Supporting Information

TiO_2 nanocrystals-embedded sulfur-doped porous carbon as high-performance and long-life anode material for sodium-ion batteries

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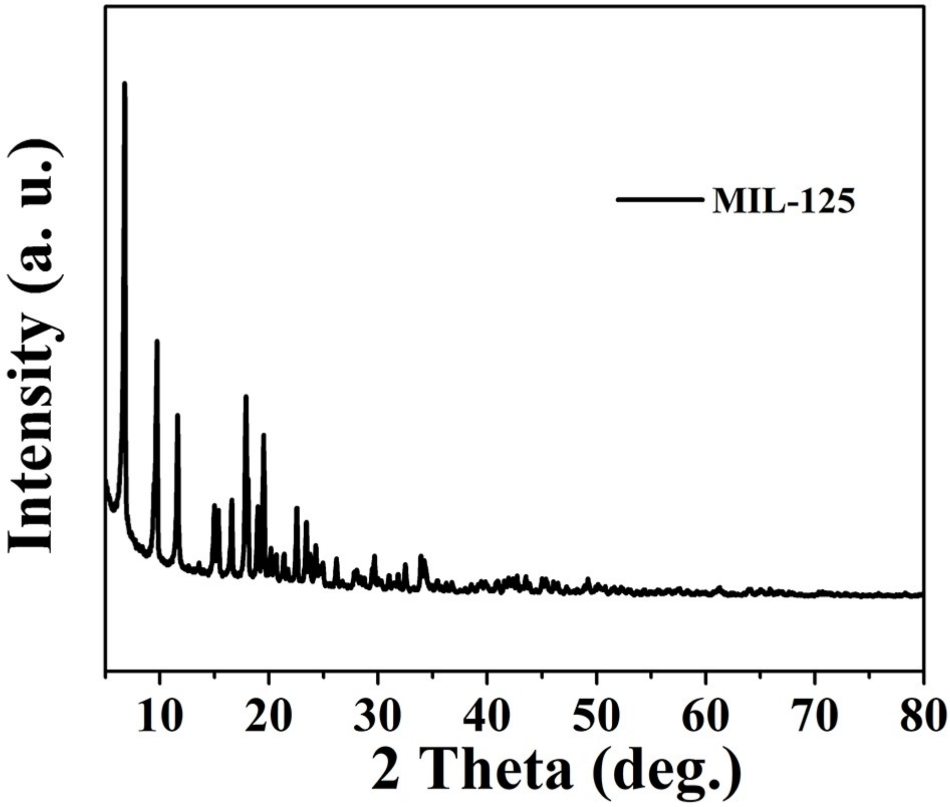

Fig. S1 XRD pattern of as-synthesized MIL-125(Ti).

