

## Supporting information

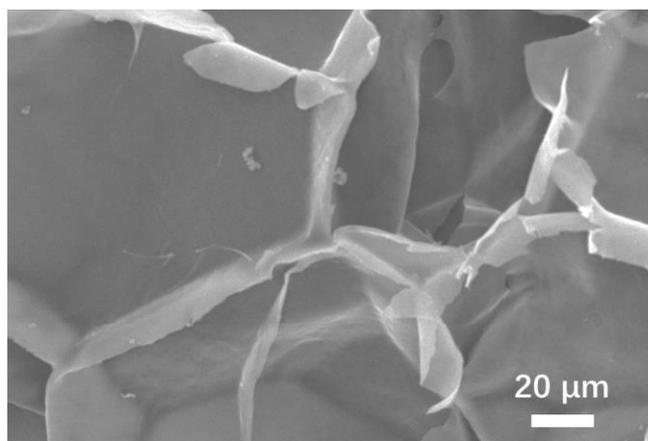
### **Fluffy carbon-coated red phosphorus as a highly stable and high rate anode for lithium ion batteries**

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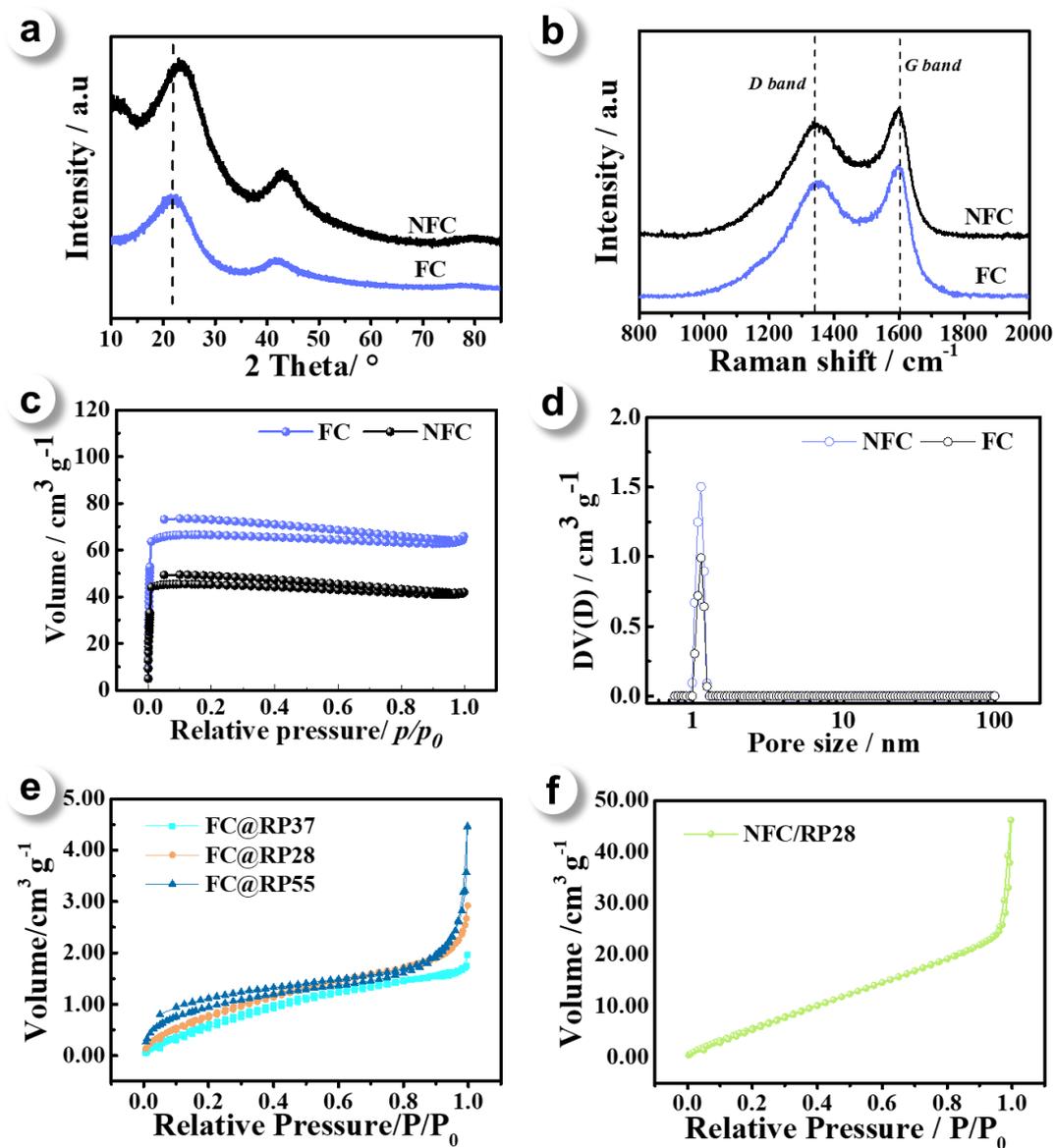
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**Fig. S1** SEM images of the FC.



