## **Support information**

## Anisotropic, low-tortuosity, ultra-thick red P@C-Wood electrodes for sodium-ion batteries

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**Fig. S1** A low-magnification SEM image of (a) the C-Wood and (b) red P@C-Wood. The thickness of (c) the C-Wood and (d) red P@C-Wood (the size of red P@C-Wood is about 5 mm  $\times$  5 mm  $\times$  0.8 mm).



Fig. S2 SEM and EDS elemental mapping of red P nanoparticles.



Fig. S3 (a) TEM image of the red P@C-Wood. (b) A high-magnification SEM image of the C-

Wood. Photo images of the thickness of the C-Wood (c) and (d) red P@C-Wood



**Fig. S4** Morphological and structural characterizations of the red P electrode at different states. The top view (a), (b), (e) and cross-section view (c), (d) of red P electrode, respectively. (f-h) Corresponding C, O, and P elemental mapping images of the red P electrode.

For the comparison, the red phosphorus is mixed with acetylene black and poly(vinylidene fluoride) (PVDF) to make a homogeneous slurry(the ratio was 8:1:1). Then the slurry is cast onto copper foil using a doctor blade, followed by drying in a vacuum 12 h at 60 °C. The mass loading of the electrodes is about 1.0 mg cm<sup>-2</sup>.



Fig. S5 XRD patterns of the C-Wood, red P and red P@C-Wood.

Table. S1 The red P loading of pure red P electrode and red P@C-Wood electrode.

Sample	Red P loading ( wt% )	Red P loading ( mg cm <sup>-</sup>
		<sup>2</sup> )
Red P electrode	15	1.522
Red P@C-Wood	30	8.371

For the pure red P electrode, the red phosphorus loading (wt%) is calculated based on 15% with half of a 12.5  $\mu$ m copper current collector, red phosphorus, acetylene black and PVDF.



**Fig. S6** (a) Cyclic voltammetry of pure red P electrode at the potential window between 0.01 and 2.0 V versus Na/Na<sup>+</sup> with a scan rate of 0.1 mV s<sup>-1</sup>; (b) cycling properties of the red P electrode at 0.01 A  $g^{-1}$ ; (c) cycling properties of the pure red P electrode at 0.1 A  $g^{-1}$ ; (d) cycling properties of red P@C-Wood electrode at 0.3 A  $g^{-1}$ .



**Fig. S7** (a) Rate capabilities and (b) cycling properties of the red P@C-Wood electrode at 1.674 mA cm<sup>-2</sup>. (c) Long cycling performance of the red P@C-Wood electrode at 16.742 mA cm<sup>-2</sup>.



Fig. S8 Cycling properties of the red P@C-Wood electrode at 0.78 A g<sup>-1</sup> based on red P@C-

Wood, red P content is about 39 wt% (Red P@C-Wood = 100:50)

Table. S2 The elemental analyzer data of wood (wt%).

Materials	С	Н	Ν	S	0
Wood	47.21	6.62	0.09	0.88	45.69



Fig. S9 Evaluation of resistance using a multimeter.

Table. S3   The resistant	ce of different materials.

Materials	Resistance
Wood	$\geq$ 40 M $\Omega$
Red P electrode	1701 Ω
C-Wood	16.8 Ω
Red P@C-Wood	26.3 Ω