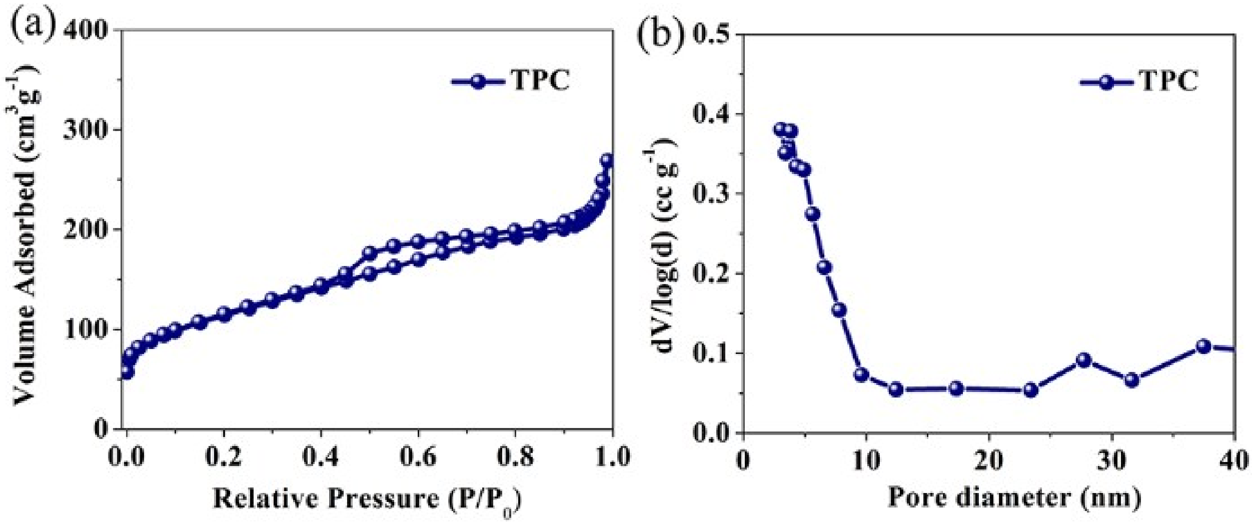

Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distribution curves of TPC.

