Supporting Information

Novel Fe_2P/graphitized carbon Yolk/shell Octahedrons for High-efficiency Hydrogen Production and Lithium Storage

Jiao Yang[#], Ya Ouyang[#], Huijuan Zhang, Haitao Xu, Yan Zhang, Yu Wang*

The State Key Laboratory of Mechanical Transmissions and the School of Chemistry and Chemical Engineering, Chongqing University, 174 Shazheng Street, Shapingba District, Chongqing City 400044, PR China

[#]these authors contributed equally to this work.

*E-mail: wangy@cqu.edu.cn; prospectwy@gmail.com

METHODS

Fabrication of Fe_2P/GC yolk/shell octahedrons composite

First, 12 mL deionized water, 12 mL glycol, 1 mL $Fe(NO_3)_3$ solution (1 M), 5 mL NaH_2PO_4 solution (1 M) and 4 mL Na_2CO_3 solution (1 M) were mixed orderly with continued stirring. Then, the precursor solution became faint yellow. After the magnetically stir for 30 min, 5 mL glucose aqueous solution (1 M) was added. Then, the mixed solution was poured into the Teflon-lined stainless-steel autoclaves (45 mL), and put into an oven for hydrothermal reaction under 180 ^oC for 20 h. The resultant sedimentation which changed into black color was collected, washed, and dried. Finally, the precursor Fe_2PO_5/polymeric layer octahedrons were then transferred into graphite boat and calcined in tube furnace at 800 ^oC under H_2 atmosphere for 200 min. (The pure Fe_2P was prepared through the above methods except the addition of glucose.)

Characterization

An X-ray diffractometer with Co Kα (λ=1.78897 Å) radiation (XRD, Bruker D8 Advance), a field-emission scanning electron microscope (JEOL, JSM-7800F, 15 kV), a transmission electron microscope (Philips, Tecnai, F30, 300 kV) coupled with an energy-dispersive spectrometer (EDS) analyzer, a BET surface-area and pore-size analyzer (Quantachrome Autosorb-6B), and a RENISHAW Invia Raman microscope (voltage (ac) 100−240 V, Power 150 W, UK) were introduced.

Electrochemical Measurements

As for HER, electrochemical measurement was fulfilled on a CHI660E

electrochemistry work-station, which was studied in a three-electrode device including a working electrode of clean glassy carbon electrode (GCE) (0.07 cm^2), a reference electrode of saturated calomel electrode (SCE), and a counter electrode of Pt foil. The catalyst suspension was prepared by following steps, 4 mg of the obtained Fe_2P/GC yolk/shell octahedrons composite as catalyst, 100 μL of Nafion solution (0.5 wt %) and 300 μL of ethanol were mixed by ultrasonication. Then, 4 μL of the suspension was dropped on the GCE (mass loading 0.48 mg cm^{-2}) and dried at room temperature as working electrode. Linear sweep voltammetry (LSV) was carried out between -0.2 to -0.6 V at a scanning rate of 50 mV s^{-1} in 0.5 M H_2SO_4 solution. The durability analysis was taken by cyclic voltammetry (CV) scanning from -0.2 to -0.6 V at 50 mV s^{-1} for 2000 cycles. The stability estimation was taken by amperometric i-t curve for 12 h at an electrostatic overpotential of 89 mV, i.e., the static voltage was 0.37 V (0.089+0.281=0.370 V). According to the equation E(RHE) = E(SCE) + 0.281 V, all the potentials were involved in reversible hydrogen electrode (RHE) in 0.5 M H_2SO_4 solution.

As for LIBs test, a mixture consisted of 80 wt % of composite, 10 wt % of carbon black, and 10 wt % of polyvinyl difluoride (PVDF) using 1- methyl-2-pyrrolidinone (NMP) as solvent was stirred overnight, and then spreaded on Cu foils. The Cu foils were then used as working electrode (mass loading 2.1 mg cm^{-2}). $LiPF_6$ (1 M) in ethylene carbonate/diethyl carbonate (1/1 in volume) was used as electrolyte. Pure Li foil was used as counter electrode and reference electrode. The cell was assembled in an argon-filled glovebox. A LAND battery program−control test system was applied to record discharge-charge curves, and a CHI660D electrochemistry workstation was utilized to record CV curves ranged of 0.01-3 V and EIS over a frequency from 0.01 Hz to 100 kHz.

