Supporting Information

Direct plasma phosphorization of Cu foam for Li ion batteries

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Experimental Procedures

1 Direct growth of Cu_3P on Cu foam (Cu_3P/CF) by low temperature plasma

Commercial Cu foam (1 cm×1 cm, 57.4~57.7 mg) is cleaned by ultra-sonication successively in 6 M HCl, water and ethanol, and then dried under vacuum at 60 °C before used. The home-made radio frequency (RF) plasma system shown in our previous report is used for Cu_3P/CF preparation. Plasma coil is already winded round the tube upstream and next to the furnace. Plasma can be generated at low pressure (1-10 Pa) by radio frequency power input into the coil.

A piece of Cu foam (1 cm×1 cm) is suspended from a small quartz tube and loaded into the center of the furnace. Red phosphorous (0.2 g) in a ceramic boat is placed upstream to the Cu foam with a gap ~ 2 cm where the temperature is same as the Cu foam. Afterwards, the tube is evacuated into 0.1 Pa using a rotary pump and is flushed with high purity Ar (99.999%) three times to remove oxygen and moisture. A mixture of Ar/H_2 flow (Ar 15 sccm and H_2 5 sccm) is made to flow into the system and the pumping rates is adjusted to keep the tube pressure ~ 18 Pa. The Cu foam is then heated to 200 °C at 10 °C/min. When the desired temperature is reached, plasma is ignited (120 W). A bright reddish violet glow is able to extend to the sample region. The treatment time is 15 min. After treatment, the plasma is turned off and the system is cooled down to room temperature in 15 sccm Ar flow. The mass loading is determined by weighting Cu foam before and after phosphorization using an analytical balance with a nominal precision of 0.01 mg. The P loading is typically 1.2-1.6 mg cm^{-2}. The taken-out sample can be directly used to test.

2 Structural characterization

The products are characterized by X-ray diffraction (XRD, Rigaku D/max 200 diffractometer, Cu Kα), scanning electron microscopy (SEM, ZEISS, Merlin Compact), high-resolution transmission electron microscopy (HRTEM, JEM 2100F, 200 kV) and X-ray photoelectron spectroscopy (XPS AXIS-Ultra spectrometer, Kratos Analytical, monochromatic Al Kα radiation). Binding energy of C1s peak from sp2-bonded carbon at 284.5 eV is the reference for correction as general. For TEM observation, the Cu_3P particles are gathered from the Cu_3P/CF sample by sonication in ethanol for 30 min. Then a few drops of the suspension are casted onto TEM grids.

3 Electrochemistry measurements

The obtained Cu_3P/CF sample is directly used as the working electrode for LIBs. Coin type cells are assembled in an argon-filled glove-box, using a lithium foil as counter electrode, 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate = 1/1 in volume with 5 wt% fluoroethylene carbonate (FEC) as the electrolyte and glass fiber (GF/D, Whatman) as the separator. The cells are tested in the voltage range of 0.005 - 2 V (versus Li/Li^+) at ambient temperature.

4 Numerical calculation

The space size is 0.9 m in the axial direction and 0.03 m in the radial direction. The coil is located from 30 cm to 43 cm away from the entrance, with a total of 14 turns. The final distribution of plasma and magnetic potential can be obtained by decoupling the magnetic potential and thermal transmission equations. Plasma is assumed to be in the local thermal equilibrium (LTE) state. Number density is obtained from the Saha equation.

Supplementary figures and tables

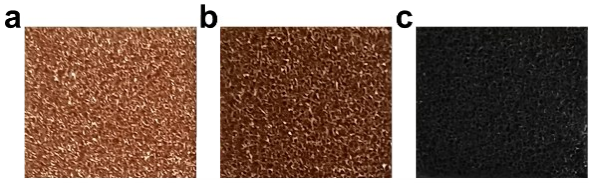


Fig. S1 Photographs of (a) bare Cu foam, (b) Cu foam after Ar plasma, (c) Cu_3P/CF.

