Supplementary Information for

Space-Confined Twin-Polymerization Enabling Homogeneous Integration of Ultrafine TiO_2 Nanoparticles into Sulfur-Doped Carbon Matrix for Boosting Lithium Storage

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Experimental section

Materials: 2-Thiophenemethanol (98%, ThM), and titanium ethoxide (TTEO) were purchased from Beijing Bailingwei Co., Ltd. Trifluoroacetic acid (CF_3COOH), toluene, dichloromethane, ethanol, acetone and *n*-hexane are commercially available from Sinopharm Group Chemical Reagent Co., Ltd., China. All chemical solvents are analytical grade, and were purified by distillation before use.

Synthesis of Ti-ThM: ThM (8.12 g, 6.7 mL), TTEO (4.01g, 3.7 mL) and 0.3 wt% KOH were mixed at 80°C for 1 h and then 100°C for 1 h under an argon atmosphere [Refs: *Macromol. Rapid Commun.*, 2015, **36**, 1623; *Macromol. Theory Simul.*, 2012, **21**, 615]. The reaction mixture was subjected to the re-crystallization by a pre-mixed solvent of toluene and *n*-hexane (1:1 v/v). The brown crystal (6.7 g) of Ti-ThM was collected by drying at 60°C overnight under vacuum.

Preparation of tp-TiO_2@SC derived from twin polymerization: Typically, Ti-ThM (2.0 g) was dissolved in toluene (10 mL) at room temperature, and the resulting mixture was slowly added to a solution of CF_3COOH (0.89 mL) in dichloromethane (5 mL) under an argon atmosphere. The brown solution was then heated to 60°C for 0.5 h and 100°C for 1 h, depositing a brownish black solid. The generated SiO_2@poly(2-thiophenemethanol) (TiO_2@PThM) composite was filtered and washed using dichloromethane, ethanol, and acetone until the filtrate was colorless. The dark TiO_2@PThM product was further yielded by drying under vacuum at 60°C overnight. Finally, the resulted powder was thermally annealed at 550°C for 5 h under argon atmosphere, producing ultrafine TiO_2 nanoparticles encapsulated in the S-doped carbon matrix (*tp*-TiO_2@SC).

Preparation of sp-TiO_2/SC *derived from simultaneous polymerization:* For comparison, *sp*-TiO_2/SC was similarly produced by simultaneous polymerization as described elsewhere [Ref: *Energy Technol.*, 2019, **7**, 1900247]. As mentioned above, Ti-ThM has a stoichiometric ratio (3.5:1) of ThM to TTEO in its chemical structure. Therefore, two individual monomers of

ThM and TTEO with an equivalent feed ratio of 3.5:1 were simultaneously initiated by CF_3COOH to perform one-pot cationic polymerization under identical experimental processes (**Fig. S4a**). The *sp*-TiO_2/SC product was finally obtained by carbonizing the TiO_2/PThM composite.

In a control experiment, bulk TiO_2 nanoparticles were also prepared using ethanol instead of ThM under similar experimental conditions as reported previously [Ref: *Energy Technol.*, 2019, **7**, 1900247].

Materials characterization: TEM images were obtained from TecnaiG20 transmission electron microscope at an acceleration voltage of 200 kV. XRD patterns were collected on a Rigaku D/Max2400 diffractometer equipped with a CuKα radiation source in the range of 2θ =5-80°. Vibrational properties were analyzed using a Renishaw Raman spectrometer by exciting at 514.5 nm. TGA was carried out on a Mettler Toledo (Switzerland) at a heating rate of 20°C min^{-1} in air atmosphere. XPS spectra were determined by X-ray photoelectron spectrometer (PHI MultiPak) with an excitation source of Mg Kα radiation.

Electrochemical measurements: Battery measurements were performed using a coin-type cell (model 2032). The electrodes were fabricated by mixing 80% active materials, 10% acetylene black, and 10% polyvinylidene fluoride in *N*-methyl pyrrolidone. The resulting uniform slurry was then coated onto a Cu foil and the solvent was evaporated at 90°C for 12 h under vacuum. The lithium foil, the porous membrane (Celgard 2400) were used as the counter electrode, and the separator, respectively. 1 M $LiPF_6$ solution in a 1:1 (volume) mixture of ethylene carbonate and dimethyl carbonate was used as the electrolyte. Charge/discharge profiles were recorded on a LAND CT2001A battery measurement system. Both CV and EIS tests were performed on a CHI 760D electrochemical work station.