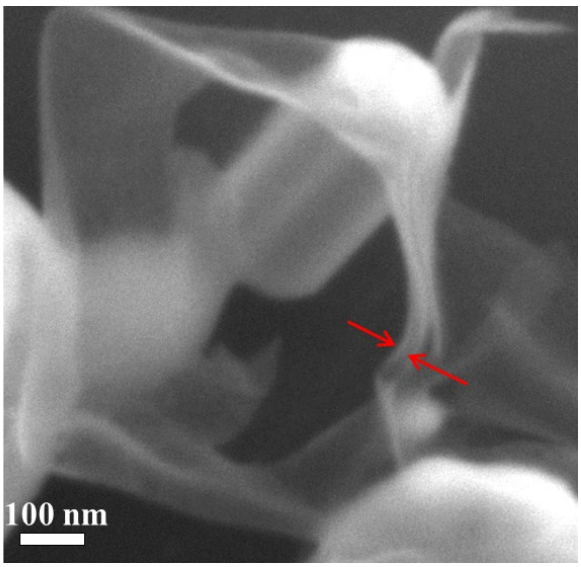

Figure S1. SEM image of broken Fe_2P/GC yolk/shell octahedrons composite.

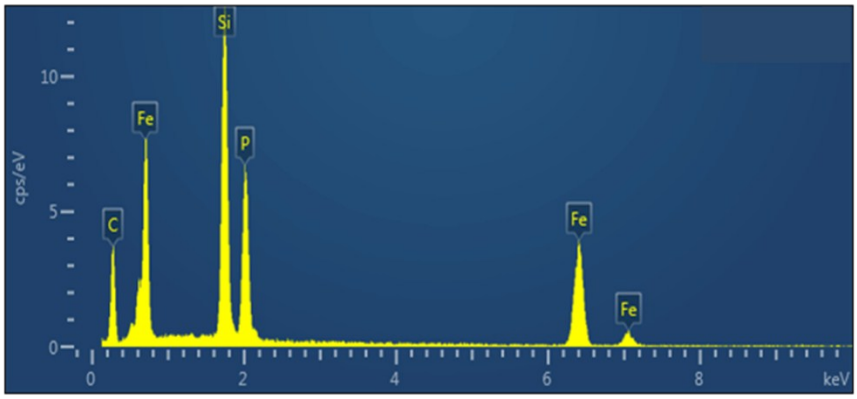

Figure S2. Energy-dispersive spectrum (EDS) of Fe_2P/GC yolk/shell octahedrons composite.

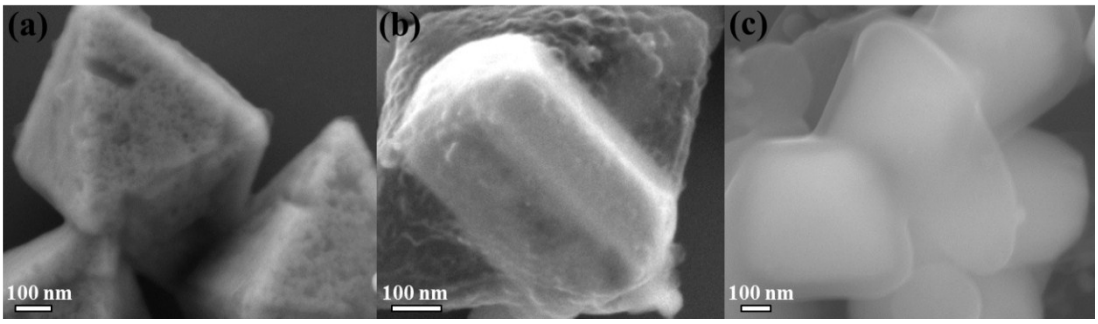

Figure S3. SEM images of Fe_2P/GC calcined at 750 °C (a), 800 °C (b) and 850 °C (c).