<b>Table.</b> 54 Comparison with red P based anodes for SIBs in literatures	Table.	<b>S4</b>	4 Comparison	with red l	P based	anodes	for \$	SIBs i	in literatures
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Materials	P content in	P content	Mass	Reversible	Reversible	Gravimetric	Gravimetric	Reference
	composites	in whole	loading of	capacity	capacity	capacity	capacity	
		electrode <sup>a</sup>	Р	(based on	(based on	(based on	(based on	
			(mg/cm <sup>-2</sup> )	P)	P/C	whole	whole	
					composites)	electrode) <sup>a</sup>	electrode) <sup>a</sup>	
Red P@C-	30 wt%	30 wt%	8.4	2239.8	791.8 mAh	791.8 mAh	18.8 mAh	This work
Wood				mAh g <sup>-1</sup> at	g-1 at 0.06 A	g-1 at 0.06 A	cm <sup>-2</sup> at 1.67	
				0.2 A g <sup>-1</sup>	g <sup>-1</sup>	g <sup>-1</sup>	mA cm <sup>-2</sup>	
				1057.8	320.5 mAh	320.5 mAh	8.9 mAh	This work
				mAh g <sup>-1</sup> at	g-1 at 0.6 A	g-1 at 0.6 A	cm <sup>-2</sup> at 16.7	
				2.0 A g <sup>-1</sup>	g-1	g <sup>-1</sup>	mA cm <sup>-2</sup>	
P/CNTs@rGO	70 wt%	70 wt%	1.5	2113 mAh	1479 mAh	1479 mAh	3.2 mAh	1
				g <sup>-1</sup> at 0.52	g <sup>-1</sup> at 0.42 A	g <sup>-1</sup> at 0.42 A	cm <sup>-2</sup> at 0.78	
				A g <sup>-1</sup>	g <sup>-1</sup>	g <sup>-1</sup>	mA cm <sup>-2</sup>	
P@N-MPC	22.6 wt%	5.2 wt%	~ 0.34	A g <sup>-1</sup> 2522.1	g <sup>-1</sup> 570 mAh g <sup>-</sup>	g <sup>-1</sup> 131.5 mAh	mA cm <sup>-2</sup>	2
P@N-MPC composites	22.6 wt%	5.2 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup>	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5	2
P@N-MPC composites	22.6 wt%	5.2 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup>	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> 1	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup>	2
P@N-MPC composites P/CNTs@rGO	22.6 wt%	5.2 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> <sup>1</sup> 1405 mAh	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh	2 3
P@N-MPC composites P/CNTs@rGO	22.6 wt% 70 wt%	5.2 wt% 10.6 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at	g <sup>-1</sup> 570 mAh g <sup>-1</sup> at 1.0 A g <sup>-1</sup> 1405 mAh g <sup>-1</sup> at 0.52 A	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6	2 3
P@N-MPC composites P/CNTs@rGO	22.6 wt% 70 wt%	5.2 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup>	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> 1 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup>	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup>	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup>	2 3
P@N-MPC composites P/CNTs@rGO P@C-GO/	22.6 wt% 70 wt% ~44.5 wt%	5.2 wt% 10.6 wt% 8.5 wt%	~ 0.34 ~ 2.2 ~0.45	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup> 1865.2	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> <sup>1</sup> 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 830 mAh g <sup>-</sup>	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 158.4 mAh	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup> 0.84 mAh	2 3
P@N-MPC composites P/CNTs@rGO P@C-GO/ MOF-5	22.6 wt% 70 wt% ~44.5 wt%	5.2 wt% 10.6 wt% 8.5 wt%	~ 0.34 ~ 2.2 ~0.45	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup> 1865.2 mAh g <sup>-1</sup> at	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> <sup>1</sup> 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 830 mAh g <sup>-</sup> <sup>1</sup> at 2.0 A g <sup>-</sup>	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 158.4 mAh g <sup>-1</sup> at 0.17 A	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup> 0.84 mAh cm <sup>-2</sup> at 2.0	2 3 4
P@N-MPC composites P/CNTs@rGO P@C-GO/ MOF-5	22.6 wt% 70 wt% ~44.5 wt%	5.2 wt% 10.6 wt% 8.5 wt%	~ 0.34	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup> 1865.2 mAh g <sup>-1</sup> at 4.5 A g <sup>-1</sup>	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> 1 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 830 mAh g <sup>-</sup> <sup>1</sup> at 2.0 A g <sup>-</sup> 1	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 158.4 mAh g <sup>-1</sup> at 0.17 A g <sup>-1</sup>	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup> 0.84 mAh cm <sup>-2</sup> at 2.0 mA cm <sup>-2</sup>	2 3 4
P@N-MPC composites P/CNTs@rGO P/CNTs@rGO P@C-GO/ MOF-5 RP/rGO	22.6 wt% 70 wt% ~44.5 wt% 57.9 wt%	5.2 wt% 10.6 wt% 8.5 wt% 57.9 wt%	~ 0.34 ~ 2.2 ~0.45 ~ 0.87	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup> 1865.2 mAh g <sup>-1</sup> at 4.5 A g <sup>-1</sup>	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> <sup>1</sup> 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 830 mAh g <sup>-</sup> <sup>1</sup> at 2.0 A g <sup>-</sup> <sup>1</sup> 897.4 mAh	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 158.4 mAh g <sup>-1</sup> at 0.17 A g <sup>-1</sup> 897.4 mAh	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup> 0.84 mAh cm <sup>-2</sup> at 2.0 mA cm <sup>-2</sup> 1.35 mAh	2 3 4 5
P@N-MPC composites P/CNTs@rGO P@C-GO/ MOF-5 RP/rGO	22.6 wt% 70 wt% ~44.5 wt% 57.9 wt%	5.2 wt% 10.6 wt% 8.5 wt% 57.9 wt%	~ 0.34 ~ 2.2 ~0.45 ~ 0.87	A g <sup>-1</sup> 2522.1 mAh g <sup>-1</sup> at 4.4 A g <sup>-1</sup> 2007.1 mAh g <sup>-1</sup> at 0.74 A g <sup>-1</sup> 1865.2 mAh g <sup>-1</sup> at 4.5 A g <sup>-1</sup> 1550 mAh g <sup>-1</sup> at 1 A	g <sup>-1</sup> 570 mAh g <sup>-</sup> <sup>1</sup> at 1.0 A g <sup>-</sup> <sup>1</sup> 1405 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 830 mAh g <sup>-</sup> <sup>1</sup> at 2.0 A g <sup>-</sup> <sup>1</sup> 897.4 mAh g <sup>-1</sup> at 0.58 A	g <sup>-1</sup> 131.5 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> 211.9 mAh g <sup>-1</sup> at 0.52 A g <sup>-1</sup> 158.4 mAh g <sup>-1</sup> at 0.17 A g <sup>-1</sup> 897.4 mAh g <sup>-1</sup> at 0.58 A	mA cm <sup>-2</sup> 0.85 mAh cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup> 4.4 mAh cm <sup>-2</sup> at 1.6 mA cm <sup>-2</sup> 0.84 mAh cm <sup>-2</sup> at 2.0 mA cm <sup>-2</sup> 1.35 mAh cm <sup>-2</sup> at 0.87	2 3 4 5

