

Hollow C@TiO₂ array nanospheres as efficient sulfur hosts for lithium-sulfur batteries

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Experimental Sections

Synthesis of hollow porous carbon nanospheres: The synthesis of hollow porous carbon nanospheres is based on a previous report with certain modifications. Specifically, 6 mL of ammonia aqueous solution (25 wt%), 140 mL of ethanol and 20 mL of DI water were mixed under magnetic stirring, after which 5.4 mL of tetraethyl orthosilicate was added to the above mixture and stirred for 20 min. Resorcinol (0.8 g) and formaldehyde (1.12 mL) were then added to the solution successively and stirring continued for 24 h. The resulting precipitate was centrifuged at 8000 rpm, washed with water and ethanol for three times, and then dried at 80 °C overnight. Hollow porous carbon nanospheres were obtained after calcination at 700 °C in a N₂ atmosphere for 5 h with a heating rate of 3 °C min⁻¹, after which SiO₂ was etched off by ammonium hydrogen fluoride (5 mol L⁻¹).

Synthesis of Hollow C@TiO₂ array nanospheres: The hollow C@TiO₂ array nanospheres were prepared by solvothermal synthesis followed by heat treatment. The obtained hollow porous carbon nanospheres were briefly added to 40 mL of isopropanol and sonicated for 1 h to obtain a black suspension, after which 40 μL of diethylenetriamine was added. After stirring for 20 min, 1.8 mL of titanium(IV) isopropoxide was added and stirred for another 20 min. Then, the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated in an electric oven at 200 °C for 24 h. After cooling down to ambient temperature naturally, the products were collected by centrifugation, washed by absolute ethanol, and dried at 60 °C overnight. The dried products were further annealed at 600 °C in Ar for 2 h at a heating rate of 4 °C min⁻¹.

Fabrication of C@TiO₂/S Cathode: The C@TiO₂/S cathode was fabricated by a simple melting-diffusion method. Briefly, the C@TiO₂ nanocomposite and sublimed sulfur powder were homogeneously mixed at a weight ratio of 1:3 by milling. The mixture was then transferred to a Teflon-lined stainless-steel autoclave, heated at 155 °C, and kept for 12 h.

Electrochemical Tests: The electrodes were prepared by coating the slurry of active material on aluminum foil. The slurry was obtained by mixing the active material, Ketjen Black and poly(vinylidene fluoride) at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidinone. The electrodes were vacuum-dried at 60 °C for 12 h. The average sulfur mass loading of the electrode is about 1.4 mg cm⁻². The 2025 coin-type cells were assembled in an argon-filled glove box with lithium foils as the counter and reference electrodes. The electrolyte was composed of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a solvent of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (volume ratio = 1:1) with 2% LiNO₃. The amount of electrolyte corresponds to the ratio of 20 μL of electrolyte to 1 mg of S. The cycle and rate performance were tested by a Neware battery test system. The CV tests were performed on a CHI 660D electrochemical workstation between 1.7 and 2.8 V. The EIS tests were performed on a PARSTAT 2273 electrochemical system in a frequency range between 100 kHz and 0.1 Hz with an AC signal amplitude of 10 mV. To compare the polysulfide adsorption abilities of the C@TiO₂ nanohybrids and bare C nanospheres, a Li₂S₄ solution (10 mmol L⁻¹) was prepared by adding sulfur and Li₂S in a mixed solvent of DOL/DME (volume ratio = 1:1), followed by vigorous stirring at ambient temperature.

Characterizations: TEM images were taken by a Hitachi HT7700 microscope, at a working voltage of 100 kV HRTEM images were taken by a JEOL JEM-2010 microscope at a working voltage of 120 kV, and SEM images were taken by a Hitachi SU8010 microscope at a work voltage of 15 kV. XRD patterns were acquired using a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). XPS data was gathered with a Thermo-Scientific K-Alpha spectrometer. TGA data was collected by a SDTQ600 analyzer in a temperature range from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. UV-visible spectra were taken by a SHIMADZU VU-2450 spectrometer within the wavelength range of 300-800 nm.