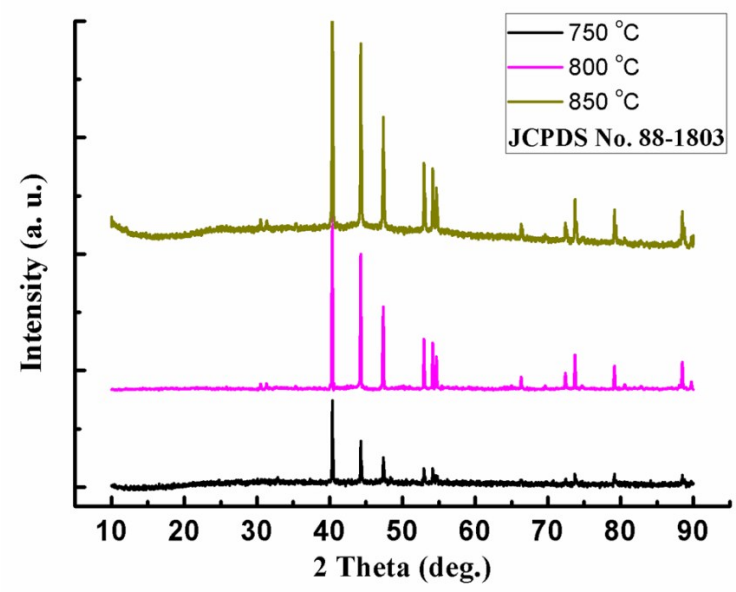

Figure S4. XRD pattern of Fe_2P/GC calcined at 750 °C , 800 °C and 850 °C .

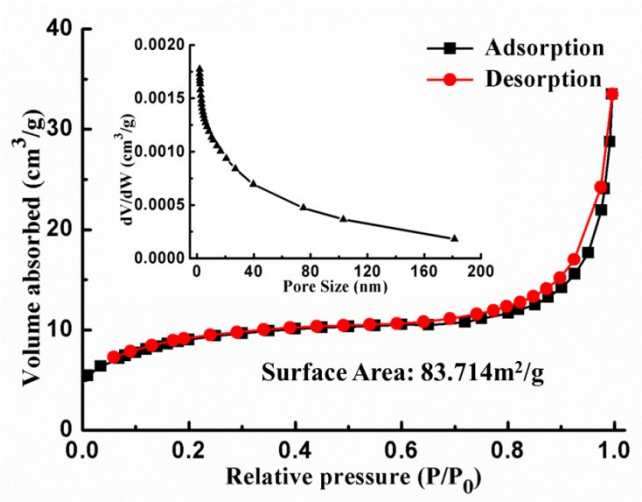

Figure S5. N_2 absorption/desorption curves of solid Fe_2P/GC octahedrons calcined and 750 ^oC. The inset exhibits its pore size distribution.

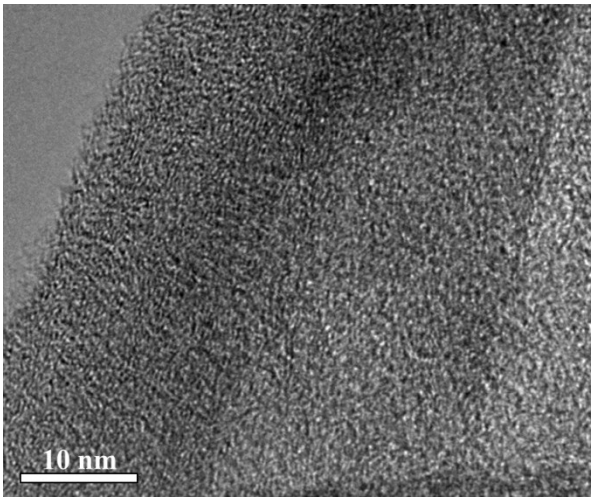

Figure S6. HRTEM image of GC shells from final Fe_2P/GC yolk/shell composite.

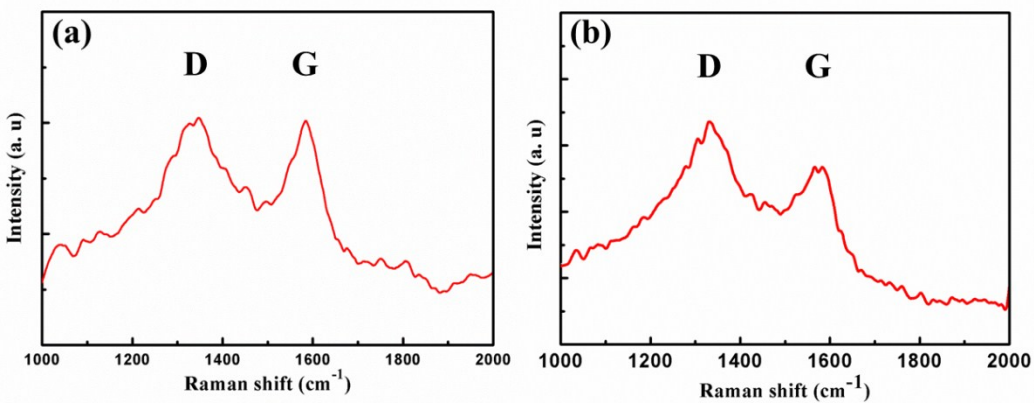

Figure S7. Raman spectrum of as-synthesized Fe_2P/GC yolk/shell octahedrons calcined at 800 °C (a) and solid Fe_2P/GC composite calcined at 750 °C (b).