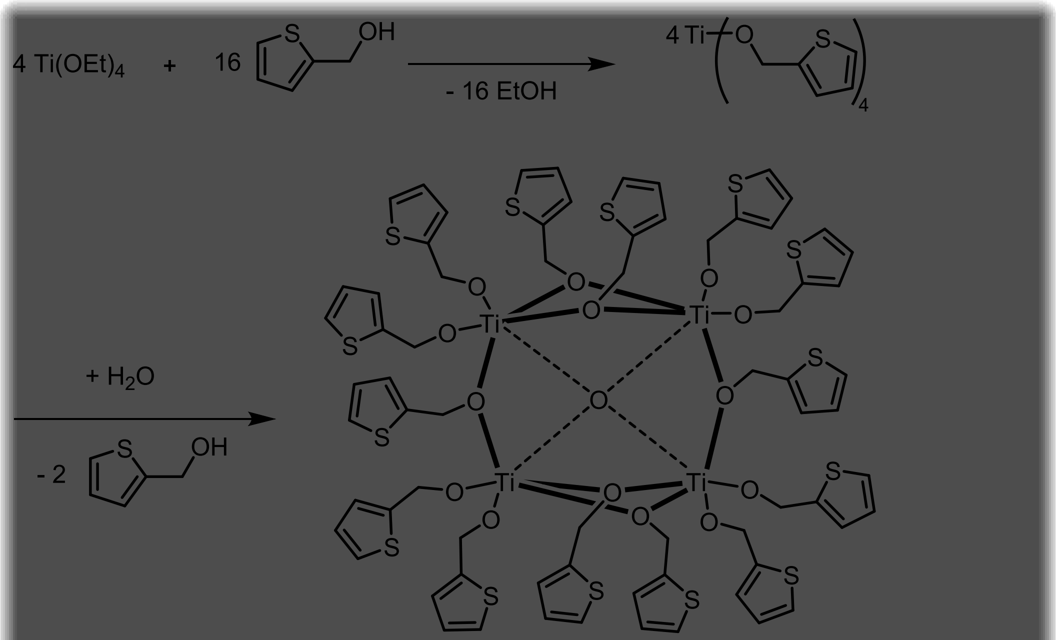

Fig. S1 Synthesis routes of (μ4-oxido)-hexakis(μ-thiophene-2-methoxo)-octakis(thiophene-2-methoxo)-tetratitanium (Ti-ThM).

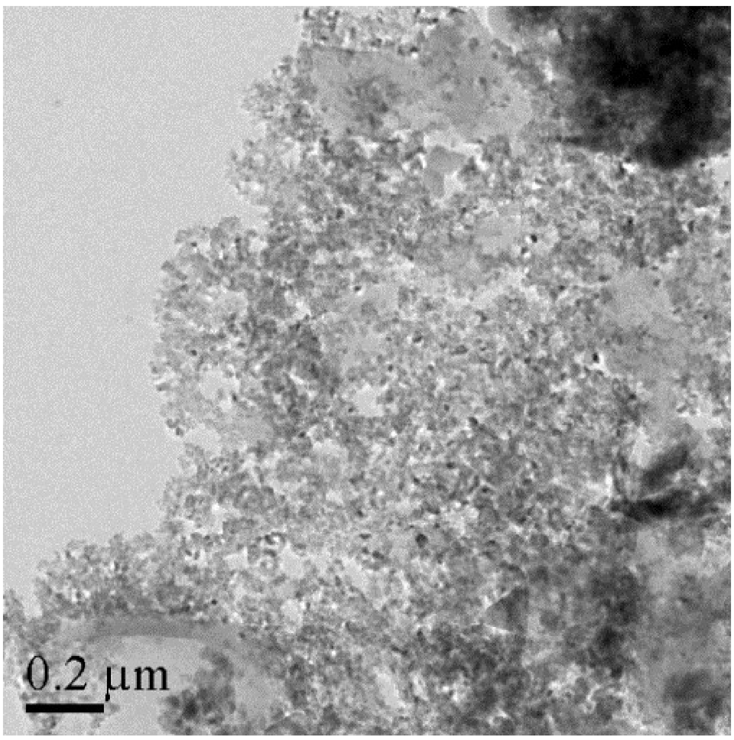

Fig. S2 Typical TEM image of the TiO_2@PThM composite.