**Fig. S2** XRD (a), Raman (b) spectra, nitrogen adsorption-desorption isotherms (c, e, f) and the pore size distribution (d) for FC and NFC sample.

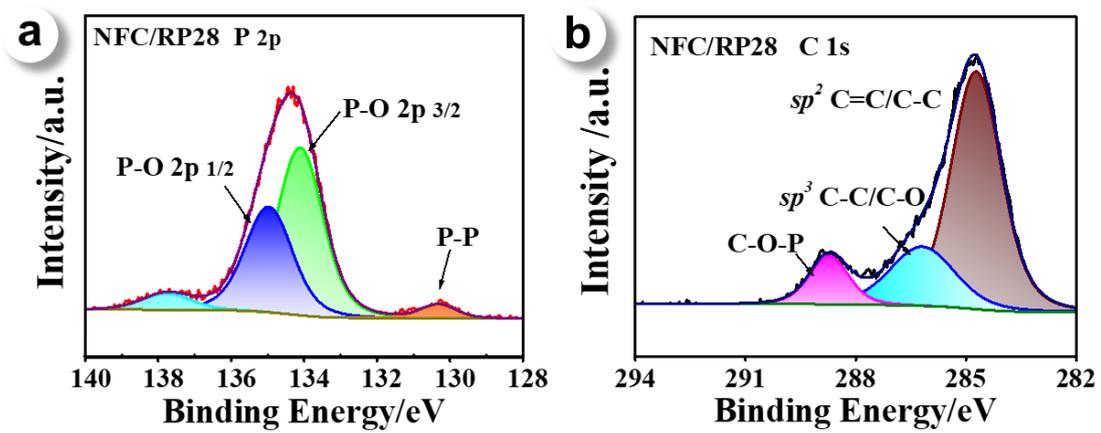
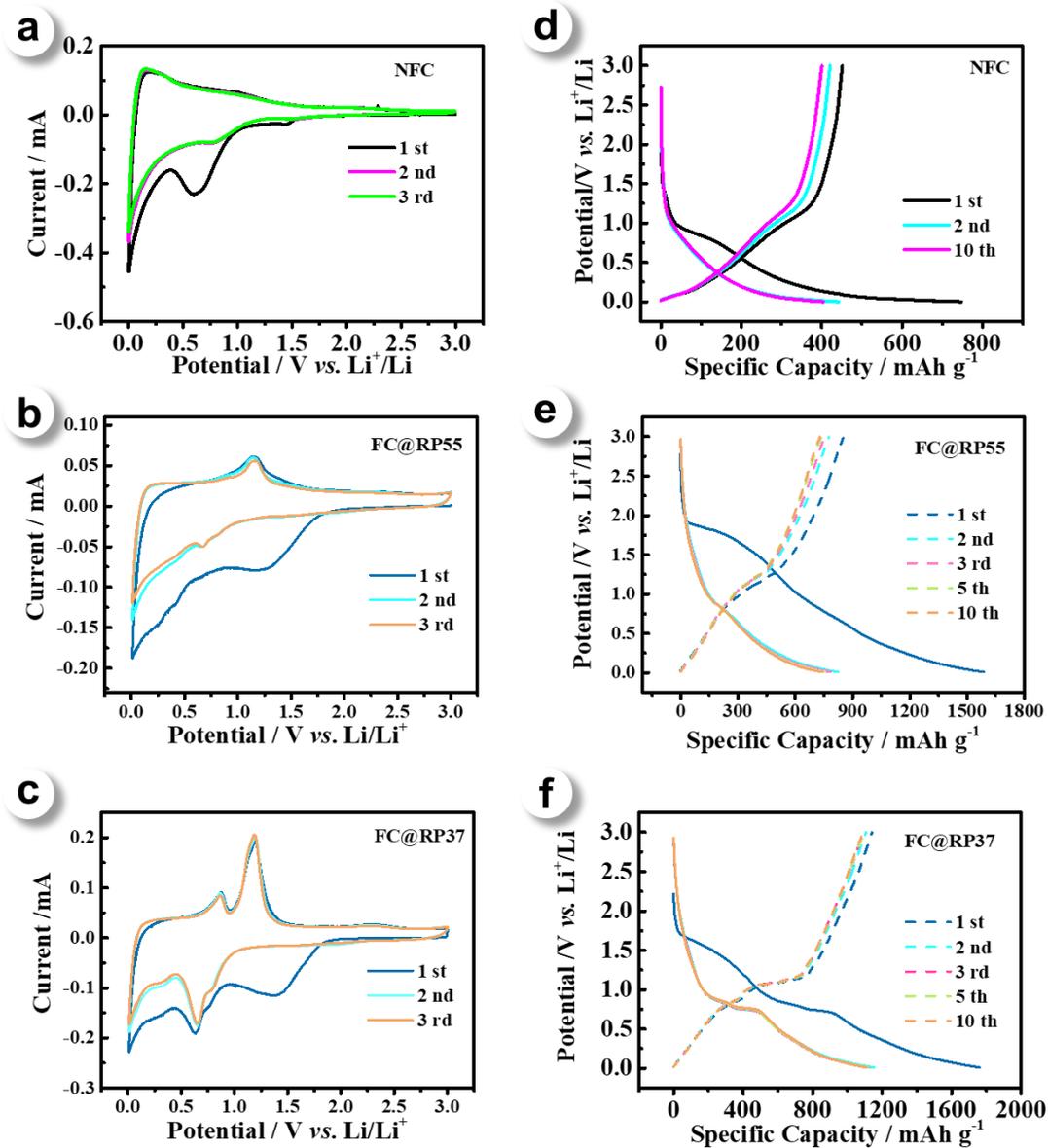
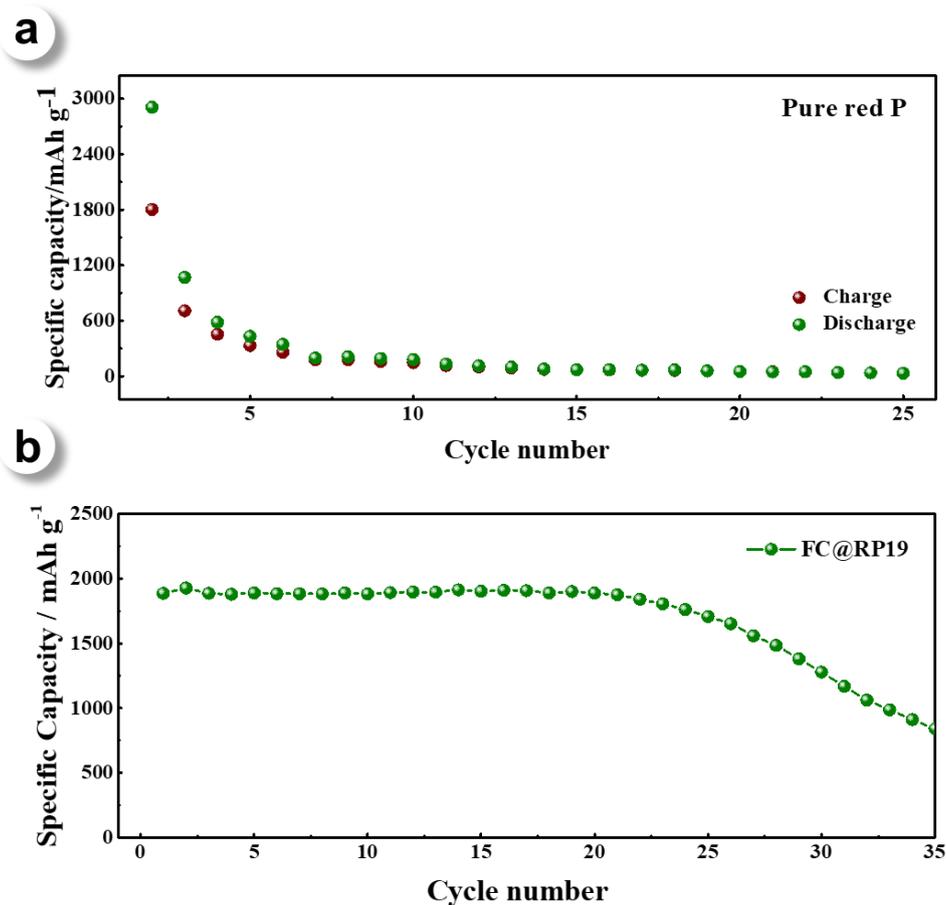