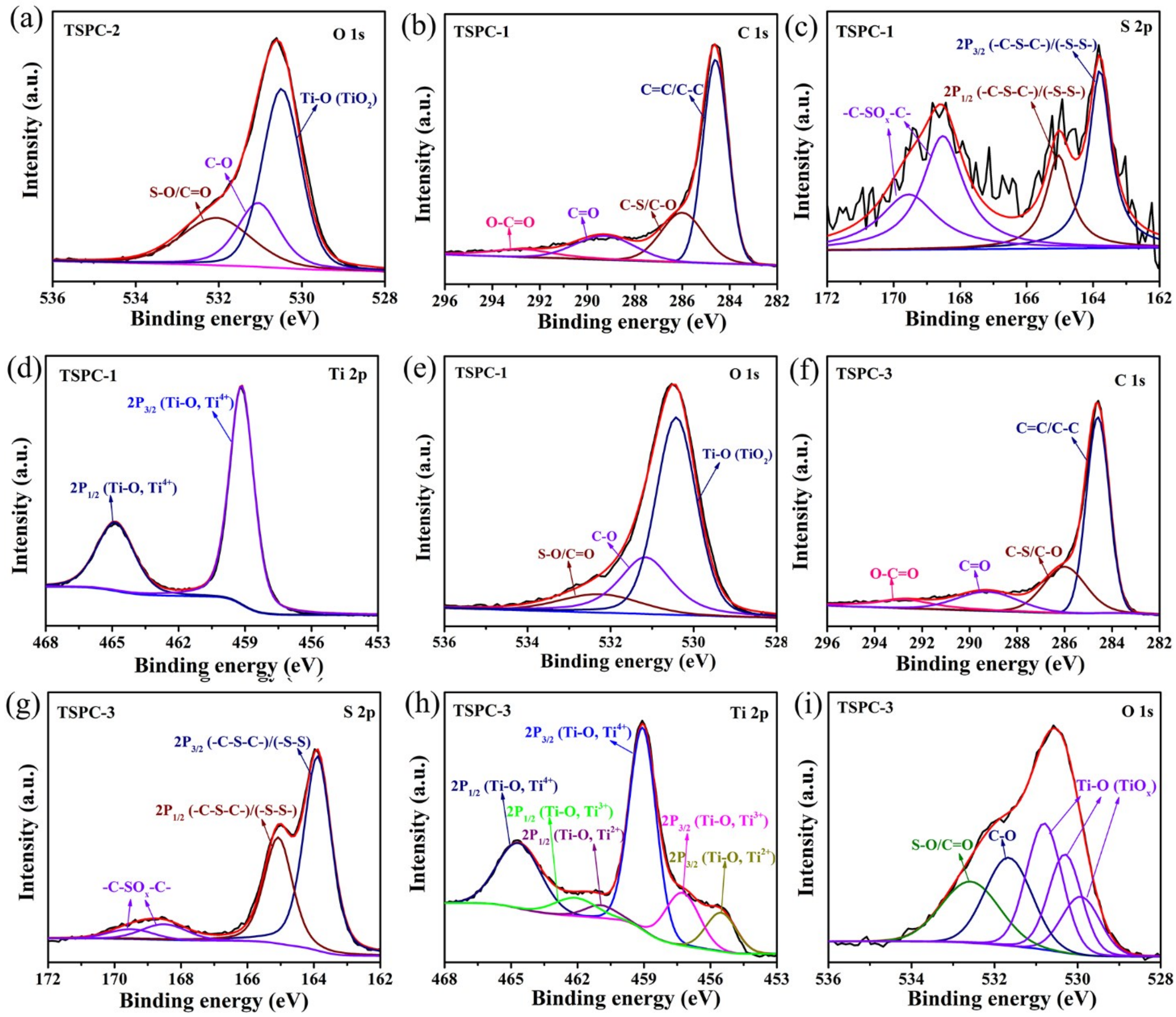

Fig. S3 XPS O 1s (a) spectra of TSPC-2. XPS C 1s (b), S 2p (c), Ti 2p (d) and O 1s (e) spectra of TSPC-1. XPS C 1s (f), S 2p (g), Ti 2p (f) and O 1s (i) spectra of TSPC-3.

The high deconvolutions of XPS C 1s, S 2p, Ti 2p, O 1s spectra of TSPC-1 and C 1s, S 2p spectra of TSPC-3 are similar to those of TSPC-2. However, for the high deconvolution of Ti 2p spectra of TSPC-3, two new fitted peaks at binding energies of 455.48 and 461.0 eV should be assigned to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti^{2+}, while the other two new fitted peaks at binding energies of 457.25 and 462.2 eV should be attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti^{3+}.[1] For the high deconvolution of O 1s spectra of TSPC-3, three new fitted peaks at binding energies of 529.9, 530.3 and 530.79 eV should be ascribed to the covalent bonds of TiO_x (TiO, Ti_2O_3 and TiO_2).[1] It should be noted that part of TiO in the outermost layer of TSPC-3 was further oxidized to Ti_2O_3 and TiO_2 due to its exposure to ambient environment.[2] The difference between XRD and XPS results of TSPC-3 is due to the fact that the measuring depth of XPS is only several nanometers but that for XRD is much deeper.[3]