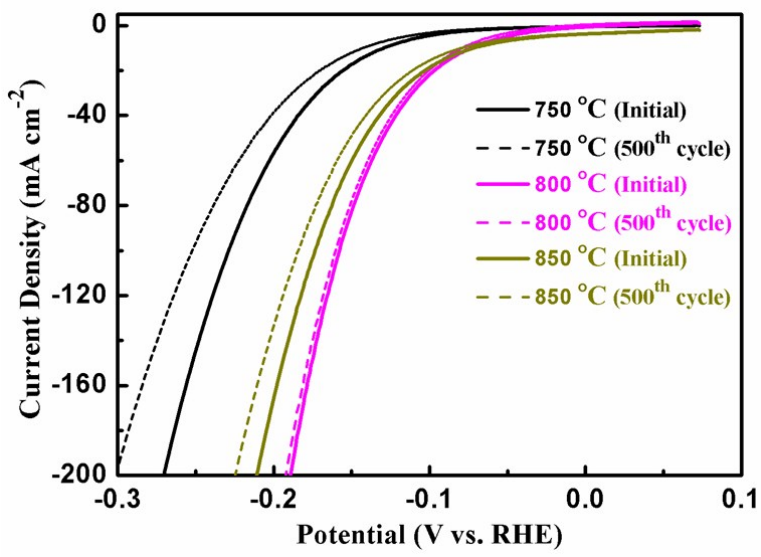

Figure S8. LSV curves of Fe_2P/GC calcinated at 750 °C , 800 °C and 850 °C at 50 mV s^{-1} over 500 cycles.

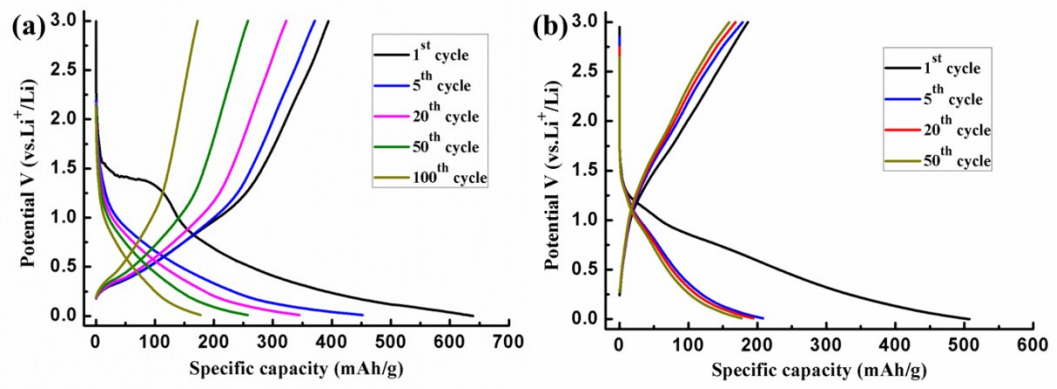

Figure S9. Discharge-charge curves of pure Fe_2P (a) and bare GC after the dissolution of Fe_2P/GC yolk/shell octahedrons in concentrated hydrochloric acid (b) at the rate of 0.1 A g^{-1}.

