with Heterostructure and Carbon Armor for Efficient and Stable Hydrogen Evolution

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n EXPERIMENT

Materials. Potassium ferricyanide ($K_3[Fe(CN)_6]$, $\geq 99\%$), sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, $\geq 99\%$), polyvinylpyrrolidone (PVP, K30, MW $\approx 40\ 000$) and hydrochloric acid (HCl, 36.0%-38.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemical materials were used without further purification. Deionized water ($18.6\ M\Omega\ cm$, DI water) can be used directly for synthesis.

Physical Characterization. The morphologies of all samples were characterized through using a SEM (FEI Quanta FEG 450 system, 20 kV) with an energy dispersive X-ray analyzer. TEM was performed on an electron microscope (Hitachi HT7700). Crystal structures were analyzed by XRD (Bruker D8) with a scanning rate of $5^\circ \cdot min^{-1}$ ranging from 5° to 90° . The valence states of the elements were authenticated by XPS (ESCALAB 250Xi) carried out on a spectrometer with an Al $K\alpha$ X-ray source.

Electrochemical Measurements. All electrochemical measurements were carried out on an electrochemical workstation (Gamry Reference 3000) with an essential three-electrode construction. The as-obtained catalysts, a carbon rod, and a saturated calomel electrode were used as the working, counter, and reference electrode, respectively. The working electrode was prepared by coating the mixed slurry of the as-obtained catalyst powder, including 5 mg sample and 20 μL Nafion solution (5 wt %) in 1 mL water-ethanol solution with volume ratio of 1:1.

The electrolyte is 0.5 M H_2SO_4 , in which the concentration of H^+ is 1 M. Thus, according to the Nernst equation:

$$E = E^\theta + \frac{2.303RT}{nF} \ln \frac{1}{c(H^+)}$$

the potential vs. RHE can be obtained by the following equation:

$$E(RHE) = E(SCE) + 0.0592pH + 0.245.$$

R: ideal gas constant, $8.314\ J \cdot K^{-1} \cdot mol^{-1}$;

T: absolute temperature;

n: number of transferred electrons;

F: Faraday's constant, $96485\ C/mol$.

The polarization curves were performed in acidic solution with a scan rate of $5\ mV\ s^{-1}$. The double-layer capacitances (C_{dl}) were tested by cyclic voltammetry (CV) which scans with different sweep rates ranging from 40 to $120\ mV\ s^{-1}$.

Electrochemical impedance spectroscopy (EIS) measurements were measured by a frequency which ranges from 0.1 to 105 Hz with an amplitude of 5 mV at a potential of -0.35 V (vs SCE).

The long-time stability was tested by continuous CV for 1000 or 5000 cycles at a sweep rate of $100\ mV\ s^{-1}$ ranging from -0.35 to -0.45 V (vs SCE).