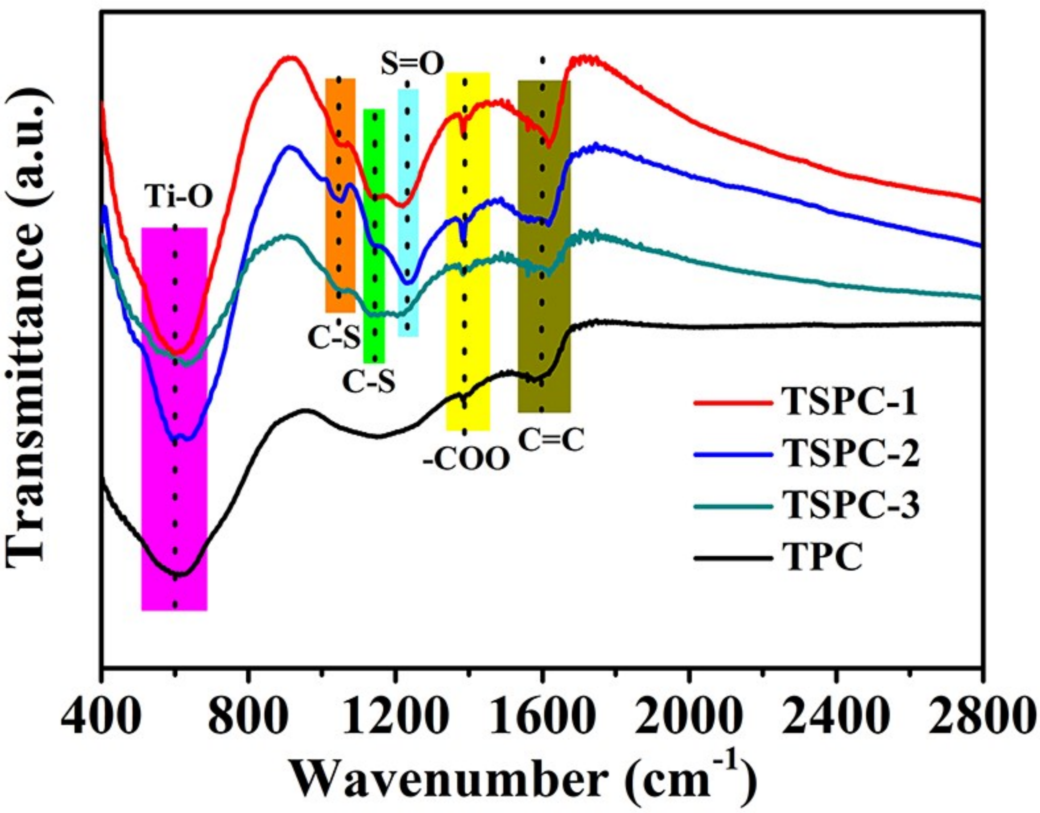

Fig. S4 FTIR spectra of TPC, TSPC-1, TSPC-2 and TSPC-3.