Supplementary Figures

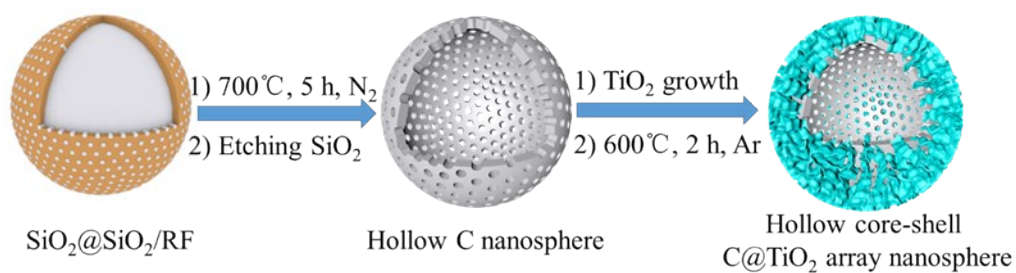


Figure S1 Illustration of hollow core-shell C@TiO₂ array nanospheres synthesis.

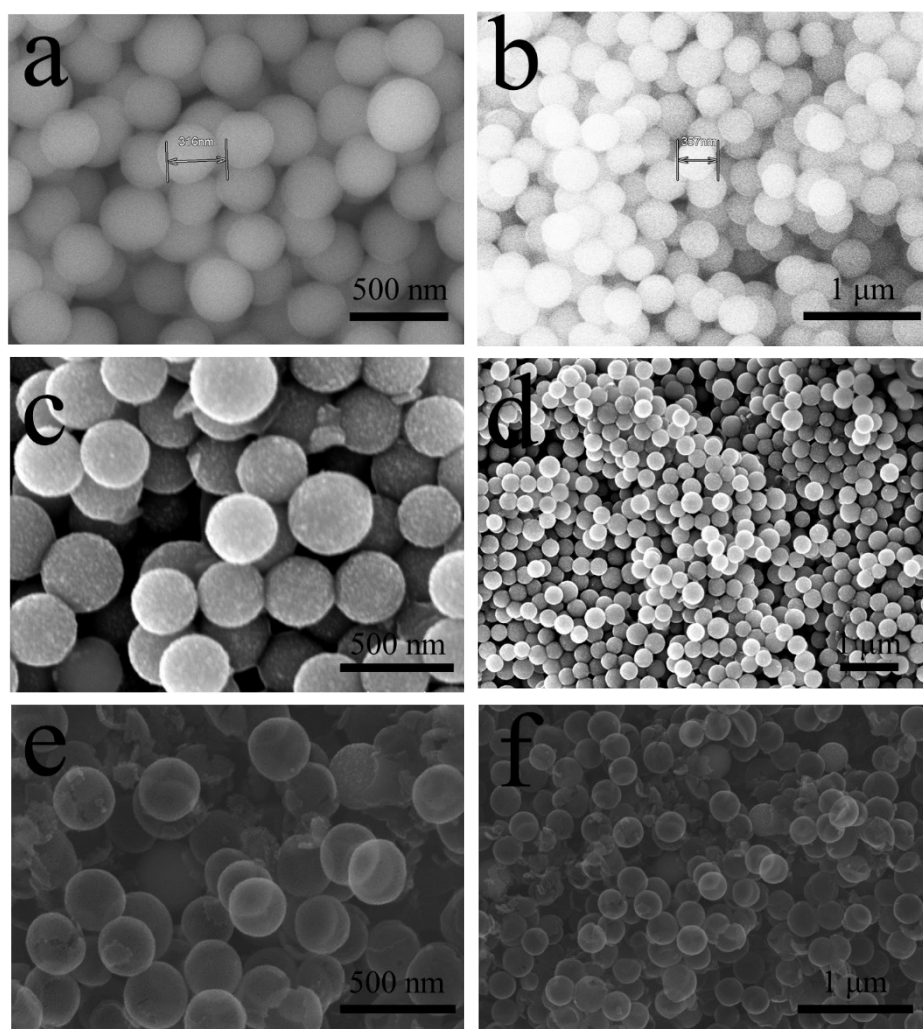


Figure S2 SEM images of (a,b) SiO₂@SiO₂/RF, (c,d) SiO₂@SiO₂/C and (e,f) hollow porous carbon nanospheres.

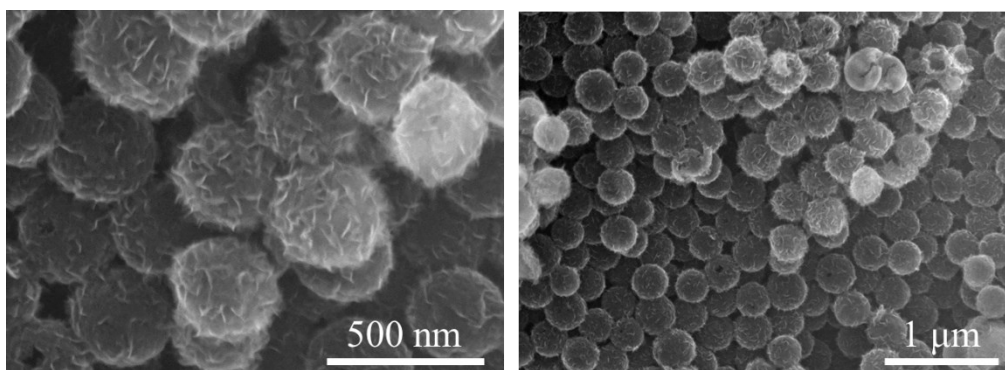


Figure S3 SEM images of C@TiO₂.