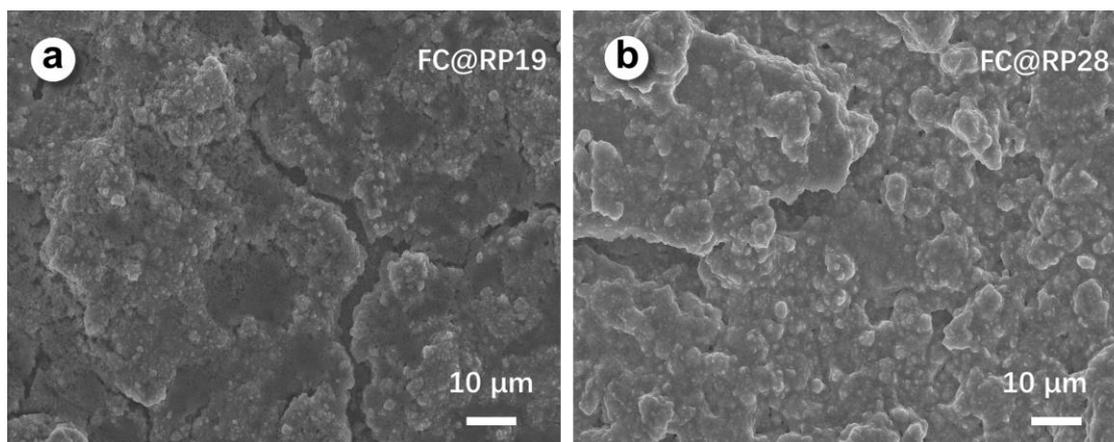
Fig. S3 XPS of P 2p (a) and C 1s (b) for NFC/RP28.