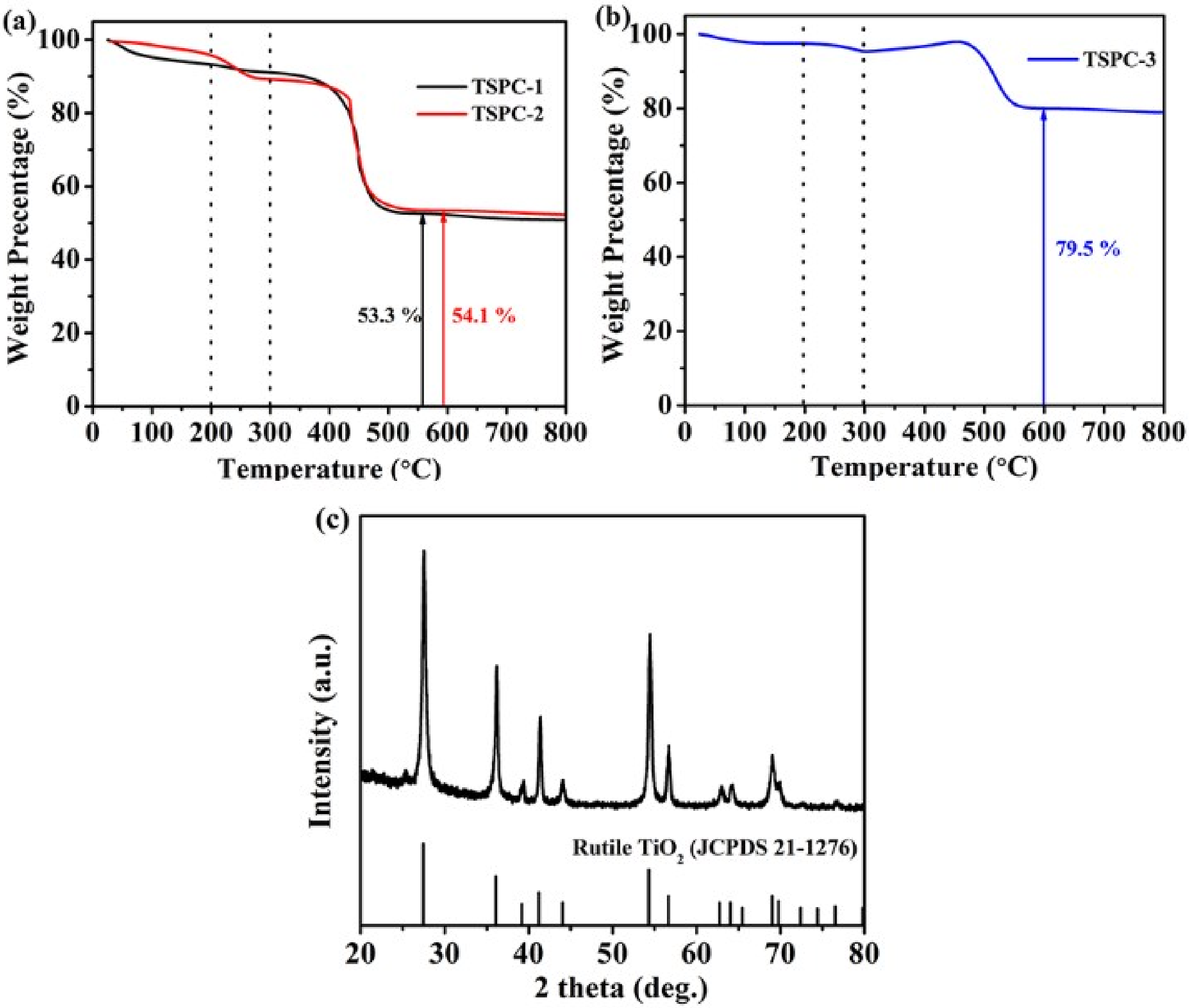

Fig. S5 (a) TG curves of TSPC-1 and TSPC-2 in air at a heating rate of 10 ˚C/min. (b) TG curves of TSPC-3 in air at a heating rate of 10 ˚C/min. (c) XRD pattern of TSPC-3 after TG test.

For TSPC-1 and TSPC-2, as sulfur-doped carbon can be completely burned in air, the resulting product will be only TiO_2. Therefore, the contents of TiO_2 in TSPC-1 and TSPC-2 are 53.3% and 54.1%, respectively. As seen in Fig. S5c, the diffraction peaks of TSCP-3 after TG test can be indexed to rutile TiO_2 (JCPDS 21-1276). Therefore, the weight loss between 330 and 600 °C is attributed to both the combustion of sulfur-doped carbon and oxidation of TiO. The content of TiO in TSPC-3 can be calculated by the following equation:

$$wt.\%(TiO) = wt.\%R \times \frac{M(TiO)}{M(TiO_2)} \tag{S1}$$

where wt.%R is the weight remaining percentage after 600 ˚C, and M represents the molecular mass of TiO and TiO_2.