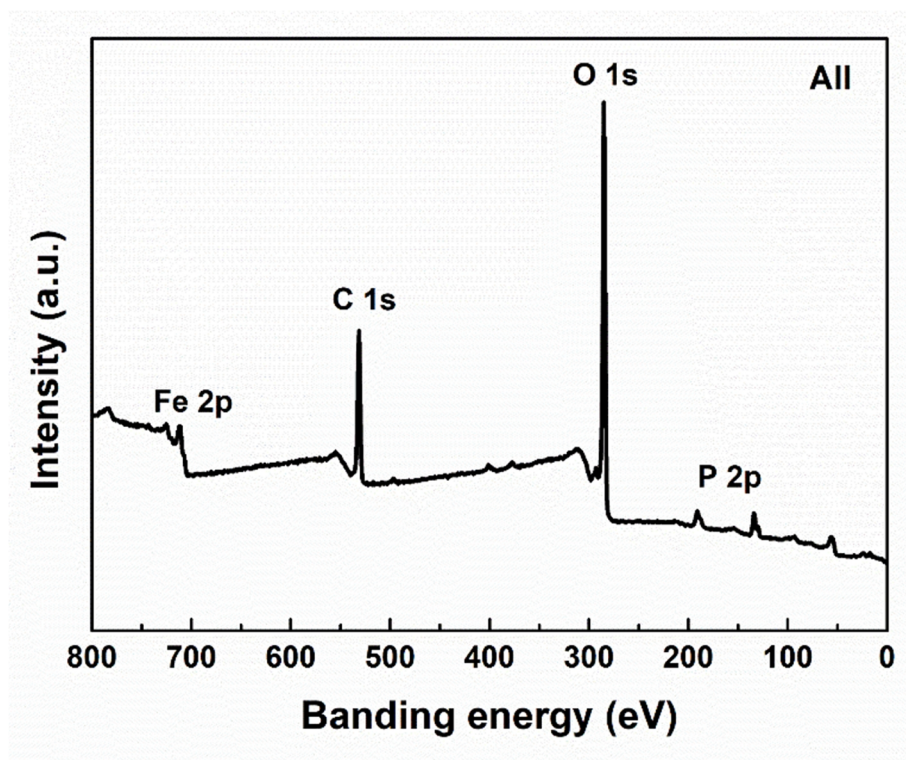


Figure S1. XPS spectra of survey in Fe₄C/FeP.

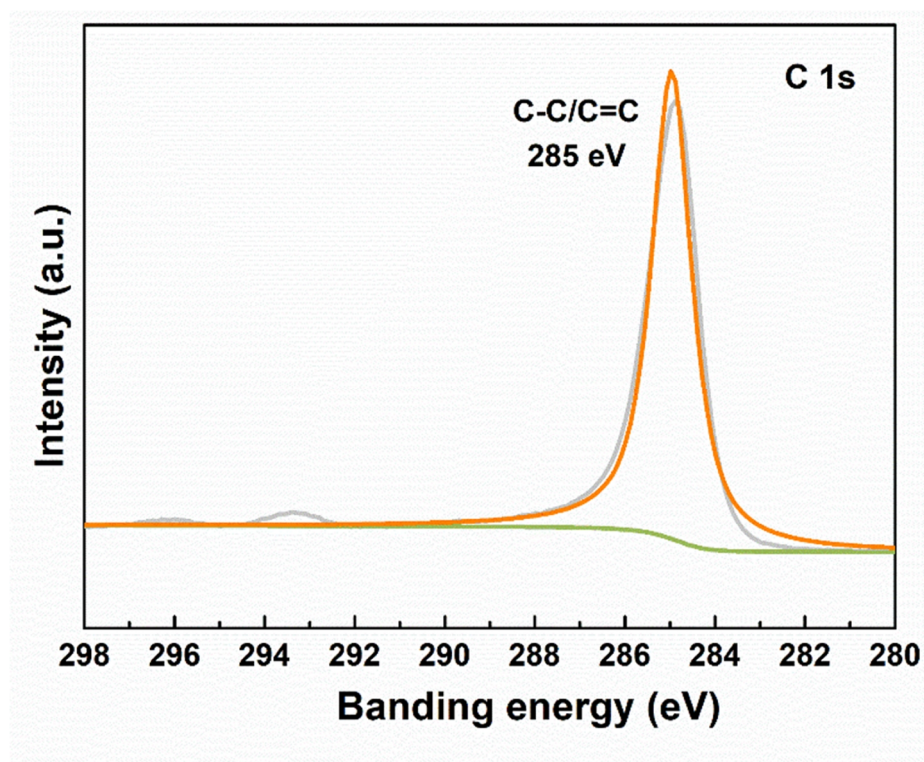


Figure S2. XPS spectra of C 1s of Fe₄C/FeP.

