

Fig. S1 Schematic diagram of various positions on (a) TA and (b) PPy. The (c) initial and (d) final positions of Li-ion diffusing from ring1 to bridge O above TA. The (e) initial and (f) final positions of Li-ion diffusing from double O to ring2 above TA. The (g) initial and (h) final positions of Li-ion diffusing from single O1 to single O2 above TA. The (i) initial and (j) final positions of Li-ion diffusing from ring1 to ring2 above PPy. The (k) initial and (l) final positions of Li-ion diffusing from N1 to N2 above PPy.

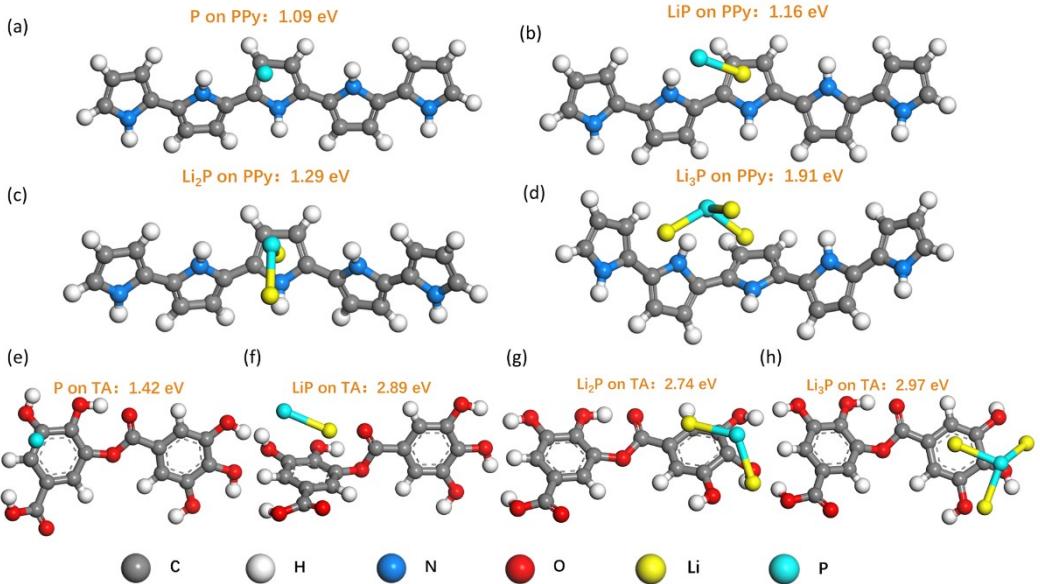


Fig. S2 Adsorption of (a) P, (b) LiP, (c) Li<sub>2</sub>P, and (d) Li<sub>3</sub>P on PPy.<sup>1</sup> Adsorption of (e) P, (f) LiP, (g) Li<sub>2</sub>P, and (h) Li<sub>3</sub>P on TA.

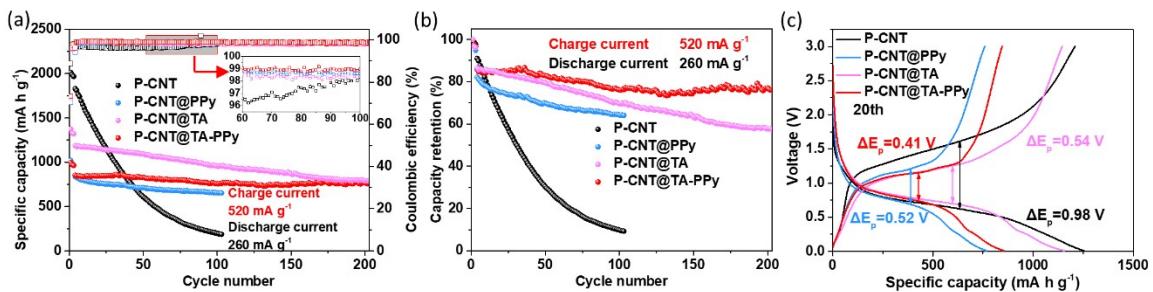


Fig. S3 (a) Cycling performances, (b) capacity retention and (c) the 20th galvanostatic charge/discharge curves of P-CNT, P-CNT@PPy, P-CNT@TA, P-CNT@TA-PPy at 520  $\text{mA g}^{-1}$  charge current density and 260  $\text{mA g}^{-1}$  discharge current density.