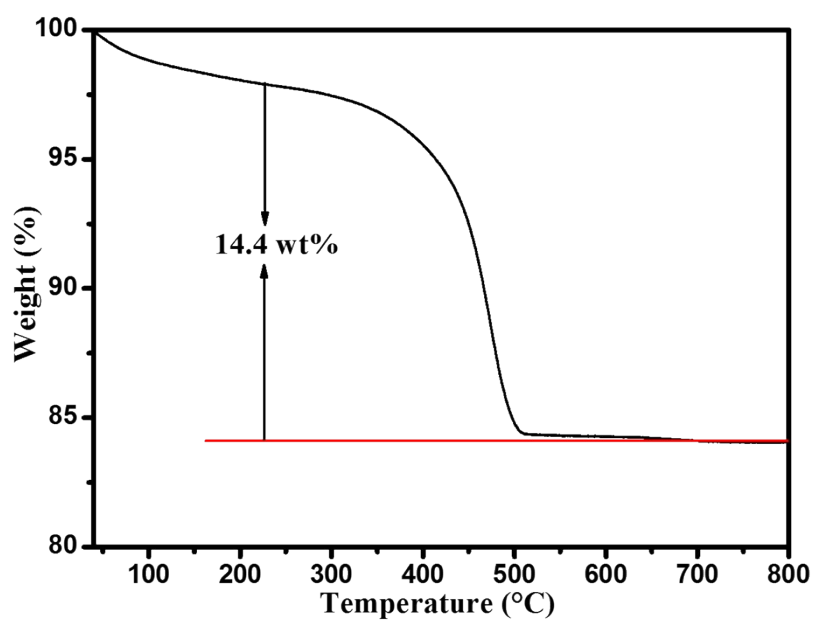
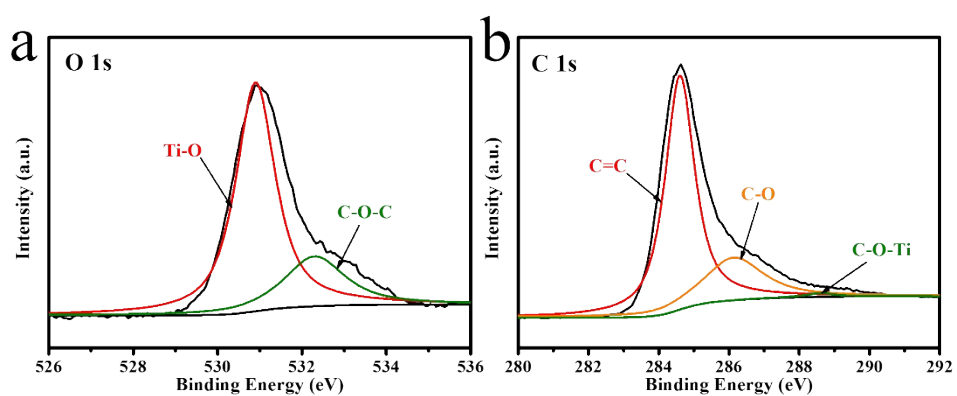


Figure S5 Thermogravimetric analysis of C@TiO₂.