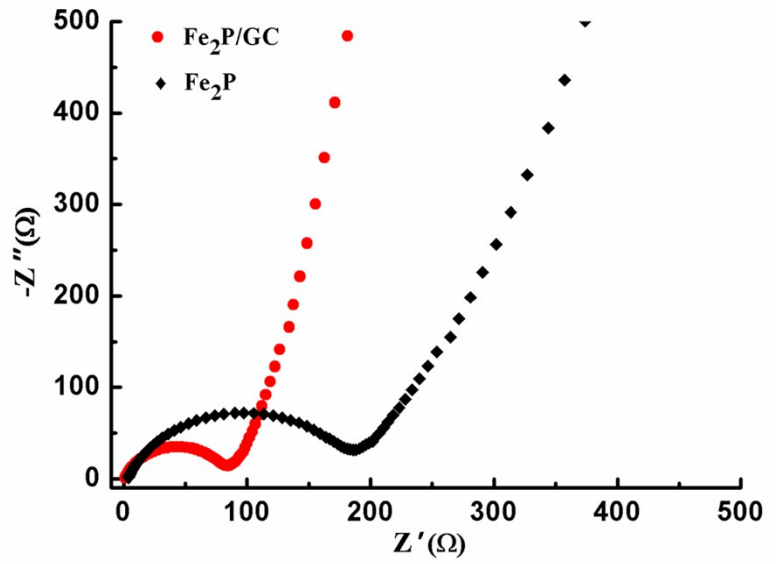

Figure S10. Nyquist plots of Fe_2P/GC yolk/shell octahedrons composite and pure Fe_2P within the frequency range from 0.01 Hz to 100 KHz.

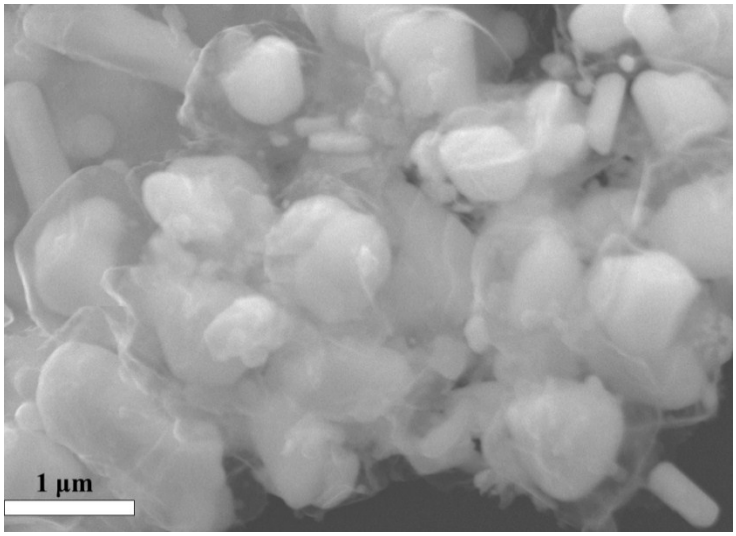

Figure S11. SEM image of Fe_2P/GC yolk/shell composite after electrochemical test.

Table S1. N_2 absorption/desorption data of other materials for comparison.

Materials	Specific surface area (SSA) (m^2 g^{-1})	Pore size (nm)
Cr_2O_3@OPC[1]	140	20
Co_3O_4-HNP/Al_2O_3[2]	207.85	4
np-Mo_2C NWs[3]	69.3	3.3
Ni_2P[4]	32.8	-
C@NiCoP[5]	110	3.8
CoP NRAs[6]	33.3	-
Fe_2P/GCS[7]	132.2	3.9
This work	243.3	4.1

Table S2. Composition of obtained Fe_2P/GC yolk/shell octahedrons

Materials	Dissolution by 12 M HCl		ICP-AES
	Weight ratio	Molar ratio	Molar ratio
Fe_2P/GC yolk/shell octahedrons	Fe:P:C 69.1:19.1:11.8	Fe:P:C 1.23:0.61:0.98	Fe:P:C 1.25:0.62:0.96

Table S3. HER performance of Fe_2P /GC yolk/shell composite compared with other transition metal compound catalysts.

Catalyst	Electrolyte	Onset Overpotential	Tafel Slope (mV dec^{-1})	η_{10}[a] (mV)	η_{20}[b] (mV)
Mo_2C/CNT[8]	0.5 M H_2SO_4	25	55.2	152	-
WC[9]		15	72	145	189
1T-MoS_2[10]		-	43	187	-
FeP/NCNT[11]		66	59	113	134
FeP NAs/CC[12]		20	45	58	79
CoP/CC[13]		30	30.1	49	59
Ni_2P/C[14]		60	54	87	115
MoP[15]		50	54	134	162
WP[16]		41	54	120	140
Fe_2P/GCS[7]		40	49	88	107
Fe_2P/NGr[17]		60	65	138	164
This work		35	45	76	98

a η_{10}: overpotential requirement for current density of 10 mA cm^{-2}.

b η_{20}: overpotential requirement for current density of 20 mA cm^{-2}.

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