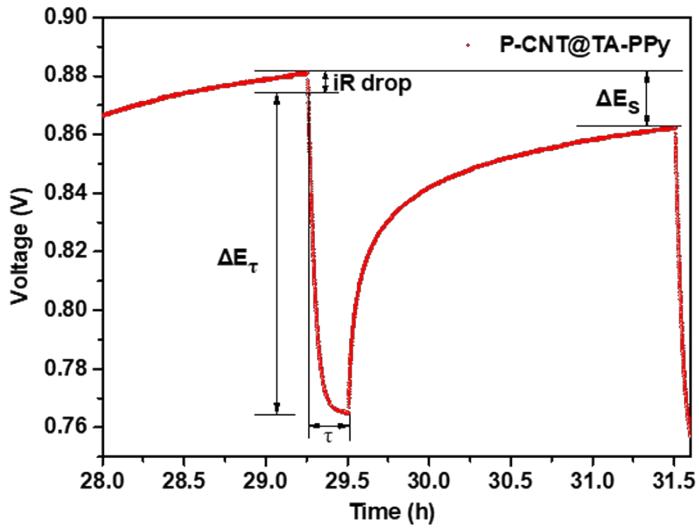


Fig. S4 Schematic labeling of different parameters in GITT.

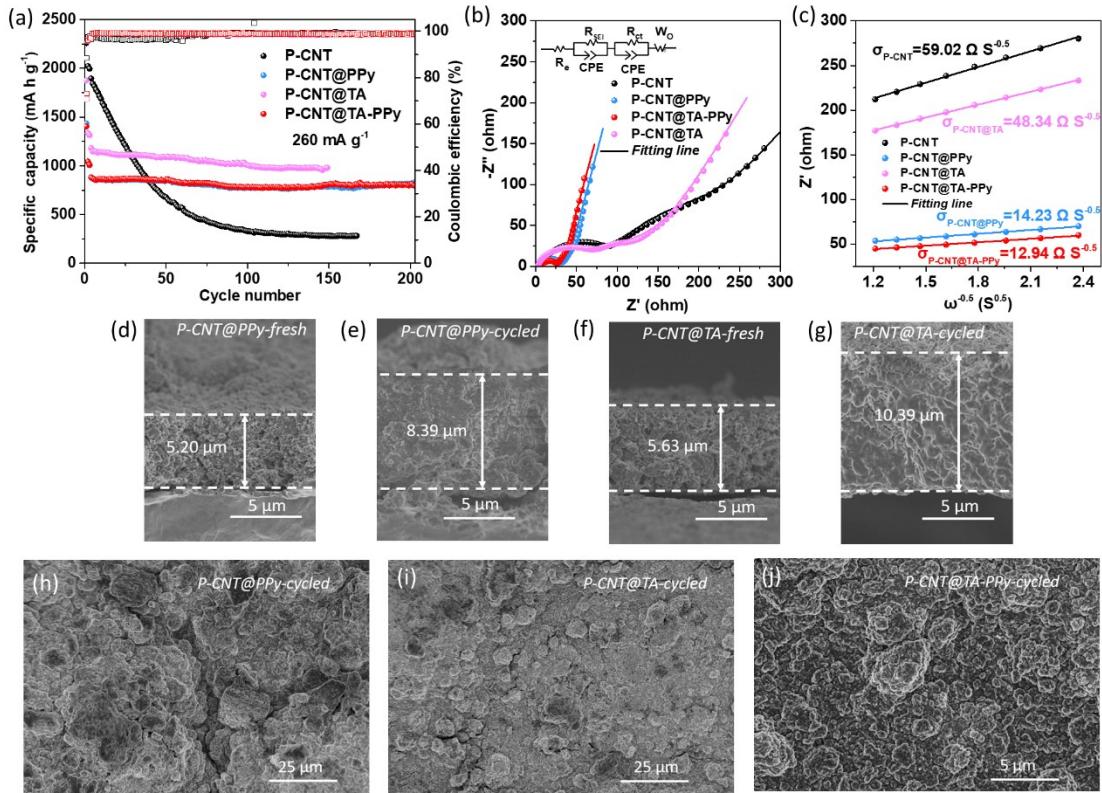


Fig. S5 The dates were tested at both charge and discharge current of 260  $\text{mA g}^{-1}$ . (a) Long cycle curves of discharge capacity of P-CNT, P-CNT@PPy, P-CNT@TA, P-CNT@TA-PPy. (b) Nyquist plots of P-CNT, P-CNT@PPy, P-CNT@TA, P-CNT@TA-PPy after 25 cycles and (c) corresponding fitting lines between frequency and  $Z'$  in the low frequency region. SEM images showing the thickness and morphology of (d) (e) (h) P-CNT@PPy, (f) (g) (i) P-CNT@TA and (j) P-CNT@TA-PPy electrodes before and after 25 cycles.

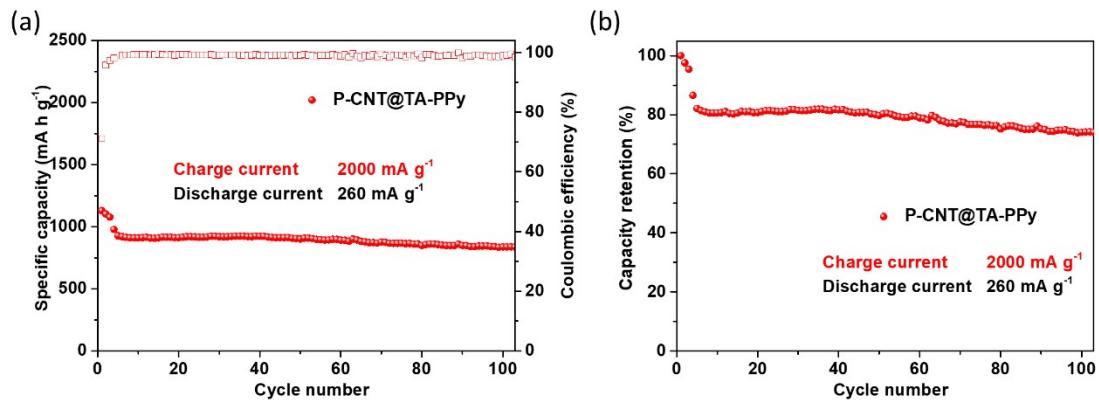


Fig. S6 (a) The cycling performance and (b) corresponding charge capacity retention of P-CNT@TA-PPy at a charge current density of  $2000 \text{ mA g}^{-1}$  and discharge current density of  $260 \text{ mA g}^{-1}$ .

Table S1 Cycling performance and multi-rate performance of this work and other works.

Materials	Phosphorus species	Cycling performance	Multi-rate performance	Reference