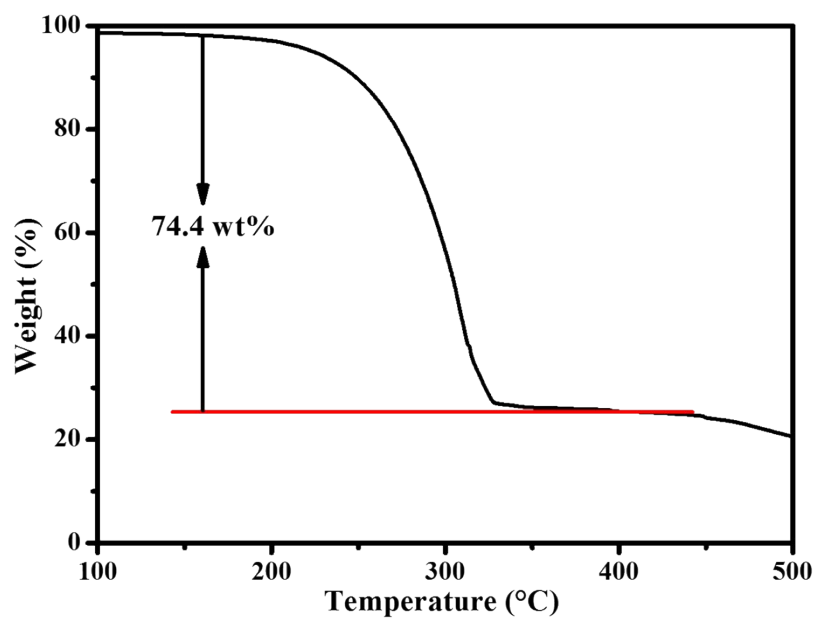


Figure S6 Thermogravimetric analysis of C@TiO₂/S.

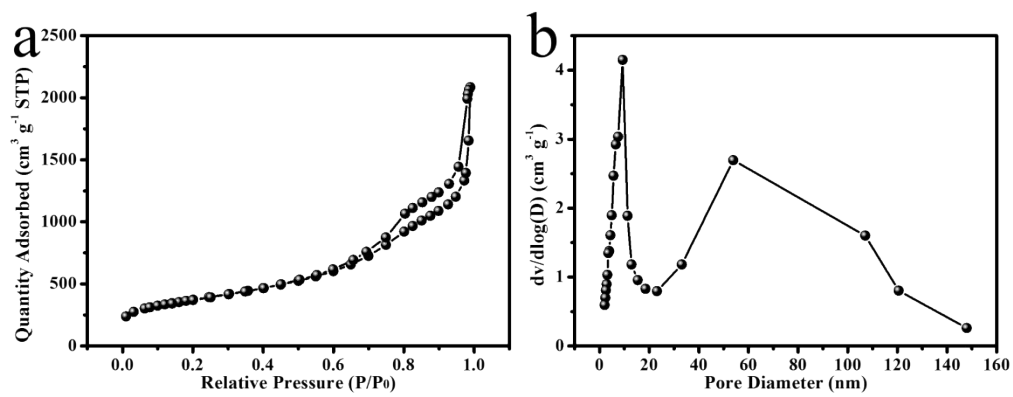


Figure S7 N₂ adsorption/desorption isotherms and corresponding pore size distribution of hollow carbon nanospheres.

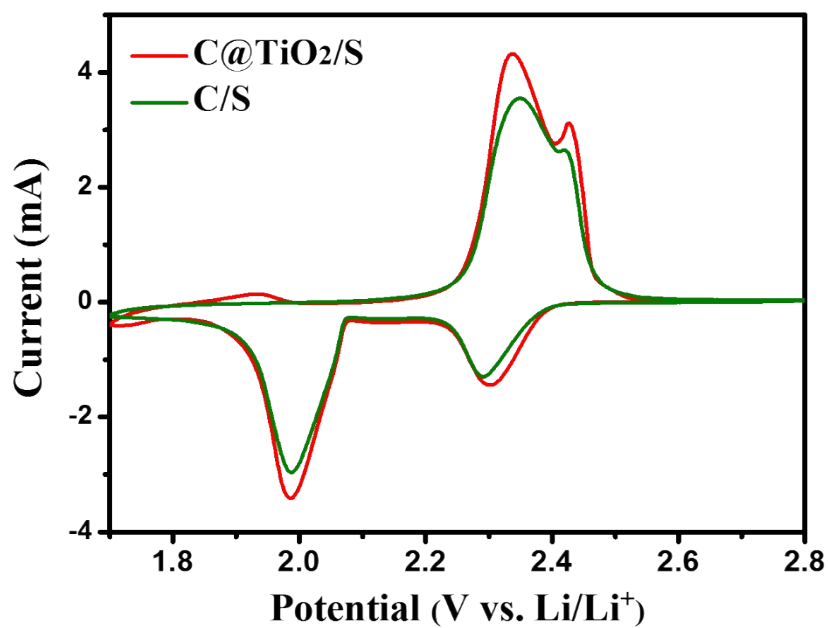


Figure S8 Comparisons of second-circle CV curves at a scan rate of 0.2 mV s^{-1} between C@TiO₂/S and C/S cathodes.