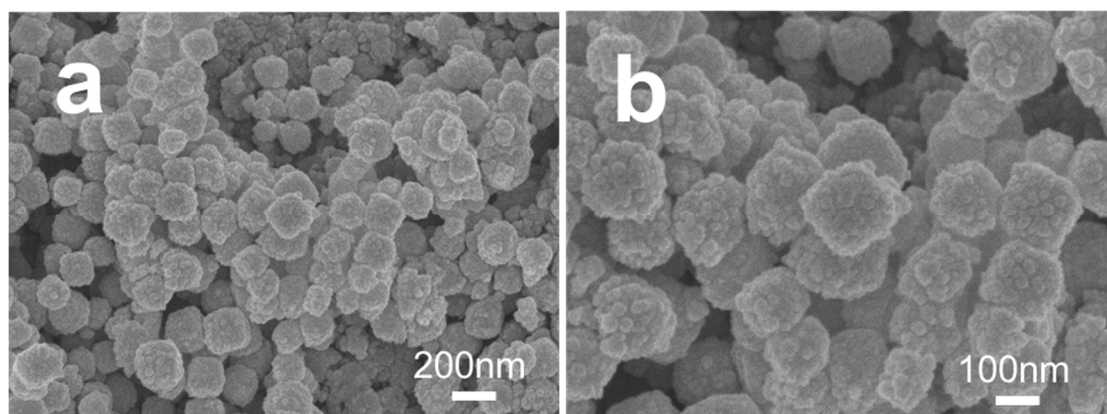


Figure S3. SEM images of FeP.

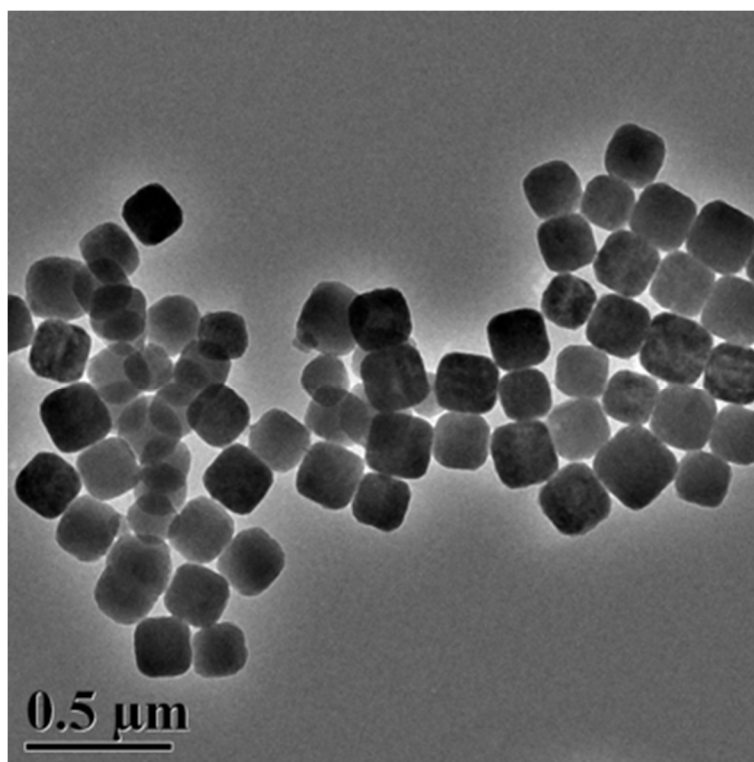


Figure S4. TEM images of PB.