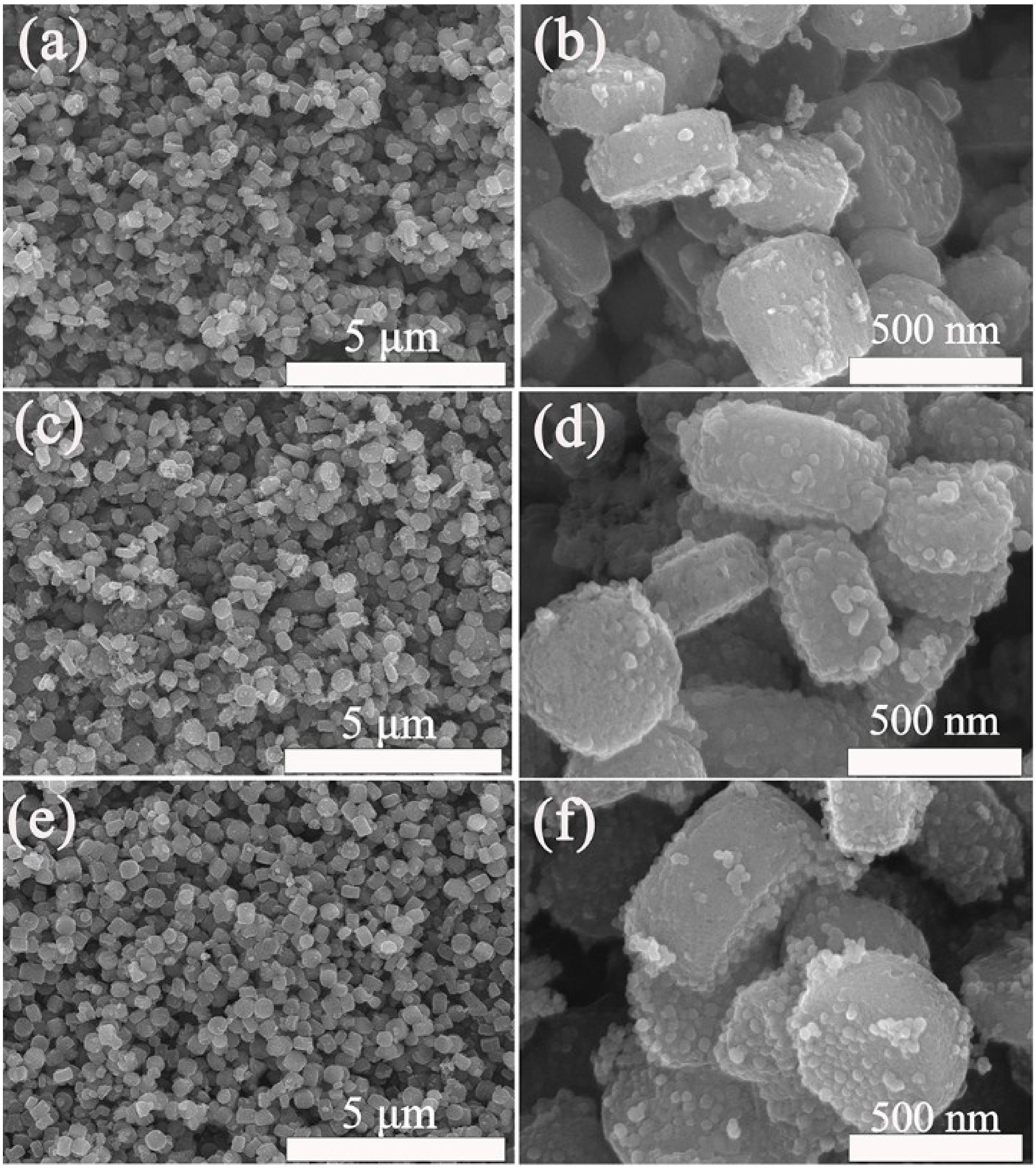

Fig. S6 FESEM images of (a,b) TPC, (c,d) TSPC-1 and (e,f) TSPC-3.

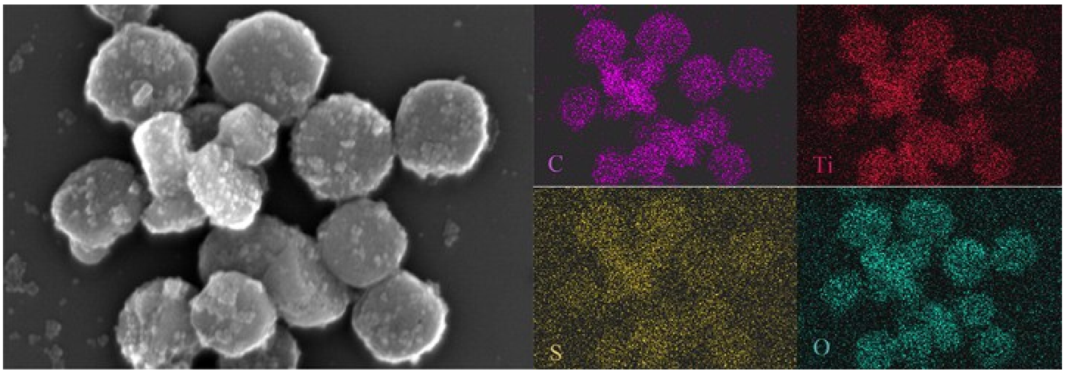

Fig. S7 EDS mapping of TSPC-2.