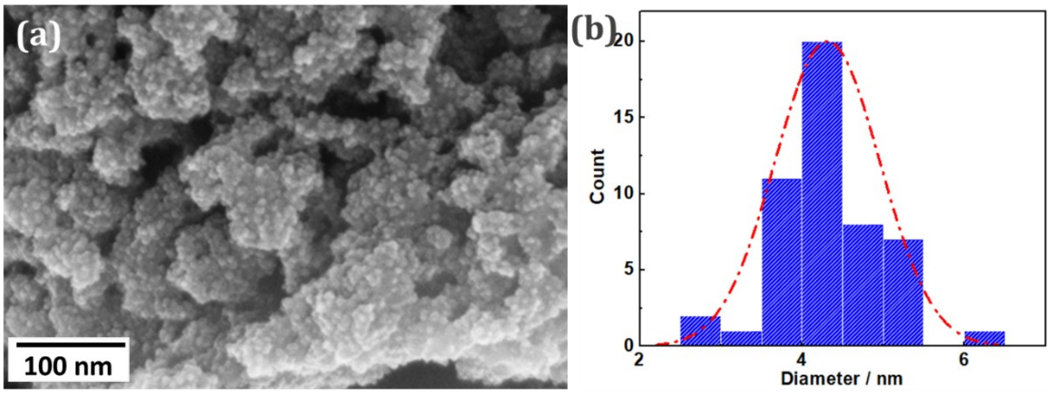

Fig. S3 (a) Typical SEM image, and (b) size distribution diagram of *tp*-TiO_2@SC.

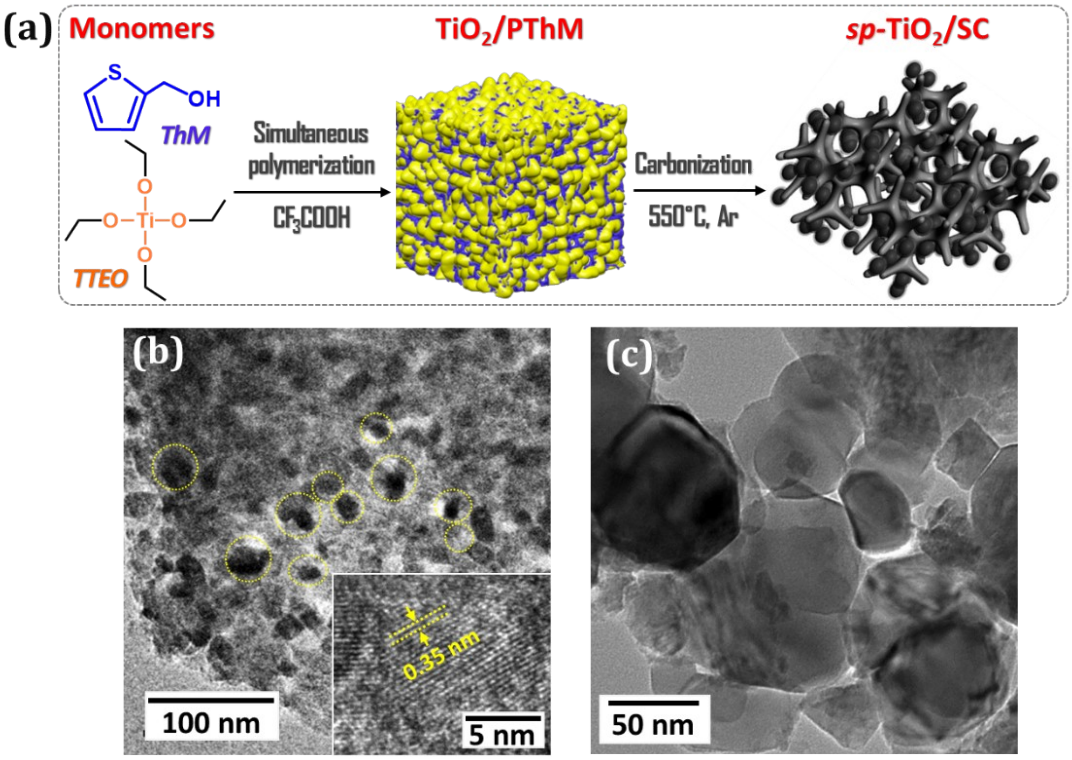

Fig. S4 (a) CF_3COOH-catalyzed simultaneous polymerization of individual ThM and TTEO with an equivalent feed ratio of 3.5:1 to produce the TiO_2/PThM composite and subsequent thermal carbonization to form TiO_2 nanoparticles in the S-doped carbon matrix (*sp*-TiO_2/SC), and typical TEM images of (b) *sp*-TiO_2/SC and (c) bulk TiO_2.

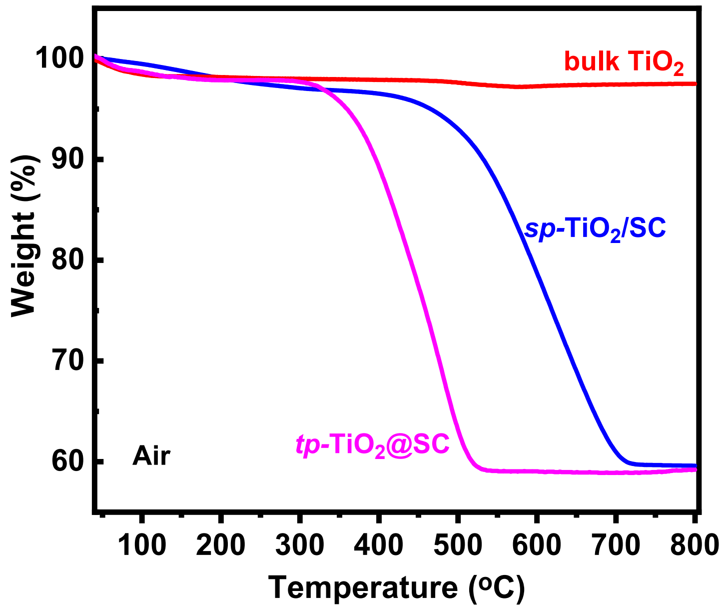

Fig. S5 TGA cures of *tp*-TiO_2@SC, *sp*-TiO_2/SC, and bulk TiO_2 meaused in air.