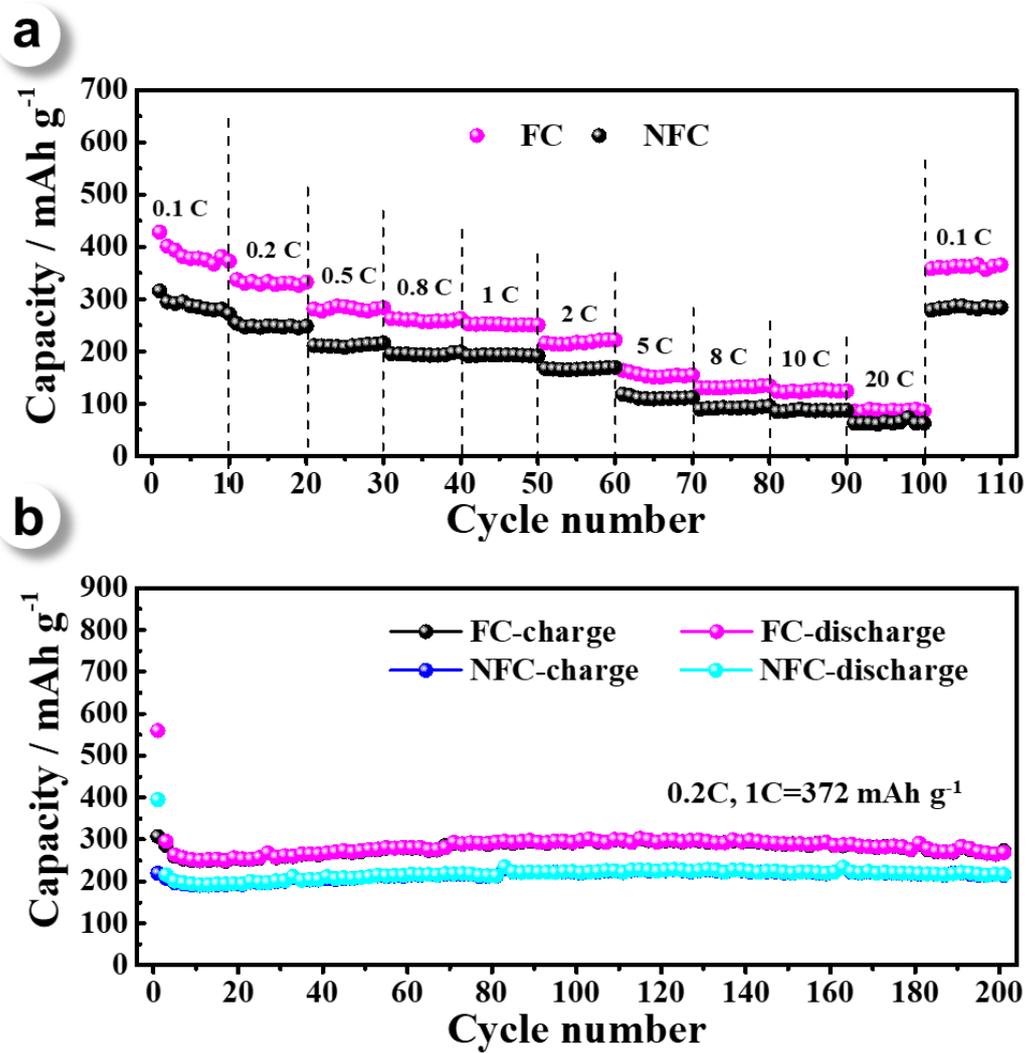
**Fig. S4** The CV curves of NFC (a), FC@RP55 (b) and FC@RP37 (c) at a scan rate of  $0.1 \text{ mV s}^{-1}$ . Voltage profiles of NFC (d) at the current density of  $0.1C$  ( $1C=372 \text{ mAh g}^{-1}$ ), FC@RP55 (e), and FC@RP37 (f) at  $0.05C$  ( $1C=2600 \text{ mA g}^{-1}$ ).