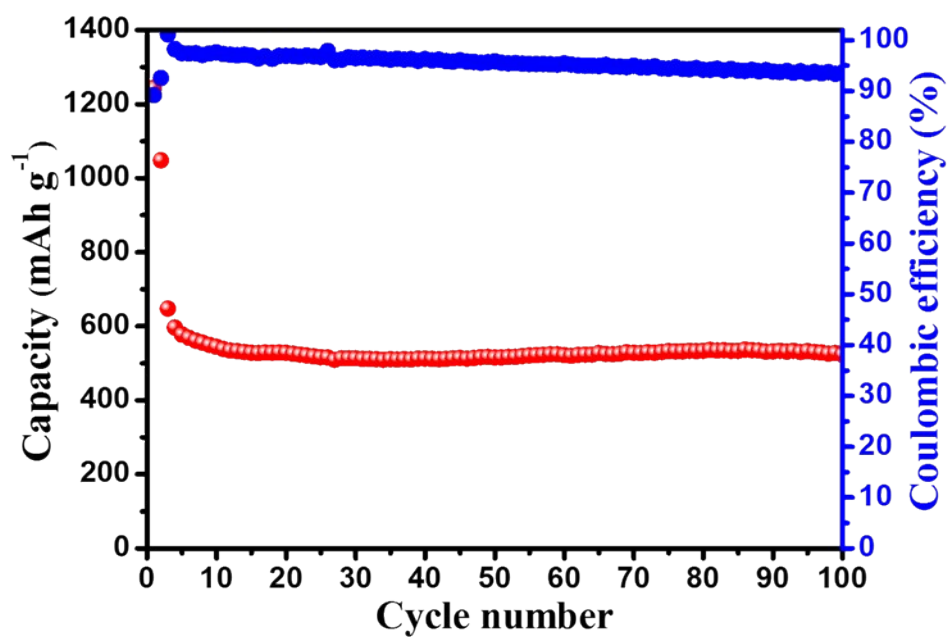


Figure S9 Cycling performance at 0.5 C of C@TiO₂/S cathode after typical activation at 0.05 C (sulfur loading $\sim 2.9 \text{ mg cm}^{-2}$).

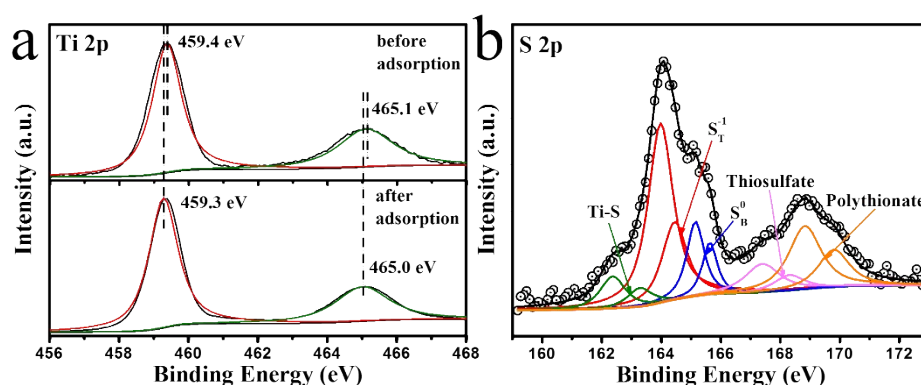


Figure S10 XPS spectra of C@TiO₂ nanoarray after Li₂S₄ adsorption test: (a) Ti 2p and (b) S 2p.

Table S1. Comparison of EIS fitting results for C@TiO₂/S and C/S cathodes.

Cathode materials	R _s (Ω)	R _{ct} (Ω)
C@TiO ₂ /S	2.17	36.63
C/S	2.66	48.74

Table S2. Electrochemical performance of Li-S batteries based on TiO₂.

Cathode	Sulfur (wt%)	Rate (C)	Cycle	Capacity (mAh g ⁻¹)	Ref.
C@TiO ₂ /S	74.4	0.5	100	815	This work
C@TiO ₂ /S	74.4	2	500	485	This work
3TiO ₂ /7S	70	0.2	200	623	1
NG/SnS ₂ /TiO ₂ -S	57.1	0.5	500	572	2
A-TiO _{2-x} NSs-S	77	0.1	100	610	3
RTMs/S	60	1	300	427	4
S-TiO ₂	68	0.5	100	480	5
HCNF@TiO ₂ -S	67.5	0.5	200	660	6
S@C-Co/TiO ₂	66	0.5	200	503	7
TG/S	60	0.5	200	631	8
GA/TiO ₂ /S	75.1	0.5	100	597	9
H-TiO _x @S/PPy	66.33	0.5	500	590	10

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