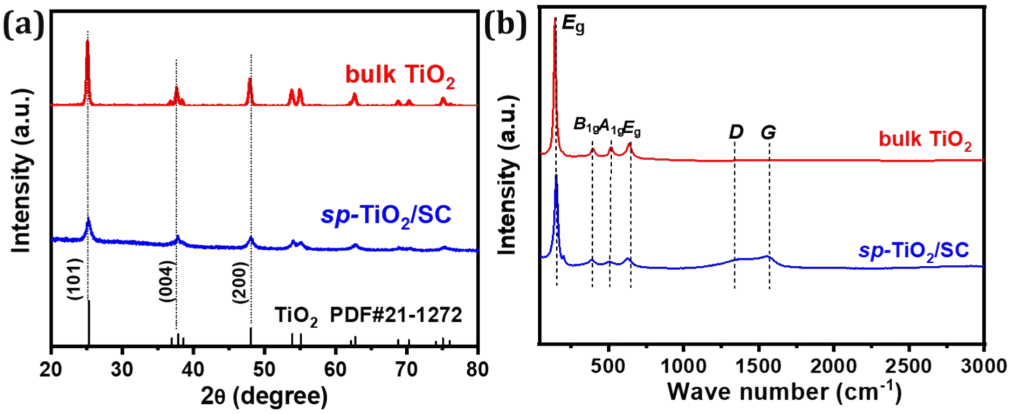

Fig. S6 (a) XRD patterns and (b) Raman spectra of *sp*-TiO_2/SC, and bulk TiO_2.

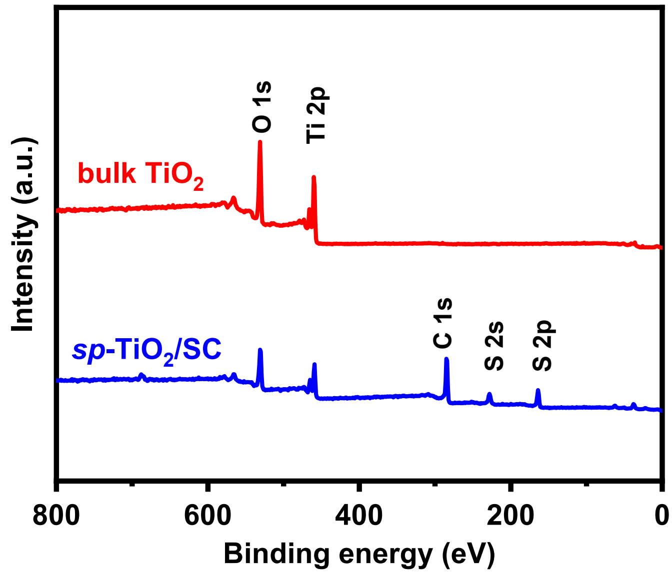

Fig. S7 XPS survey spectra of *sp*-TiO_2/SC, and bulk TiO_2.

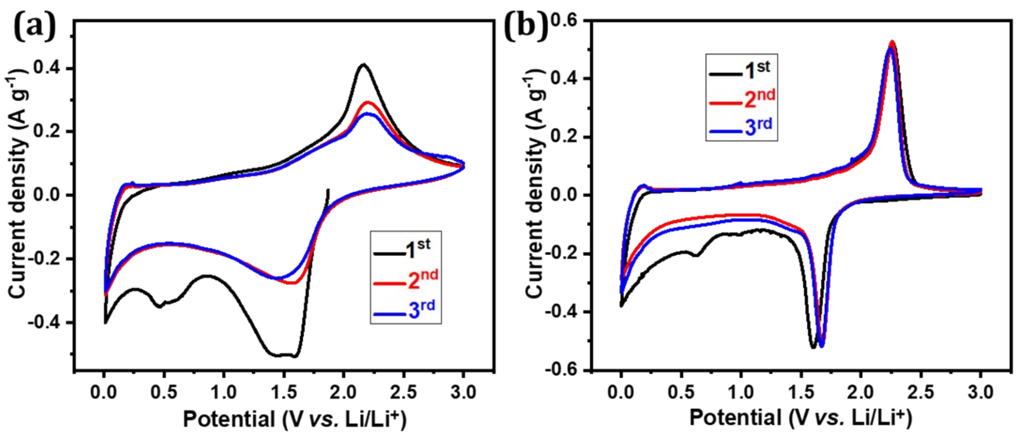

Fig. S8 CV profiles of (a) *sp*-TiO_2/SC, and (b) bulk TiO_2 at 0.2 mV s^{-1}.