**Fig. S5** Cycle performance of pure red P and FC@RP19 electrode at 0.05C.



**Fig. S6** SEM images of FC@RP19 and FC@RP28 electrodes after 20<sup>th</sup> cycle.



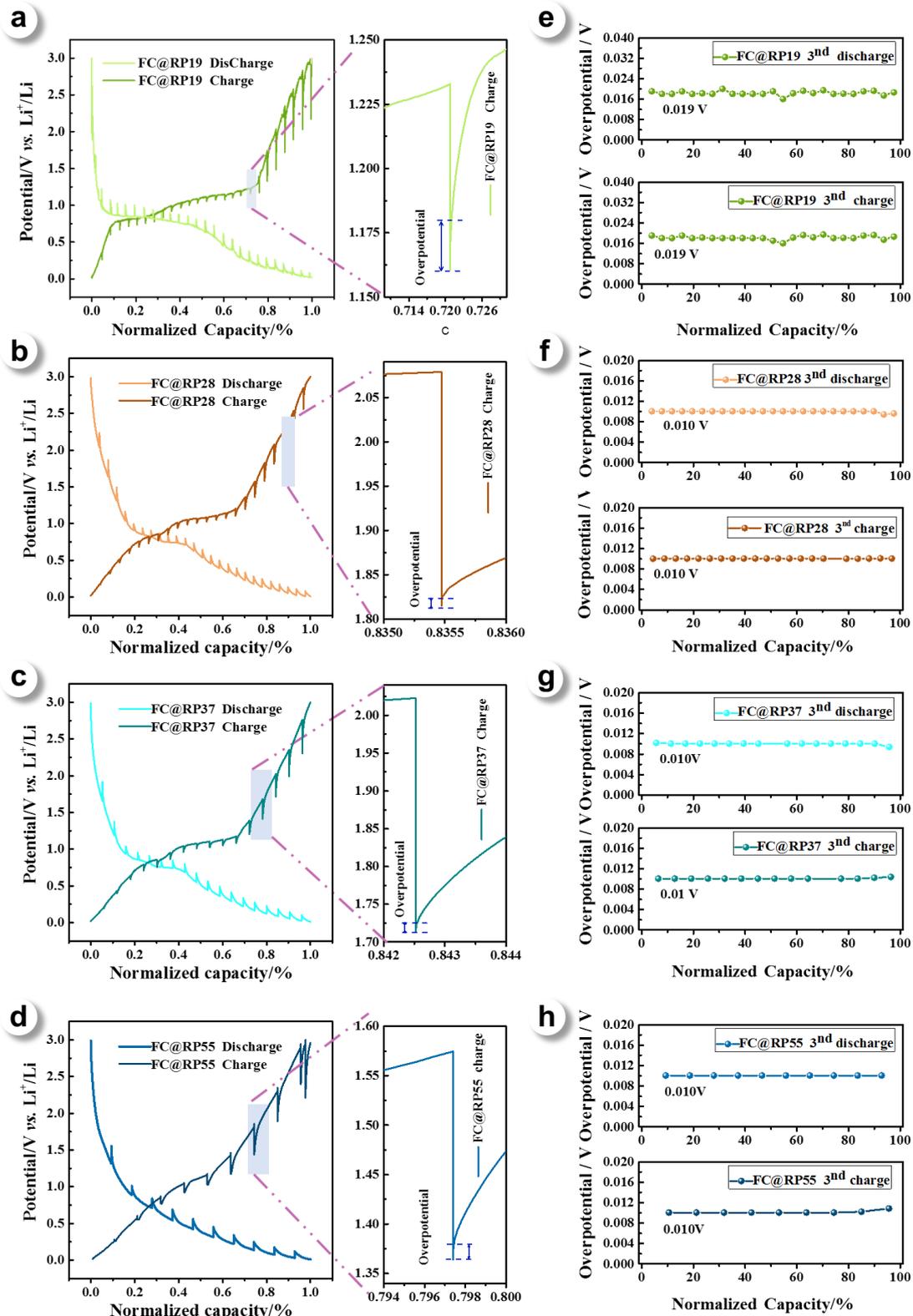
**Fig. S7** Rate performance of FC and NFC at different current density (a). Cycle performance of FC and NFC electrode at a current density of 1C (372 mA g<sup>-1</sup>).