P-CNT@TA-PPy	Black phosphorus	815 $\text{mA h g}^{-1}$ at 260 $\text{mA g}^{-1}$ ; 757 $\text{mA h g}^{-1}$ at 520 $\text{mA g}^{-1}$ ; 821 $\text{mA h g}^{-1}$ at 1000 $\text{mA g}^{-1}$ ; 837 $\text{mA h g}^{-1}$ at 2000 $\text{mA g}^{-1}$	893, 840, 760, 446 $\text{mA h g}^{-1}$ at 260, 520, 1300, 5200 $\text{mA g}^{-1}$	This work
P/CNT-10% LiF	Black phosphorus	821 $\text{mA h g}^{-1}$ at 50 $\text{mA g}^{-1}$ ; 783 $\text{mA h g}^{-1}$ at 200 $\text{mA g}^{-1}$	1060, 945, 866, 798, 754 and 703 $\text{mA h g}^{-1}$ at 25, 50, 100, 200, 500, 1000 $\text{mA g}^{-1}$	[S2]
BP/HPC	Black phosphorus	350 $\text{mA h g}^{-1}$ at 1000 $\text{mA g}^{-1}$	580, 450, 360, 300, 210 $\text{mA h g}^{-1}$ at 50, 200, 500, 1000, 2000 $\text{mA g}^{-1}$	[S3]
BP@CNTs	Black phosphorus	750 $\text{mA h g}^{-1}$ at 100 $\text{mA g}^{-1}$ ; 522 $\text{mA h g}^{-1}$ at 500 $\text{mA g}^{-1}$	1450, 950, 800, 550, 420, 380 $\text{mA h g}^{-1}$ at 100, 250, 500, 1000, 1500, 2500 $\text{mA g}^{-1}$	[S4]
RP-HC(70%)@TiO <sub>2</sub>	Red phosphorus	795 $\text{mA h g}^{-1}$ at 100 $\text{mA g}^{-1}$ ; 447 $\text{mA h g}^{-1}$ at 1000 $\text{mA g}^{-1}$	841, 716, 657, 608, 554, 518, 460 $\text{mA h g}^{-1}$ at 100, 200, 400, 600, 800,	[S5]