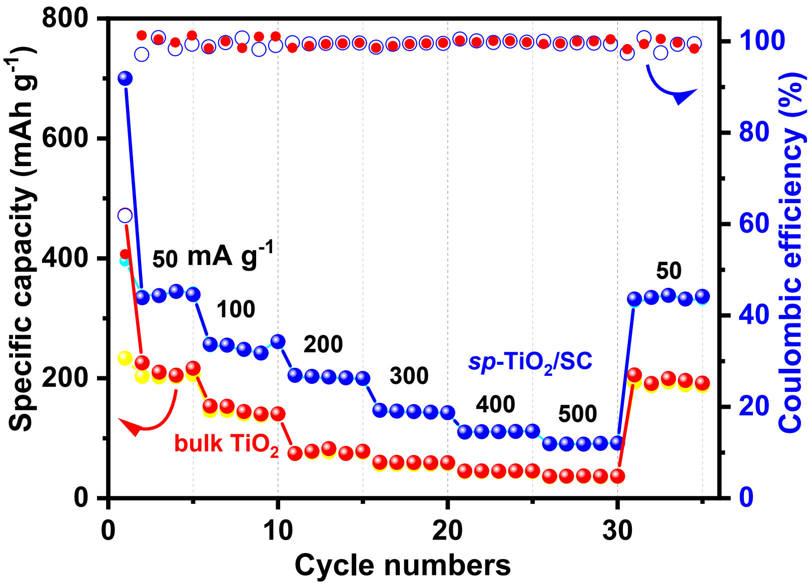

Fig. S9 Rate performance of *sp*-TiO_2/SC and bulk TiO_2 in the range of 50 to 500 mA g^{-1}.

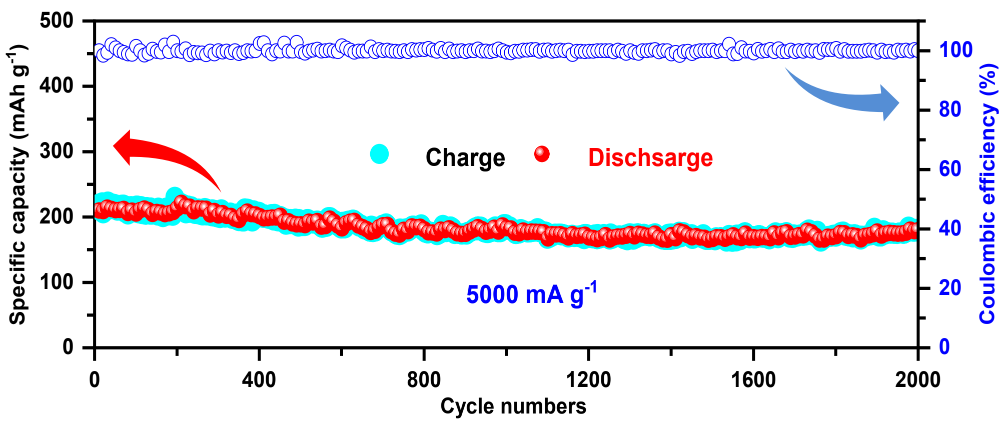

Fig. S10 Cycling stability after running 2000 cycles at 5000 mA g^{-1} for *tp*-TiO_2@SC.

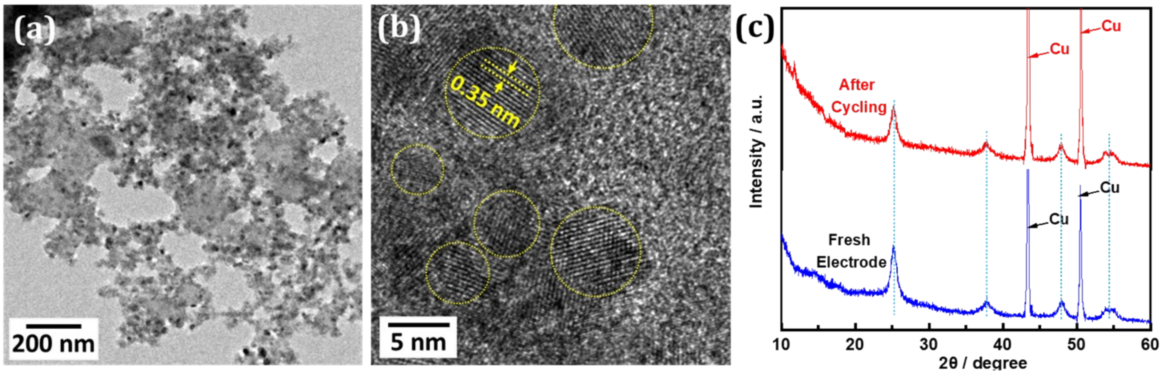

Fig. S11 Typical TEM images (a, b) and (c) XRD patterns of the *tp*-TiO_2@SC electrode after running 200 cycles at 50 mA g^{-1}.

