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Accelerated Li–S chemistry at a cooperative interface built *in situ*†

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The performances of lithium–sulfur (Li–S) batteries have been markedly impaired by intricate multi-electron sulfur chemistry involving reversible conversion of polysulfides (LiPSs) to Li_2S upon discharge and back to S_8 upon charge. Herein, graphene *in situ* coated TiO_2 nanotubes are realized via a direct chemical vapor deposition (CVD) technique, leading to the design of a graphene– TiO_2 (G– TiO_2) promotor for Li–S chemistry. With the aid of detailed experimental and theoretical characterization, we reveal that the direct CVD-derived G– TiO_2 realizes not only the coupling of Li^+ -ion diffusion and electron transfer but also efficient regulation of LiPSs, thereby producing a synergistic catalyzing effect on both LiPS conversion and Li_2S decomposition. As a result, S/graphene– TiO_2 (S/G– TiO_2) presents a remarkable rate capability and an ultralow capacity decay rate of 0.052% over 1000 cycles at 2.0C. Even at a high sulfur loading of 9.4 mg cm^{-2} , such a cathode still delivers a superior areal capacity of 8.7 mA h cm^{-2} . This work would motivate the deep-seated revisiting of the sulfur reaction mechanism and offer a rational strategy to construct high-energy and long-life Li–S batteries.

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Introduction

The rapid development of portable electronics and electric vehicles has stimulated ever-growing explorations of advanced battery systems. Lithium–sulfur (Li–S) batteries have been considered as one of the most promising candidates because of their high theoretical capacity (1672 mA g^{-1}) and excellent energy density (2600 Wh kg^{-1}), as well as the natural abundance of sulfur.^{1–3} A multielectron conversion chemistry involving the sulfur dissolution and lithium polysulfide (LiPS) evolution contributes to the high energy density of Li–S batteries.^{4,5} However, accompanying problems, mainly pertaining to the notorious LiPS shuttle and low areal sulfur loading, have posed a fatal threat to the real implementation of Li–S batteries.

To tackle these issues, extensive investigations have centered on the rational design of host materials and electrode structures.^{6–9} Augmenting the interaction between LiPSs and sulfur hosts is in general regarded as an effective strategy.^{10,11} In this respect, carbonaceous frameworks with heteroatom doping¹² and metal-based textural architectures encompassing oxides,¹³ sulfides,¹⁴ and nitrides^{15,16} have been employed to physically confine and chemically anchor LiPSs. For instance, Li *et al.*¹⁷ fabricated nepenthes-like N-doped hierarchical graphene by using diatomite as the growth template. Benefiting from the incorporation of N atoms and the formation of the devious morphology, LiPS shuttle was markedly mitigated. Ma *et al.*¹⁵ developed a carbon-sphere-templating route to synthesize porous VN nanobubbles, which accordingly functioned as an efficient LiPS immobilizer toward favorable cycling stability of the Li–S system.

Despite alleviating the LiPS shuttle to a certain extent, the anchoring effect is solely unsatisfactory to realize high-performance Li–S batteries.^{18–20} Note that the Li_2S_4 conversion process contributes to nearly three quarters of the theoretical capacity (1672 mA h g^{-1}), suggesting its vital role in the electrochemical reaction of Li–S systems.²¹ However, both the high concentration of accumulated Li_2S_4 in the electrolyte and liquid–solid phase transformation of Li_2S_4 into Li_2S would cause retarded reaction kinetics, resulting in inferior capacity and short lifespan. In light of this, the design of various mediators to guide the electrocatalysis of Li–S chemistry toward propelled sulfur redox kinetics is indeed appealing.^{19,22–26} Specifically, the development of heterostructured hosts enables

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to achieve comprehensive regulations of electrochemical performances, and they have thus emerged as a new frontier in catalysis chemistry.^{27–29} A recent study by us reported that a VO₂-VN binary host could serve as an effective promoter for sulfur redox.³⁰ Nevertheless, in-target interface engineering and in-depth understanding of the electrocatalytic process in Li-S systems still remain in a nascent stage.