P@AC@PPy	52 wt%	10 wt%	0.62	800 mAh	416 mAh g-	80 mAh g <sup>-1</sup>	0.5 mAh	6
				g-1 at 0.1 A	<sup>1</sup> at 0.05 A	at 0.01 A g <sup>-1</sup>	cm <sup>-2</sup> at 0.06	
				g-1	g-1		mA cm <sup>-2</sup>	
RH-3-1-RP/CS	60 wt%	23.4 wt%	3	1027 mAh	616.2 mAh	240.3 mAh	3.1 mAh	7
				g-1 at 4 A	g-1 at 2.4 A	g-1 at 0.9 A	cm <sup>-2</sup> at 12	
				g <sup>-1</sup>	g <sup>-1</sup>	g <sup>-1</sup>	mA cm <sup>-2</sup>	
NRP-rGO	56.3 wt%	18 wt%	0.39	1176 mAh	662 mAh g-	211.7 mAh	0.46 mAh	8
				g-1 at 3.6 A	<sup>1</sup> at 2 A g <sup>-1</sup>	g <sup>-1</sup> at 0.65 A	cm <sup>-2</sup> at 1.4	
				g-1		g-1	mA cm <sup>-2</sup>	
S-P/ rGO	45.6 wt%	12 wt%	0.9	1364.1	622 mAh g-	163.7 mAh	1.2 mAh	9
				mAh g <sup>-1</sup> at	<sup>1</sup> at 1.2 A g <sup>-</sup>	g-1 at 0.31 A	cm <sup>-2</sup> at 2.3	
				2.6 A g <sup>-1</sup>	1	g <sup>-1</sup>	mA cm <sup>-2</sup>	

a. The calculated gravimetric capacity of whole electrode is based on the mass of active materials, binder, conductive additive and current collectors (Capacity <sub>electrode</sub> = capacity <sub>active materials</sub>/ (mass <sub>active materials</sub> + mass <sub>binder</sub> + mass <sub>conductive additive</sub> + mass <sub>current</sub> <sub>collectors</sub>)). The current density of whole electrode is according to the reported current density based on the P multiplying by the weight ratio of P in composites, such as : Current density <sub>electrode</sub> = Current density <sub>active materials</sub> × weight ratio <sub>active materials</sub>. All the loading mass is according to the reported value in references.

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