Supplementary Information

Stable Polypyridinopyridine-Red Phosphorus Composite as a Superior Anode for Long-Cycling Lithium-Ion Batteries

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Table S1 FTIR wavenumbers (cm^{-1}) and assignments for PAN, RP, PPyPy, PPyPy-RP and PPyPy/RP, respectively.

Wave number (cm^{-1})	Bonds	Wave number (cm^{-1})	Bonds
2942.0	C - H	1245.5	C = N
2245.5	C ≡ N	1075.1	P - O
1630.0	C = C	1040.2	P- P
1451.9	CH_2	978.7	P - O - C
1385.3	P = O	652.4	P - C
1361.5	C - C	503.4	P- C=N

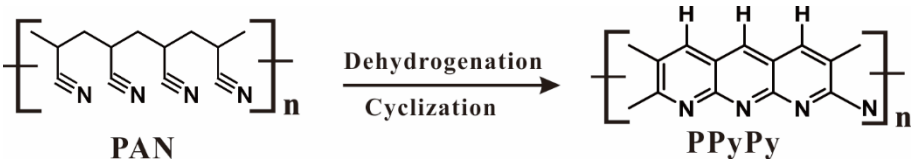

Fig. S1 Schematic illustration of the formation of PPyPy from PAN under dehydrogenation and cyclization process

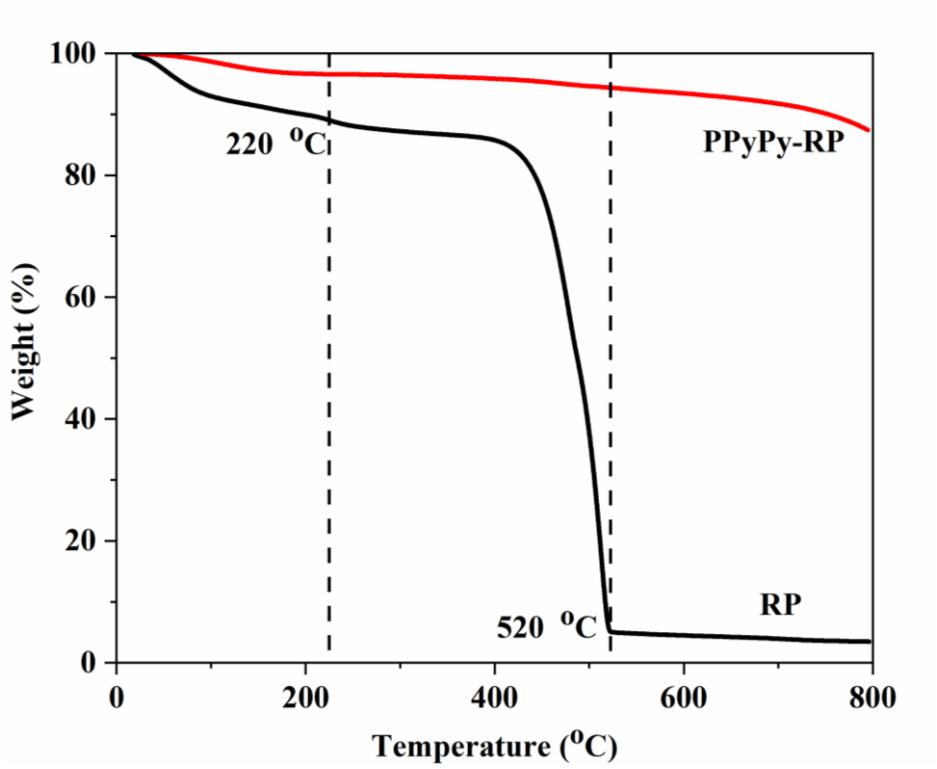

Fig. S2 TGA curves of the PPyPy-RP and pure red phosphorus. The content of pure phosphorus in the PPyPy-RP calculated from the TGA is 1.9 wt%. This analysis was taken in N_2 atmosphere with a heating rate of 10 °C min^{-1}.