The “synergistic catalysis” is an emerging research field that deals with electrochemical reactions occurring at the interface normally between semiconducting oxides and two-dimensional mediators such as graphene, MoS₂ and h-BN.^{31–33} In such a strategy, the catalytic process could be kinetically improved owing to the enrichment of active species and enhanced transport of carriers, *i.e.*, ions and electrons. In addition, such a catalysis relies heavily upon the properties of the interface and the existence of defects.³⁴ Inspired by this conceptual advance, we herein explore the electrocatalytic behaviours of heterostructure hosts in Li-S realm throughout the direct construction of the graphene-TiO₂ interface with the aid of catalyst-free plasma-enhanced chemical vapor deposition (PECVD). In contrast to previous studies employing wet chemical routes for the fabrication of graphene/TiO₂ composites, PECVD allows the direct formation of defective graphene over TiO₂ nanotubes in a conformal manner, resulting in synergistic catalysis for Li-S chemistry. Our practical experimentations and theoretical calculations reveal that G-TiO₂ manifests bifunctional electrocatalytic functionalities: (i) enabling the storage of abundant interface charges due to the difference in the work function between graphene and TiO₂, thereby enhancing the electrical conductivity of the interface and hence, promoting LiPS conversion; (ii) synergizing the advantages of adsorptive TiO₂ and conductive graphene, in turn framing a smooth adsorption-diffusion-conversion pathway for LiPSs. The thus-derived S/graphene-TiO₂ (S/G-TiO₂) cathode exhibits a low average capacity decay of 0.052% per cycle at 2.0C for 1000 cycles. A high areal capacity of 8.7 mA h cm⁻² is further attained at 0.1C even with a high sulfur loading of 9.4 mg cm⁻².

Experimental methods

Synthesis of TiO₂ nanotubes

In a typical synthesis, 0.1 g commercial TiO₂ powder was added into NaOH aqueous solution, followed by vigorous stirring to generate a uniform solution mixture. The mixed solution was then placed in a Teflon-lined autoclave with a stirrer and subsequently kept at a temperature of 130 °C for 24 h. It was found that the concentration of the precursor was key to generating a nanotubular morphology and the stirring rate had a critical influence on the formation of the viscous cross-linking network, implying a controllable process for synthesizing TiO₂ nanotubes. In this work, the concentration of the precursor was adjusted to 1 : 130 g mL⁻¹ and the stirring rate was controlled within the range of 800 to 1000 rpm throughout the wet-chemistry reaction. The final product was obtained after rinsing, hydrogen ion exchange, cyro-drying and gentle annealing procedures.

Synthesis of G-TiO₂ nanotubes

G-TiO₂ nanotubes were synthesized through a designed low-temperature PECVD route. Typically, the as-prepared TiO₂ nanotubes served as the growth substrate and were transferred into a CVD tube furnace. The system was pumped to a base pressure of 1 Pa and then purged with pure Ar. The CVD furnace was then heated to 500 °C under an argon flow. A mixed gas consisting of Ar (100 sccm) and CH₄ (10 sccm) was introduced in the presence of plasma (60 W) to trigger the reaction. The direct PECVD process was maintained for 40 min to obtain the final G-TiO₂ product.

Fabrication of sulfur cathodes with G-TiO₂ and TiO₂

Briefly, 0.25 g carbon nanotubes (CNTs), 0.05 g G-TiO₂ (TiO₂) nanotubes and 0.7 g sulfur were mixed and sealed in a glass vessel. The mixed powder was kept at a temperature of 155 °C for 6 h to form S/G-TiO₂ and S/TiO₂ hybrids. Such hybrids were further vigorously mixed with the LA132 aqueous binder at a weight ratio of 9 : 1 for 60 min on a twin-shaft mixer. The as-prepared slurry was coated on an aluminium current collector and then dried at 50 °C for 14 h under vacuum. The cathode was further punched into disks with a diameter of 13 mm. The sulfur mass in the entire cathode was 63 wt% and the areal sulfur loading was 1.4–1.6 mg cm⁻² for the typical electrochemical measurements. To evaluate their high-loading potential toward practical applications, the cathodes with high areal sulfur loadings of 3.1–9.4 mg cm⁻² were also prepared. In addition, a pure sulfur cathode was also fabricated as the control.

Characterization

The morphologies and corresponding elemental maps were obtained by using a Hitachi SU8010 Scanning Electron Microscope (SEM). The detailed structure and corresponding elemental maps of the samples were recorded on a Titan Themis Cubed G2 300 and Tecnai G2 F20 S-TWIN Transmission Electron Microscope (TEM). The X-ray diffraction (XRD) patterns of the samples were analyzed by using a Bruker D8 Advance Diffractometer. The Raman spectra of the samples were recorded on an HR Evolution Raman spectrometer. The nitrogen adsorption-desorption isotherms were recorded through Brunauer-Emmett-Teller BET measurements at 77 K in a N₂ atmosphere on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System. The surface states of the samples were probed using an Escalab 250Xi X-ray photoelectron spectroscopy (XPS).