**Table S1.** Electrochemical performance comparison of phosphorus/carbon composites as anode for lithium-ion batteries.

Sample	P/C ratio <i>or</i> P wt %	Preparation method	Initial charge capacity / mAh g <sup>-1</sup>	Cycle performance	Ref.
Ring-shaped phosphorus/MWCNTs	16	Vapor phase reaction	1206 at 0.5 A g <sup>-1</sup>	58.8 % capacity retention over 10 cycle	[1]
Red phosphorus/graphene	40	Electro-spraying and far-infrared reduction	~1763 at 0.1 A g <sup>-1</sup>	Capacity of ~1542 mAh g <sup>-1</sup> is retained after 100 cycles	[2]
Red P/ carbon film	21	Vapor phase polymerization	~1511 at 0.1 A g <sup>-1</sup>	Capacity of 903 mAh g <sup>-1</sup> after 640 cycles	[3]
Hollow red-phosphorus nanospheres	60	Wet solvothermal method	1285.7 at 0.52 A g <sup>-1</sup>	Capacity (based on P) of 1048.4 mA h g <sup>-1</sup> at 1 C after 600 cycles	[4]
Red phosphorus/RGO films	10	Sonication technique	~850 at 50 mA g <sup>-1</sup>	Capacity of 706 mA h g <sup>-1</sup> at 50 mA g <sup>-1</sup> after 200 cycles.	[5]
Phosphorus/ carbon nanotubes	70	Wet ball-milling	1396.6 at 50 mA g <sup>-1</sup>	~90 % capacity retention over 50 cycles.	[6]
Phosphorus/carbon composites	60	Ball-milling	1585.3 mAh g <sup>-1</sup> at 0.1 C	Capacity retention of 68.3% over 200 cycles	[7]
Phosphorus/graphene composites	80	Solution-based method	~1555 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	Capacity of 1286 mA h g <sup>-1</sup> after 100 cycles at 0.2 A g <sup>-1</sup>	[8]
Phosphorus/active carbon	47	Vaporization–condensation	2130 mAh g <sup>-1</sup> at 0.15A g <sup>-1</sup>	Capacity of 1370 mAh g <sup>-1</sup> after 85 cycles at 0.3 A g <sup>-1</sup>	[9]
Phosphorus/ carbon nanotubes	80	Ball-milling	2133.4 mA h g <sup>-1</sup> at 0.05C	Capacity of 998.5 mAh g <sup>-1</sup> after 50 cycles	[10]
Phosphorus/graphene	70	High-pressure-assisted spraying	1876 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	Capacity of 990 mAh g <sup>-1</sup> after 50 cycles	[11]
Amorphous red phosphorus@ fluffy hard carbon composites	80	Ball-milling	1699.5 mAh g <sup>-1</sup> at 0.05C	~1230 mAh g <sup>-1</sup> at 1C over 1000 cycles with 96% of capacity retention	This work

**Table S2.** The  $R_s$  and  $R_{ct}$  for all the FC@RP electrodes.

Sample	$R_s$ /Ohm	$R_{ct}$ /Ohm
FC@RP19	4.18	135.9
FC@RP28	4.09	43.13
FC@RP37	4.02	48.67
FC@RP55	3.92	77.58

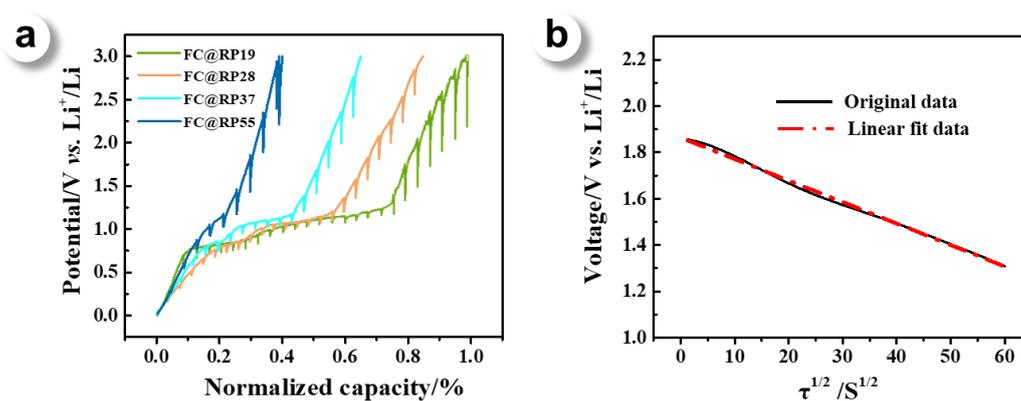


**Fig. S8** The potential response curves of FC@RP during GITT measurements with the inset of the magnified area illustrating the overpotential (a-d). Overpotential values estimated from the GITT results for 5<sup>th</sup> cycle (e-h).