To calculate the specific capacity contribution of phosphorus in the electrodes, a formula can be carried out as:

$$C_P = (C_C - C`_S) / W_P \qquad (1)$$

where the capacity contribution of Substrate in the electrode is calculated by the following equation as:

$$C`_S = C``_S \times W_S \qquad (2)$$

Where the C_C and $C``_S$ are the capacity of Composite and Substrate, while W_P and W_S are the percentage of Phosphorus and Substrate, respectively.

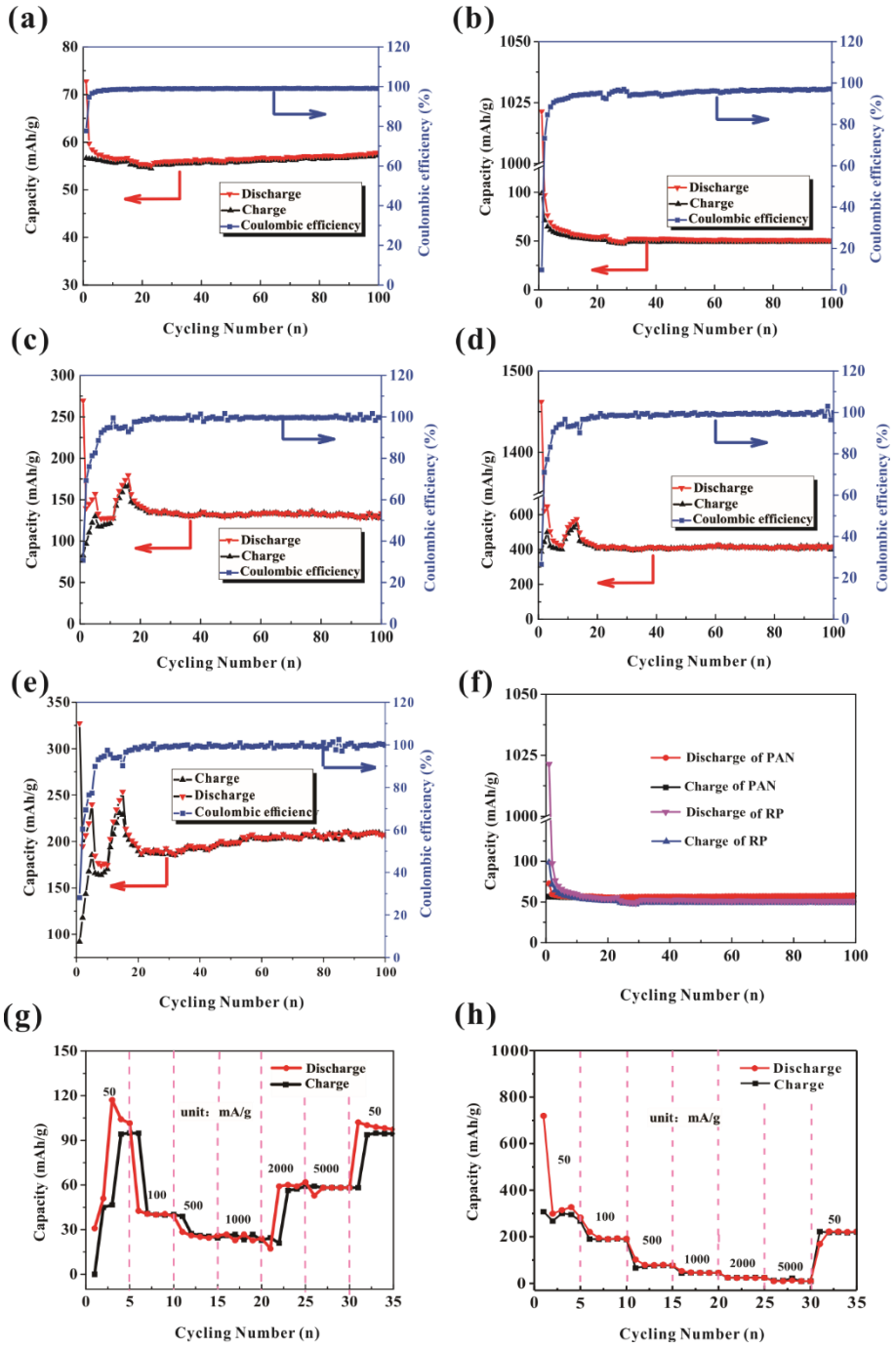

Fig. S3 Cycling stability and Coulombic efficiency of corresponding electrode for LIBs cycled 100 cycles at a current density of 100 mA/g; PAN (a), RP (b), PPyPy (c), PPyPy/RP (d), acetylene black (e); Compare discharge/charge capacities of PAN and RP at a current density of 100 mA/g (f); Rate capabilities of PAN (g) and AC (h) electrode for LIBs cycled at various current densities.