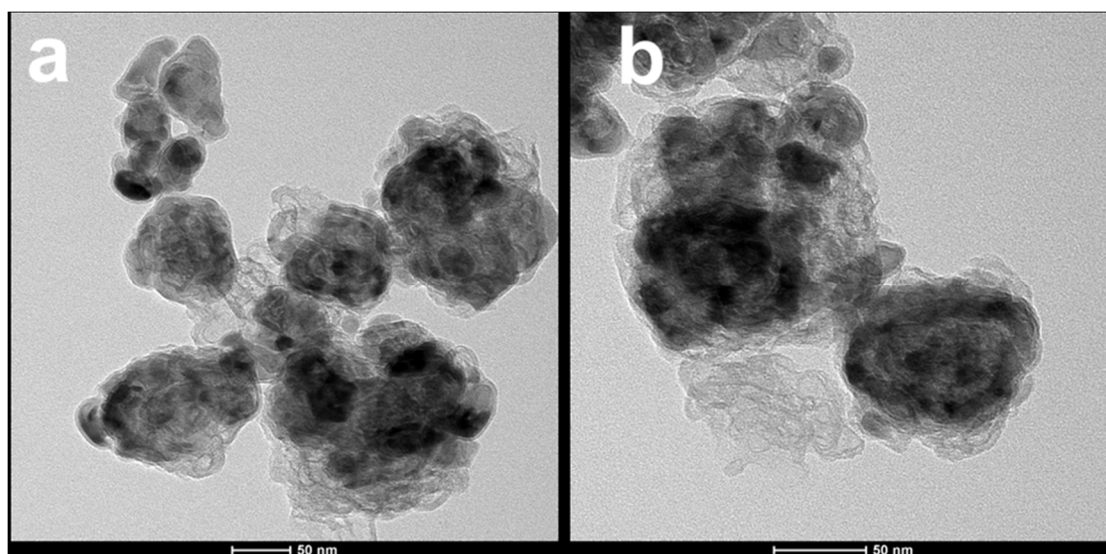


Figure S5. TEM images of Fe_3C .

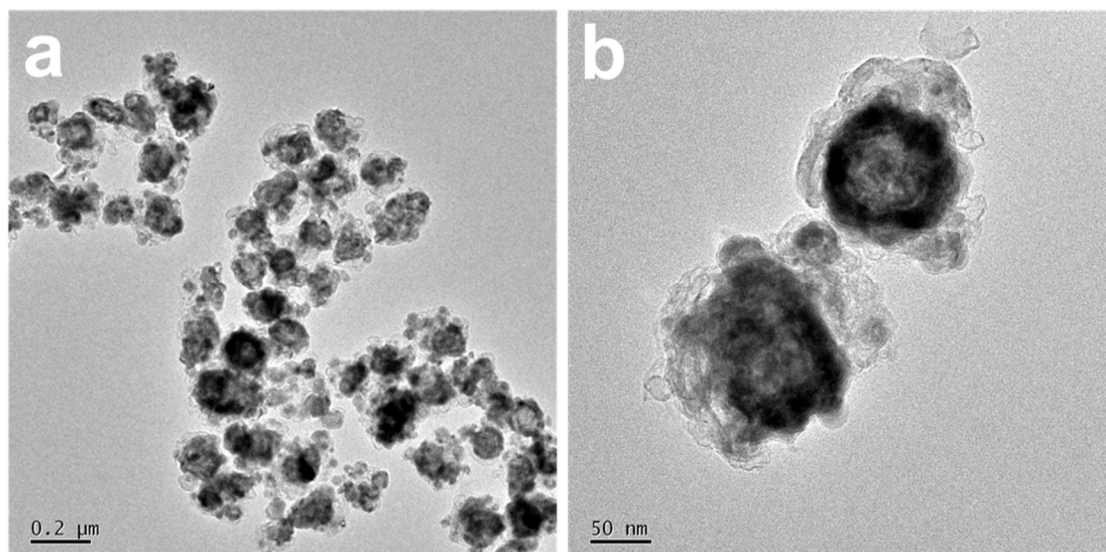


Figure S6. TEM image of FeP.