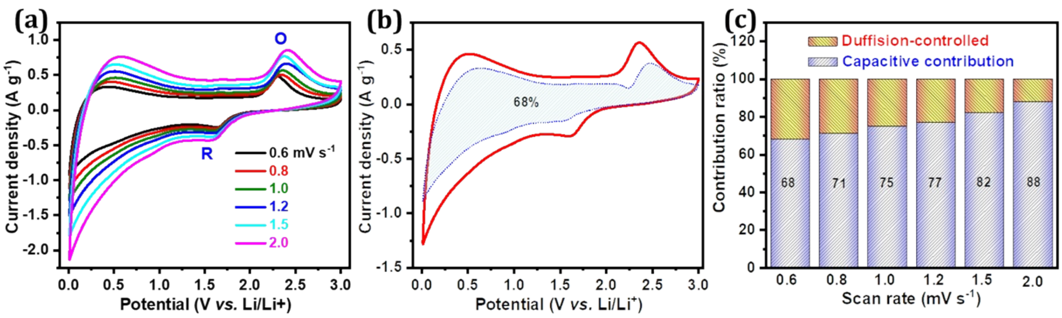

Fig. S12 (a) CV curves of *tp*-TiO_2@SC at sweep rates of 0.6 to 2.0 mV s^{-1}, (b) the capacitive- (blue) and diffusion-controlled contribution (blank) at 0.6 mV s^{-1}, and (c) the normalized capacitive-/diffusion-controlled contribution fractions at various scan rates.

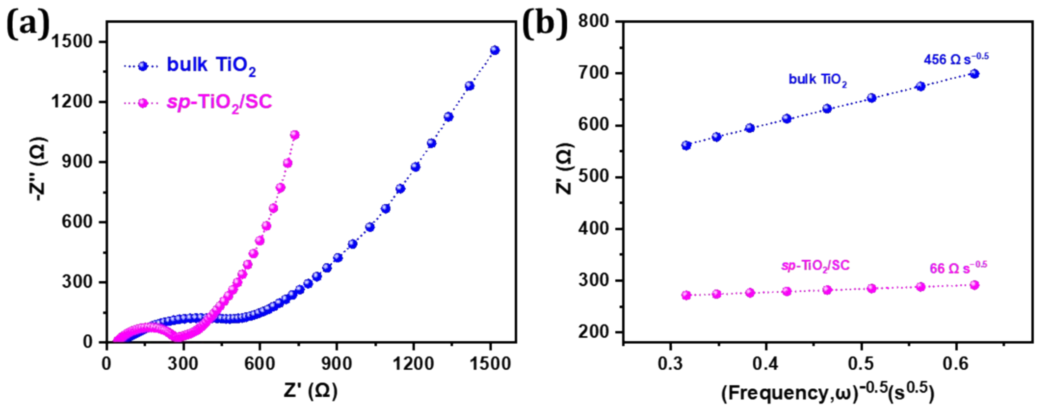

Fig. S13 (a) Nyquist plots and (b) the relationship between the real part of impedance (*Z*') and the reciprocal of square root of frequency ($\omega^{-0.5}$) of *sp*-TiO_2/SC and bulk TiO_2.