			1000 mA g <sup>-1</sup>	2000 mA g <sup>-1</sup>
BP	Black phosphorus	440 mA h g <sup>-1</sup> at 740 mA g <sup>-1</sup> ;	636, 566, 540, 504, 470, 407 mA h g <sup>-1</sup> at 460, 1440, 1830, 2750, 3430, 4120 mA h g <sup>-1</sup>	[S6]
Red phosphorus nanodot/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Red phosphorus	500 mA h g <sup>-1</sup> at 50 mA g <sup>-1</sup> ; 818 mA h g <sup>-1</sup> at 200 mA g <sup>-1</sup> ;	599, 434, 347, 260, 197 mA h g <sup>-1</sup> at 50, 100, 200, 500, 1000 mA g <sup>-1</sup>	[S7]
BPNs@TiO <sub>2</sub> @G	Black phosphorus	502 mA h g <sup>-1</sup> at 1250 mA g <sup>-1</sup> ;	491, 425, 383, 329 mA h g <sup>-1</sup> at 300, 500, 1000, 2000 mA g <sup>-1</sup>	[S8]
FP	Fibrous phosphorus	817 mA h g <sup>-1</sup> at 100 mA g <sup>-1</sup> ;	1302, 940, 509, 262, 150 mA h g <sup>-1</sup> at 100, 200, 500, 1000, 2000 mA g <sup>-1</sup>	[S9]
TGC-SiC@graphene@P	Fibrous phosphorus	553 mA h g <sup>-1</sup> at 200 mA g <sup>-1</sup> ;	734, 572, 453, 346 mA h g <sup>-1</sup> at 100, 200, 500, and 1000 mA g <sup>-1</sup>	[S10]

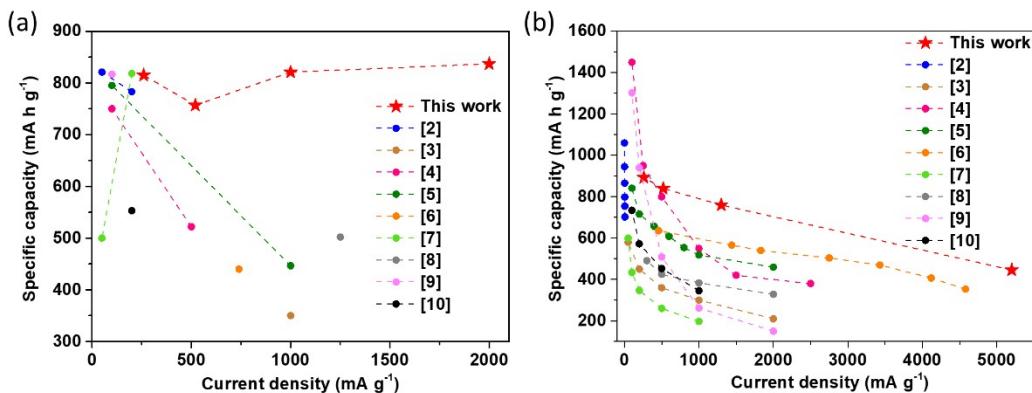


Fig. S7 (a) The cycling performance and (b) multi-rate performance compared with other works.<sup>2-10</sup>

## Reference

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