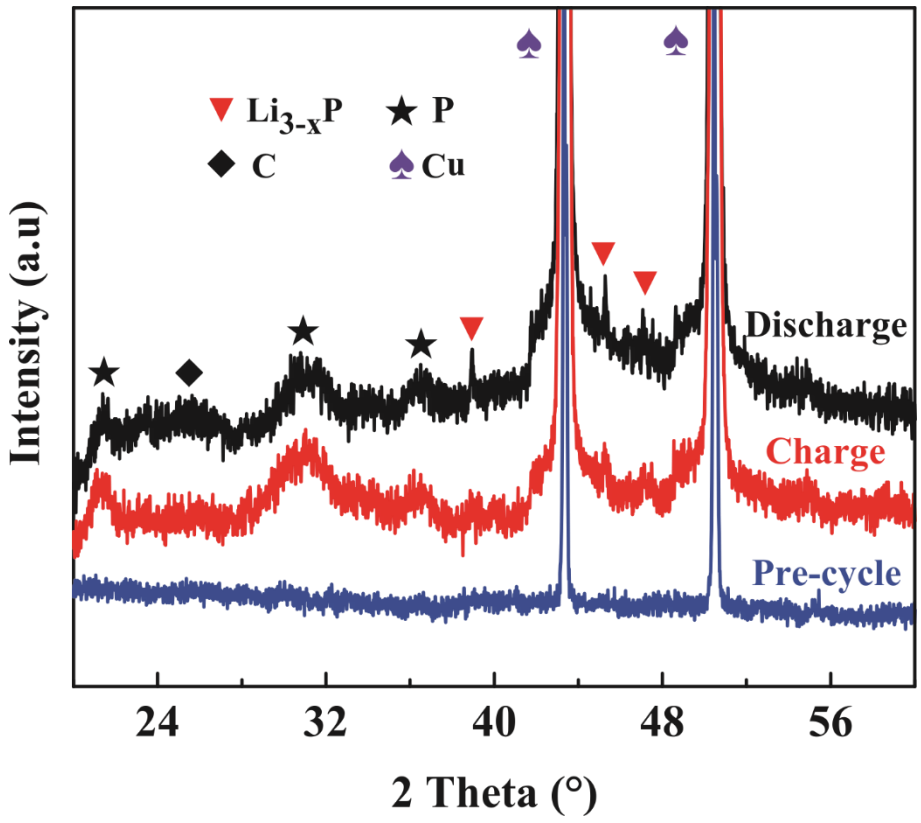

Fig. S4 The XRD patterns with the corresponding pre-cycle and first charge–discharge of PPyPy-RP as anode of LIBs;