Table S1 Lithium storage performance of TiO_2/carbon composites

Materials	**TiO_2 size (nm)**	**Carbon (wt%)**	**Cycle performance**	**Rate capability**	References
***sp*-TiO_2@SC**	**5**	**40.9**	**582 mAh g^{-1} after 200 cycles at 0.05 A g^{-1} 144 mAh g^{-1} after 2000 cycles at 5 A g^{-1}**	**667 mAh g^{-1} at 0.05 A g^{-1} 313 mAh g^{-1} at 0.5 A g^{-1}**	**This work**
TiO_2/metal-organic frameworks	9.9	35.7	446 mAh g^{-1} after 1000 cycles	646 mAh g^{-1} at 0. 017 A g^{-1} 335 mAh g^{-1} at 3.36 A g^{-1}	[1] *Chem. Eng. J.* 2022, 430,132689
TiO_2/porous carbons	-	72	377 mAh g^{-1} after 50 cycles	377 mAh g^{-1} at 0.035 A g^{-1} 117 mAh g^{-1} at 0.7 A g^{-1}	[2] *Res. Chem. Intermed.* 2017, 43,2891
TiO_2/graphitic carbons	-	-	321 mAh g^{-1} after 1000 cycles	434 mAh g^{-1} at 0.1 A g^{-1} 255 mAh g^{-1} at 5 A g^{-1}	[3] *Surf. Interfaces* 2022, 35,102404
TiO_2/N-rich carbons	60~150	54.8	303 mAh g^{-1} after 125 cycles	297 mAh g^{-1} at 0.034 A g^{-1} 87 mAh g^{-1} at 3.35 A g^{-1}	[4] *Electrochim. Acta* 2017, 255, 417
TiO_2@N-doped C	-	17	462 mAh g^{-1} after 300 cycles	382 mAh g^{-1} at 0.05 A g^{-1} 112 mAh g^{-1} at 10 A g^{-1}	[5] *Electrochim. Acta* 2019, 299, 540
TiO_2@N-doped carbon coaxial nanotubes	-	33.6	480 mAh g^{-1} after 80 cycles	480 mAh g^{-1} at 0.1 A g^{-1} 140 mAh g^{-1} at 2 A g^{-1}	[6] *Appl. Surf. Sci.* 2018, 458, 1018
S-doped carbon@TiO_2	4~8	78.1	648 mAh g^{-1} after 200 cycles	768 mAh g^{-1} at 0.1 A g^{-1} 442 mAh g^{-1} at 2 A g^{-1}	[7] *Energy Storage Mater.* 2018, 13, 215
carbon@mesoporous TiO_2@CNTs	5~6	39.8	191 mAh g^{-1} after 200 cycles	223 mAh g^{-1} at 0.017 A g^{-1} 115 mAh g^{-1} at 0.85 A g^{-1}	[8] *Electrochim. Acta* 2019, 312, 119
R-TiO_2@C hollow spheres	>10	5.7	191 mAh g^{-1} after 200 cycles	310 mAh g^{-1} at 0.668 A g^{-1} 50 mAh g^{-1} at 3.34 A g^{-1}	[9] *J. Alloy. Compd.* 2023, 969, 172258
TiO_2 on graphene	-	18.9	573 mAh g^{-1} after 600 cycles	373 mAh g^{-1} at 0.1 A g^{-1} 199 mAh g^{-1} at 5 A g^{-1}	[10] *J. Mater. Chem. A* 2018, 6, 7070
Watermelon-like TiO_2@carbon sphere	~25	65.9	312 mAh g^{-1} after 200 cycles	496 mAh g^{-1} at 0.085 A g^{-1} 180 mAh g^{-1} at 3.4 A g^{-1}	[11] *Nanotechnology* 2020, 31, 215407
Nanowires embedded porous TiO_2@C	-	88	128 mAh g^{-1} after 2500 cycles	271 mAh g^{-1} at 0.105 A g^{-1} 32 mAh g^{-1} at 10.5 A g^{-1}	[12] *Ceram. Int.* 2020, 46, 9119
TiO_2/Carbon nanosheets	-	~40	273 mAh g^{-1} after 1500 cycles	575 mAh g^{-1} at 0.1 A g^{-1} 79 mAh g^{-1} at 12.8 A g^{-1}	[13] *ACS Appl. Nano Mater.* 2021, 4, 11288
TiO_2/S-doped carbon fibers	-	78.9	607 mAh g^{-1} after 150 cycles	738 mAh g^{-1} at 0.1 A g^{-1} 454 mAh g^{-1} at 2 A g^{-1}	[14] *Small* 2019, 15, 1902201