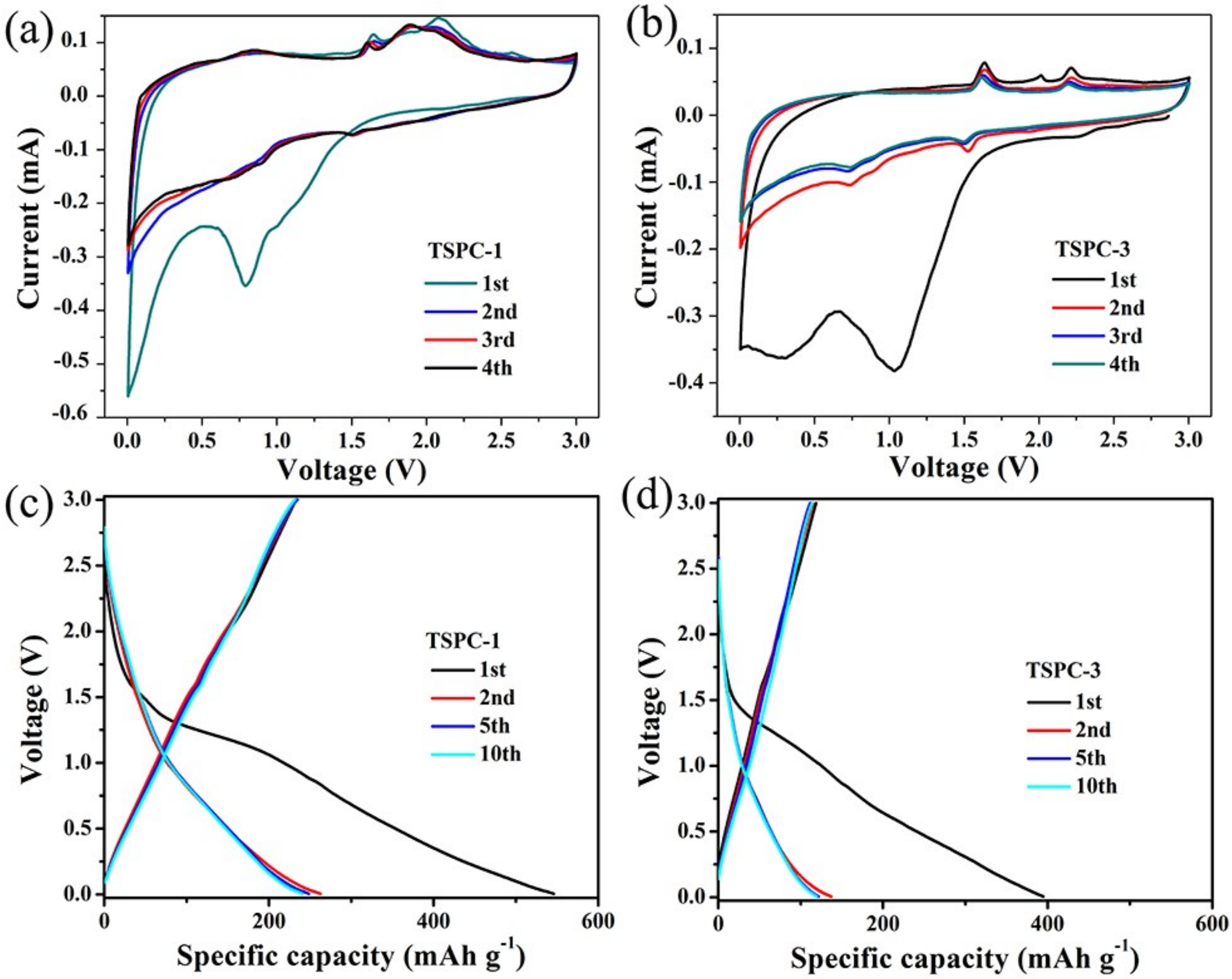

Fig. S8 CV curves of (a) TSPC-1 and (b) TSPC-3 at a scan rate of 0.2 mV s^{-1} between 0.005 and 3 V. Charge /discharge profiles of (c) TSPC-1 and (d) TSPC-3 at different cycles at a current density of 50 mA g^{-1}.