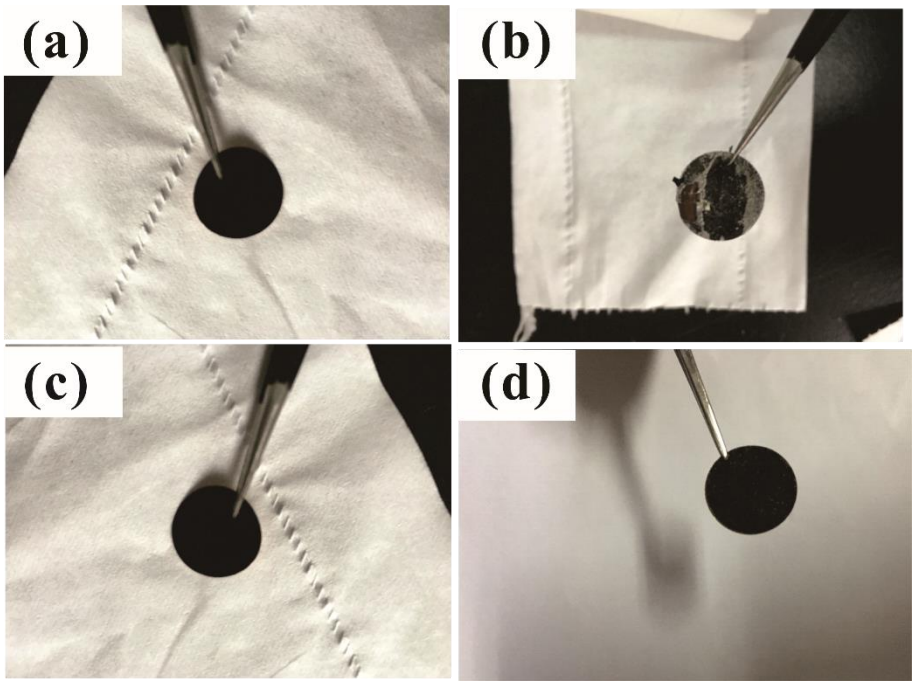

Fig. S5 The photographs of RP electrode and PPyPy-RP electrode after different discharge. Pre-cycle RP electrode (a) and after

100 th discharge (b); Pre-cycle PPyPy-RP electrode (c) and after 2000 th discharge (d)

Table S2 The R_e, R_f, and R_{ct} were obtained by fitting experimental data using the corresponding equivalent circuit (Figure. 6c) for RP, PPyPy, PPyPy-RP and PPyPy/RP cell pre-cycling.

	R_e (Ω)	R_f (Ω)	R_{ct} (Ω)
RP	1.53	147	140
PPyPy	1.23		72.5
PPyPy-RP	1.73		77.0
PPyPy/RP	1.68	61.7	27.5

Table S3 The Re, Rf, and Rct were obtained by fitting experimental data using the corresponding equivalent circuit (Figure. 5c) for PPyPy-RP cell after different cycles.

	R_e (Ω)	R_f (Ω)	R_{ct} (Ω)
Pre-cycle-PPyPy-RP	1.73		77.0
1 st-PPyPy-RP	1.51	6.59	33.2
20 th- PPyPy-RP	1.82	4.77	8.75
100 th- PPyPy-RP	1.85	21.3	16.4

Table S4 Electrochemical performance of phosphorus–carbon composites in lithium half-cells

Electrode material	Current density (mA/g)	*Initial Coulombic Efficiency (%)*	Reversible capacity ($mAh/g_{phosphorus}$) /Cycles	Reference
P/CNTs	130	74.3	998.5/50	[1]
P/graphite (P-C bond)	500	85.5	1849/100	[2]
P/Carbon Matrix	300	80	1370/100	[3]
P-Graphene Nanosheet	130	84	1283/300	[4]
P/carbon cloth/graphene oxide	259.6	82.7	910/200	[5]
Densely Packed Phosphorene–Graphene	500	60.2	725/200	[6]
	100	86.2	1870.2/100	
PPyPy-RP	1000	84.4	1632.8/800	This work
	5000	67.9	518.3/2000	

References

[1] Y. Kim, Y. Park, A. Choi, N. S. Choi, J. Kim, J. Lee, J. H. Ryu, S. M. Oh and K. T. Lee, *Adv. Mater.*, 2013, **25**, 3045-3049.

[2] J. Sun, G. Zheng, H. W. Lee, N. Liu, H. Wang, H. Yao, W. Yang and Y. Cui, *Nano Lett.*, 2016, **14**, 4573-4580.

[3] J. Li, L. Wang, X. He and J. Wang, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 4217-4223.

[4] Z. Yu, J. Song, M. L. Gordin, R. Yi, D. Tang and D. Wang, *Adv Sci (Weinh)*, 2015, **2**, 1400020.

[5] Y. Du, Y. Tang and C. Chang, *J. Electrochem. Soc.*, 2016, **163**, A2938-A2942.

[6] Y. Zhang, X. Rui, Y. Tang, Y. Liu, J. Wei, S. Chen, W. R. Leow, W. Li, Y. Liu, J. Deng, B. Ma, Q. Yan and X. Chen, *Adv. Energy Mater.*, 2016, **6**, 1502409.