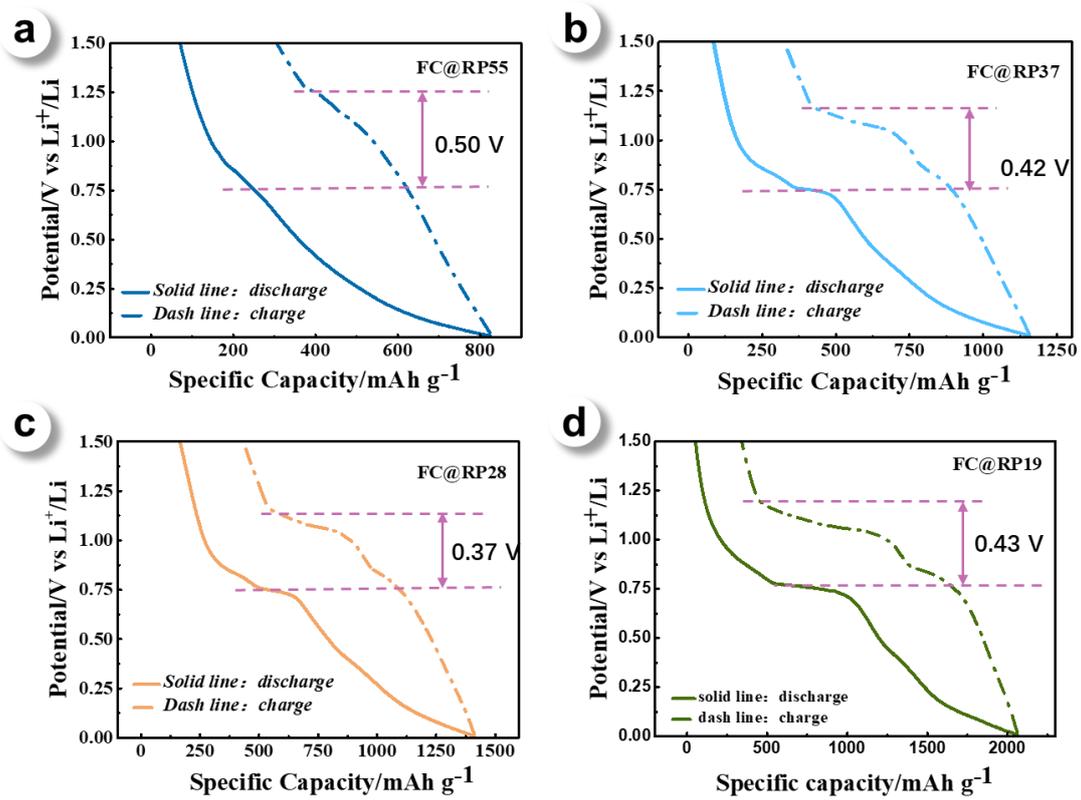
The cell voltage is linearly proportional to  $\sqrt{\tau}$ , as shown in Figure S8b. The diffusion coefficient (D) can be calculated from the GITT potential profiles by Fick's second law, as the following equation:

$$D = \frac{4}{\pi\tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_S}{\Delta E_\tau} \right)^2 \quad (\text{equation S1})$$

The  $\tau$  is the titration time,  $m_B$  is the electrode active material mass,  $S$  is the geometric area of the Cu foil electrode,  $\Delta E_S$  is the quasi-thermodynamic equilibrium potential difference before and after the current pulse,  $\Delta E_\tau$  is the potential difference during current pulse,  $V_M$  is the molar volume,  $M_B$  is the molar mass.



**Fig. S9** GITT profile of the FC@ RP electrodes in the charge state (a), and linear behavior of the potential vs.  $\sqrt{\tau}$  relationship in GITT at 1.824 V vs. Li<sup>+</sup>/Li of fourth lithiation process of FC@RP28 for LIBs.



**Fig. S10** Voltage profiles of all FC@RP electrodes show the voltage hysteresis between the charge and discharge at 1C.

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