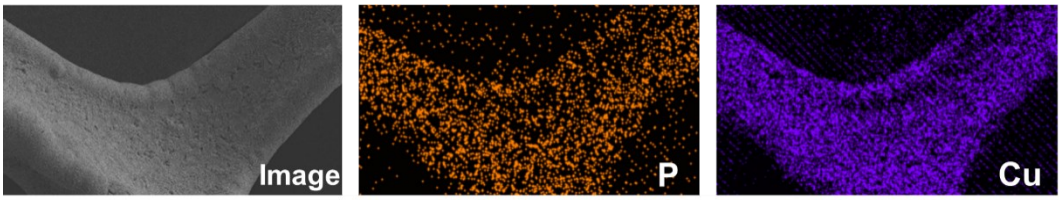


Fig. S2 SEM images of Cu_3P/CF and elemental mapping images of P and Cu.

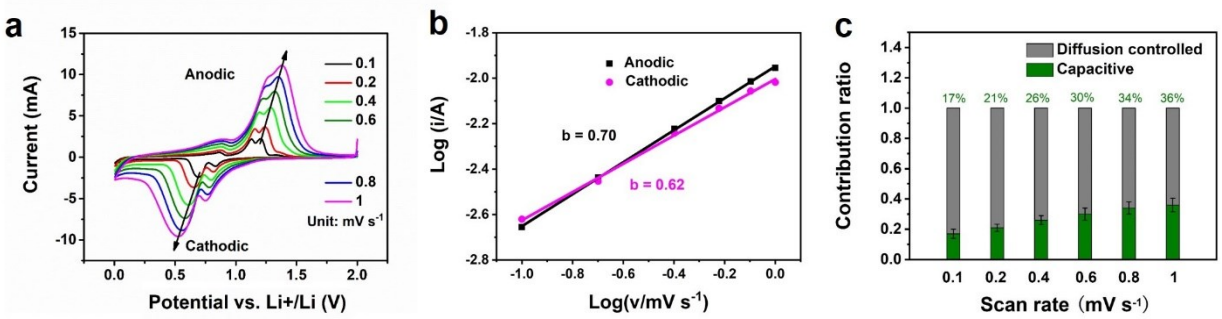
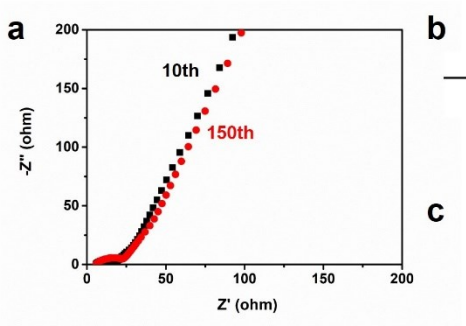


Fig. S3 (a) The CV curves at different sweep rates (from 0.1 to 1.0 mV s^{-1}). (b) The relationship between peak current and scan rate. (c) The normalized capacity contribution ratio of the capacitive- and diffusion-controlled charge versus scan rate.



c

Cycle number	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)
10	11.8	12.3	5
150	10.2	14.7	4

Fig. S4 (a) Nyquist profiles of the honeycomb Cu_3P / Cu electrode after 10 and 150 cycles. (b) An equivalent electrical circuit used for fitting the Nyquist profiles. (c) Fitted electrochemical impedance parameters. Generally, the equivalent circuit includes the impedance of pure Ohmic nature (R_s) corresponding to the overall Ohmic resistance of the cell, an interface impedance corresponding to the SEI layer (including a resistive component R_f and a capacitive component CPE_1) and an electrochemical impedance (including a charge-transfer impedance R_{ct}, a capacitive component CPE_2 and a Warburg impedance Z_w), respectively.