TiO_2@CNTs	-	-	201 mAh g^{-1} after 650 cycles	272 mAh g^{-1} at 0.1 A g^{-1} 133 mAh g^{-1} at 40 A g^{-1}	[15] *Adv. Mater. Interfaces* 2016, 3, 1600375
TiO_2@N-doped carbon foams	10	-	149 mAh g^{-1} after 100 cycles	203 mAh g^{-1} at 0.1 A g^{-1} 104 mAh g^{-1} at 2 A g^{-1}	[16] *Small* 2016, 12, 6724
Carbon nanolayer-wrapped TiO_2	30	15.5	403 mAh g^{-1} after 1000 cycles	474 mAh g^{-1} at 0.1 A g^{-1} 182 mAh g^{-1} at 5 A g^{-1}	[17] *ACS Appl. Nano Mater.* 2021, 4, 7832
TiO_2@carbon microspheres	20-50	28.2	322 mAh g^{-1} after 100 cycles	351 mAh g^{-1} at 0.1 A g^{-1} 145 mAh g^{-1} at 2 A g^{-1}	[18] *Diam. Relat. Mater.* 2023, 136, 109913
TiO_2/carbon nanosheets	100	1.6	89 mAh g^{-1} after 500 cycles	287 mAh g^{-1} at 0.05 A g^{-1} 169 mAh g^{-1} at 2 A g^{-1}	[19] *Adv. Mater. Interfaces* 2022, 9, 2102375
N-doped carbon-coated TiO_2 hollow spheres	-	10.1	166 mAh g^{-1} after 2000 cycles	390 mAh g^{-1} at 0.1 A g^{-1} 141 mAh g^{-1} at 10 A g^{-1}	[20] *Nanoscale.* 2021, 13, 2 368
Carbon-coated TiO_2	14.5	3.5		225 mAh g^{-1} at 0.168 A g^{-1} 91 mAh g^{-1} at 8.4 A g^{-1}	[21] *ACS Appl. Mater. Interfaces* 2019, 11, 11391
TiO_2 encapsulated by sawdust-derived biochar	10	-	100 mAh g^{-1} after 2500 cycles	418 mAh g^{-1} at 0.1 A g^{-1} 60 mAh g^{-1} at 5 A g^{-1}	[22] *Sci. Total Environ.* 2021, 794, 148688
TiO_2 in pomegranate- like carbon sphere	10~20	68.9	203 mAh g^{-1} after 2000 cycles	~300 mAh g^{-1} at 0.1 A g^{-1} ~100 mAh g^{-1} at 5 A g^{-1}	[23] *J. Colloid Interf. Sci.* 2023, 633 546-554
TiO_2 in carbon nanospheres	-	67.6	895 mAh g^{-1} after 100 cycles	959 mAh g^{-1} at 0.062 A g^{-1} 244 mAh g^{-1} at 1.55 A g^{-1}	[24] *Ionics* 2022, 28, 1635
TiO_2@holely carbon nanofibers	-	19	354 mAh g^{-1} after 100 cycles	473 mAh g^{-1} at 0.1 A g^{-1} 147 mAh g^{-1} at 5 A g^{-1}	[25] *J. Alloy. Compd.* 2022, 926, 166943
Carbon modified hierarchical hollow tubes composed of TiO_2	-	-	177 mAh g^{-1} after 100 cycles	188 mAh g^{-1} at 0.175 A g^{-1} 106 mAh g^{-1} at 3.5 A g^{-1}	[26] *J. Alloy. Compd.* 2021, 857,158048
TiO_2/carbon nanosheet	10~20	6.3	110 mAh g^{-1} after 2000 cycles	220 mAh g^{-1} at 0.168 A g^{-1} 38 mAh g^{-1} at 8.4 A g^{-1}	[27] *J. Mater Sci. Technol.* 2019, 35, 1977
Graphene-boosted defective rutile TiO_{2-x}	200~300	-	157 mAh g^{-1} after 1400 cycles	254 mAh g^{-1} at 0.084 A g^{-1} 134 mAh g^{-1} at 0.84 A g^{-1}	[28] *Mater. Chem. Front.* 2021, 5, 3226
TiO_2 quantum dots confined in 3D carbon	-	12.1	76 mAh g^{-1} after 10000 cycles	421 mAh g^{-1} at 0.1 A g^{-1} 108 mAh g^{-1} at 5 A g^{-1}	[29] *J. Colloid Interf. Sci.* 2021, 582, 874
TiO_2-carbon hybrid nanostructures	-	28	321 mAh g^{-1} after 100 cycles	447 mAh g^{-1} at 0.06 A g^{-1} 251 mAh g^{-1} at 1.2 A g^{-1}	[30] *Adv. Funct. Mater.* 2016, 26, 1338
TiO_2 nanofibers decorated with N-doped carbon	8	9.2	176 mAh g^{-1} after 2000 cycles	401 mAh g^{-1} at 0. 034 A g^{-1} 97 mAh g^{-1} at 6.7 A g^{-1}	[31] *ACS Appl. Mater. Interfaces* 2018, 10, 35060
CNT-C@TiO_2	9~13	22.8	206 mAh g^{-1} after 200 cycles	414 mAh g^{-1} at 0.1 A g^{-1} 72 mAh g-1 at 1.6 A g^{-1}	[32] *J. Mater. Sci.* 2019, 54, 592.
Mesoporous TiO_2/carbon spheres	-	1.9	140 mAh g^{-1} a fter 600 cycles	161 mAh g^{-1} at 0.34 A g^{-1} 103 mAh g^{-1} at 1.7 A g^{-1}	[33] *ACS Sustainable Chem. Eng.* 2022, 10, 10955
Carbon coated TiO_2 aerogel	~5	8.6	133 mAh g^{-1} after 3000 cycles	215 mAh g^{-1} at 0.017 A g^{-1} 127 mAh g^{-1} at 3.35 A g^{-1}	[34] *Chem. Eng. J.* 2018, 351, 825