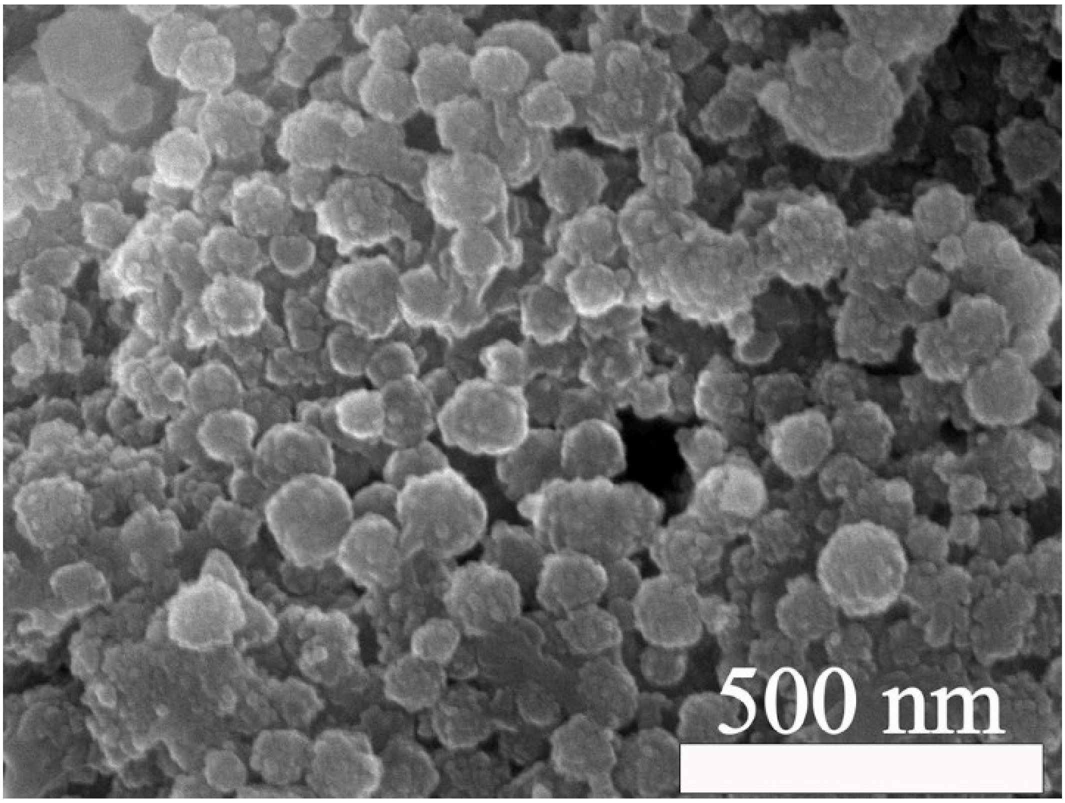

Fig. S9 FESEM images of TSPC-2 electrode after 100 cycles at a current density of 50 mA g^{-1}.

Table S1 Specific surface areas, pore volumes and mean pore diameters of TSPC-1, TSPC-2 and TSPC-3 measured by BET method.

Sample	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Mean pore diameter (nm)
TPC	404.5	0.27	3.06
TSPC-1	343.5	0.58	3.45
TSPC-2	380.2	0.40	3.40
TSPC-3	401.7	0.38	3.20

Table S2 Weight percentages of carbon and sulfur in TSPC determined from the EA.

Sample	C (wt.%)	S (wt.%)
TSPC-1	25.9	8.3
TSPC-2	19.7	14.2
TSPC-3	18.1	4.3

Table S3 Sodium-storage performance of TSPC-2 in this work compared with other reported TiO_2-based anode material in the literatures.

Anode	Discharge capacity (mA h g^{-1})	Current Density (mA g^{-1})	Cycle number (cycles)	Reference
TiO_2/C nanofibers	237.1	200	1000	Ref. S4
C-TiO_2 microspheres	155	20	50	Ref. S5
Hybrid TiO_2@graphene	186.6	100	100	Ref. S6
Carbon-coated TiO_2 nanoparticles	210.7	30	100	Ref. S7
Anatase/bronze TiO_2/C	143	167.5	300	Ref. S8
Carbon-coated rutile TiO_2	175	84	200	Ref. S9
Graphene@nitrogen doped carbon@TiO_2	263	50	200	Ref. S10
Anatase TiO_2@C composites	167.4	100	110	Ref. S11
Graphene-supported TiO_2 nanospheres	208	20	200	Ref. S12
TSPC-2	323	50	100	This work
Anatase/bronze TiO_2/C	104	3350	6000	Ref. S8
Carbon-coated rutile TiO_2	70	3360	2000	Ref. S9

Graphene@nitrogen doped carbon@TiO_2	108.8	1000	5000	Ref. S10
Anatase TiO_2@C composites	148	500	500	Ref. S11
Nitrogen doped graphene grafted TiO_2	425.6	2000	200	Ref. S13
TSPC-2	207.6	2500	1500	This work

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