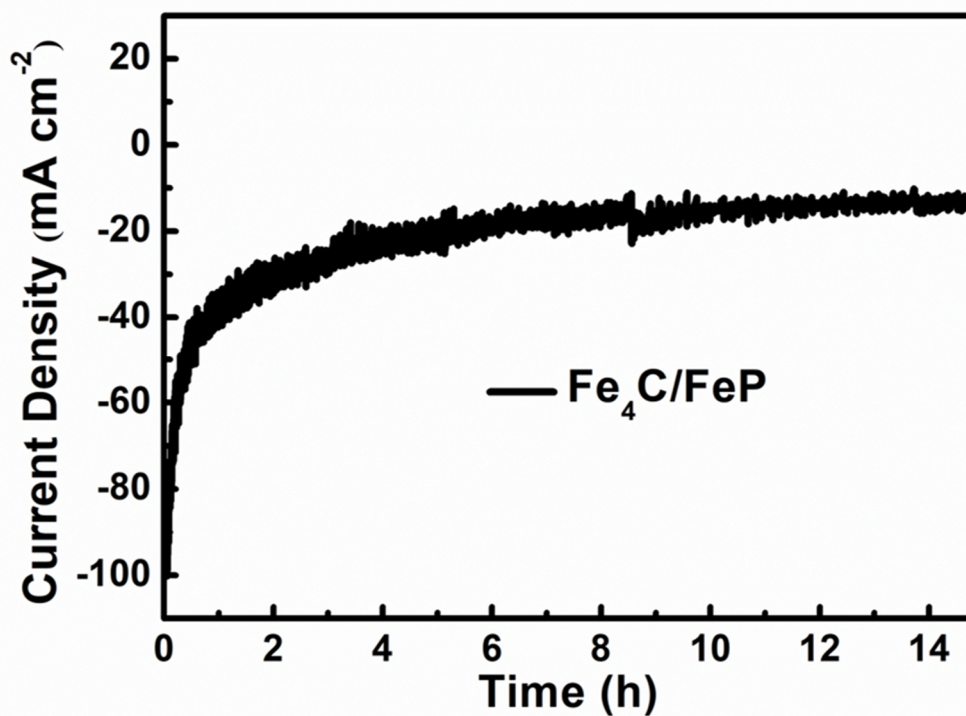


Figure S7. Chronoamperometry curve of Fe₄C/FeP for 15 h in 0.5 M H₂SO₄.

Table S1. Comparison of the HER Performance of Fe₄C/FeP with Other Recently Reported HER Electrocatalysts in Acidic Media

Electrocatalyst	j (mA cm ⁻²)	η (mV)	Electrolyte solution	Ref.
Fe ₄ C/FeP	10	180	0.5 M H ₂ SO ₄	This work
FeP nanosheets	10	250	0.5 M H ₂ SO ₄	[1]
Fe ₂ P/Fe	10	191	0.5 M H ₂ SO ₄	[2]
Fe _x P@NPC	10	227	0.5 M H ₂ SO ₄	[3]
MOF-derived Ni ₂ P	10	200	0.5 M H ₂ SO ₄	[4]
MoP@NPC/rGO/GCE	10	218	0.5 M H ₂ SO ₄	[5]
MoS ₂ /MoO ₃ /FTO	10	310	0.5 M H ₂ SO ₄	[6]
Metallic MoS ₂ nanosheets	10	195	0.5 M H ₂ SO ₄	[7]

n REFERENCES

- (1) Xu, Y.; Wu, R.; Zhang, J.; Shi, Y.; Zhang, B. Anion-exchange synthesis of nanoporous FeP nanosheets as electrocatalysts for hydrogen evolution reaction. *Chem. Commun.* **2013**, 49, 6656-6658.
- (2) Read, C. G.; Callejas, J. F.; Holder, C. F.; Schaak, R. E. General strategy for the synthesis of transition metal phosphide films for electrocatalytic hydrogen and oxygen evolution. *ACS Appl. Mater. Interfaces* **2016**, 8, 12798-12803.
- (3) Cheng, Y. H.; Guo, J. N.; Huang, Y.; Liao, Z. J.; Xiang, Z. H. Ultrastable hydrogen evolution electrocatalyst derived from phosphide postmodified metal-organic frameworks. *Nano Energy* **2017**, 35, 115-120.
- (4) Tian, T.; Ai, L. H.; Jiang, J. Metal-organic framework-derived nickel phosphides as efficient electrocatalysts toward sustainable hydrogen generation from water splitting. *RSC Adv.* **2015**, 5, 10290-10295.
- (5) Li, J. S.; Sha, J. Q.; Du, B.; Tang, B. Highly efficient hydrogen evolution electrocatalysts based on coupled molybdenum phosphide and reduced graphene oxide derived from MOFs. *Chem. Commun.* **2017**, 53, 12576-12579.
- (6) Chen, Z.; Cummins, D.; Reinecke, B. N.; Clark, E.; Sunkara, M. K.; Jaramillo, T. F. Core-shell MoO₃-MoS₂ nanowires for hydrogen evolution: a functional design for electrocatalytic materials. *Nano Lett.* **2011**, 11, 4168-4175.
- (7) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS₂ nanosheets. *J. Am. Chem. Soc.* **2013**, 135, 10274-10277.