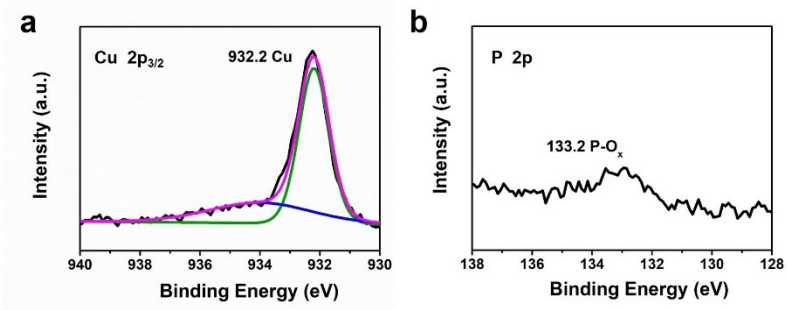


Fig. S5 XPS spectra of Cu foam of Cu $2p_{3/2}$ and P 2p after Ar plasma treatment.

Table S1. Comparisons of some recently reported transition metal phosphides for lithium ion anode material

	Preparation method	**Conductive additive and binder**	**ICE[a] (%)**	**Capacity (mAh g^{-1}) (cycles)**	**Current densities (mA g^{-1})**	**Mass loading (mg cm^{-2})**	**Current densities(mA cm^{-2})**	**Capacity (mAh cm^{-2})**	**Ref.**
Cu_3P/CF	Plasma phosphorization at 200 °C for 15 min by using red P	no	90	200 (50/2V)	280	11.4	3.2	2.3	This work
Cu_3P@C	Phosphorus-containing resin and Cu foam heated to 900°C for 1 h	acetylene black, PVDF[b]	78	540 (50/3V)	37	0.85	0.03	0.46	[1]
Cu_3P	Cu membrane and red P heated at 429°C for 0.5 h under vacuum	no	76	250 (20/3V)	75	10.5	0.79	2.6	[2]
Cu_3P/RGO	One-pot method in autoclave heated to 140°C for 12 h by using yellow P, $CuCl_2$ and GO	carbon black, PVDF[b]	86	756 (80/3V)	500	0.65-0.97	0.32-0.48	0.5~0.73	[3]
Cu_3P	Red phosphorus were sprayed over electrodeposited copper plates, and heated under 250°C	no	44	-	-	-	0.02	~0.3	[4]

	for 5h.								
Cu_3P	Cu powder and red P through ball milling process at 350 rpm for 24 h	carbon black, PVDF[b]	-	220 (50/2V)	24.2	-	-	-	[5]
Cu/P	$CuSO_4·5H_2O$, super P and $NaH_2PO_2·H_2O$ by using microwave oven to 200°C, dried under 200°C over night	oxidized graphite, PVDF[b]	-	175 (25/1.5, -30°C)	36	2.5	0.09	0.44	[6]
Cu_3P	Red P and Cu foils be heated under 400 °C for 8 h in Ar	carbon black, TEFLON	46	150 (30/2V)	73	-	-	-	[7]
CoP	$Co(CO_3)_{0.5}(OH)$ covered stainless steel foil heated to 350 °C for 2h in Ar by using $NaH_2PO_2·H_2O$	no	70	510 (400/2.6V)	400	1.3	0.52	0.66	[8]
CoP@C	$Co(acac)_2$ and Triphenylphosphine (PPh_3) heated to 400 °C for 1h under vacuum	acetylene black, CMC[c]	76	655 (100/3V)	180	0.7	0.13	0.46	[9]
Ni_5P_4@C	$Ni(acac)_2$ and Triphenylphosphine (PPh_3) heated to 370 °C for 1h under vacuum	acetylene black, CMC[c]	65	600 (100/2.5V)	150	0.7	0.1	0.42	[9]
NiP_2@C	Ni-MOF-74 and red P heated to 600 °C for 2 h under Ar flow	carbon black, PVDF[b]	68	483 (100/2.5V)	500	-	-	-	[10]
Ni_2P⊂pGN	Annealing at 650 °C for 2 h in Ar/H_2 by using $NiNH_4PO_4$□H_2O and GO	carbon black, PVDF[b]	63	511 (250/3V)	100	-	-	-	[11]

[a] ICE: Initial Coulombic Efficiency

[b] PVDF: polyvinylidene fluoride in *n*-methyl-2-pyrrolidone solvent

[c] CMC: carboxy methyl cellulose sodium

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