Li₂S₄ adsorption test

Li₂S₄ solution with a concentration of 7.0 mmol L⁻¹ was prepared beforehand by completely dissolving sulfur and lithium sulfide in a molar ratio of 3 : 1 in 1,2-dimethoxyethane (DME). 25 mg of G-TiO₂ and TiO₂ were added into 2 mL Li₂S₄ solution, respectively. The Li₂S₄ adsorption tests were carried out in an Argon-filled glove box.

Li₂S nucleation tests

Li₂S₈ solution was first achieved by dissolving sulfur and lithium sulfide at a molar ratio of 7 : 1 in tetraglyme solvent,

followed by vigorous magnetic stirring for 24 h. The amount of [S] in Li_2S_8 was 2.0 mol L^{-1} . Commercial carbon paper (CP) was punched into disks with a diameter of 13 mm. G- TiO_2 and TiO_2 nanotubes were loaded on the CP disks and denoted as CP-G- TiO_2 and CP- TiO_2 , respectively. Briefly, the CP-G- TiO_2 and CP- TiO_2 were used as the cathodes whilst lithium foil acted as the anode. 20 μL Li_2S_8 electrolyte was dropped onto the cathode and 20 μL LiTFSI (1.0 mol L^{-1}) without Li_2S_8 was added onto the anode side. The assembled batteries were first galvanostatically discharged at 0.112 mA to 2.06 V and subsequently maintained potentiostatically at 2.05 V until the current was below 10^{-5} A. The Li_2S_4 conversion process was evaluated by calculating the Li_2S deposits according to Faraday's law.

Electrochemical measurements

The as-prepared cathodes were assembled into coin-type (LIR2032) cells with the employment of lithium foil as the anode and the Celgard 2400 membrane as the separator. The electrolyte was composed of 1.0 mol L^{-1} LiTFSI and 1 wt% LiNO_3 in a mixed solution of DME/DOL. The electrolyte/sulfur ratio was precisely controlled to $15 \mu\text{L mg}^{-1}$ for common cathodes and $8 \mu\text{L mg}^{-1}$ for cathodes with high sulfur loadings. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) curves were collected on an Autolab potentiostat PGSTAT302N. The frequency range for EIS tests was 10^5 to 10^{-2} Hz. Galvanostatic discharge/charge measurements, and rate and cycling performance experiments of cathodes were carried out on a Land CT2001A battery testing system in a voltage range of 1.7–2.8 V.

Theoretical calculations

The first principles method based on density functional theory (DFT) was adopted to simulate the Li-S battery system, executed using the Vienna *Ab initio* Simulation Package (VASP). Projector augmented wave pseudopotential (PAW) was applied to handle the electron-core interactions and the exchange-correlation interactions were employed by generalized gradient approximation of the PBE functional. The kinetic energy cutoff with a plane wave was 400 eV. The constructed geometric structure was relaxed until the total energy and force per atom were less than 10^{-5} eV and $-0.01 \text{ eV \AA}^{-1}$ for TiO_2 using an anatase configuration and graphene (G) system, 10^{-4} eV and $-0.02 \text{ eV \AA}^{-1}$ for the TiO_2/G compound system, respectively. The first Brillouin zone integrations were employed using $3 \times 3 \times 1$ and $5 \times 5 \times 1$ k -grid points in TiO_2 , $2 \times 2 \times 1$ and $4 \times 4 \times 1$ k -grid points in G, $2 \times 3 \times 1$ and $3 \times 6 \times 1$ k -grid points in the TiO_2/G system for the geometry optimizations and static computations, respectively. We further evaluated charge transfer using Bader charge and difference charge density analysis. The adsorption of lithium polysulfides (LiPSs) on the TiO_2 (101) surface with a $1 \times 3 \times 1$ supercell and G with a $8 \times 8 \times 1$ supercell was adopted. For the TiO_2/G compound system, 2×2 supercell TiO_2 (101) was used to match G using a 3×5 supercell with a mismatch rate of $\sim 4\%$ for the a direction and $\sim 2.5\%$ for the b direction. The thickness of the vacuum layer is 15 $\text{\AA}$; the bottom layer with O-Ti-O three atomic layer thickness was fixed to the bulk position, and other

layers and adsorbates were allowed to relax fully. The adsorption energy of LiPSs on the above surface was calculated by the below equation. $E_{\text{ads}} = E_{\text{surf}} + E_{\text{LiPS}} - E_{\text{total}}$, where the E_{total} and E_{surf} are the total energy with and without the adsorption of LiPSs, and E_{LiPS} is the energy of LiPSs. The Climbing Image Nudged Elastic Band (CI-NEB)³⁵ method was adopted to calculate the diffusion kinetics of the Li atom on the TiO_2 and G- TiO_2 .

Results and discussion

Fig. 1 schematically illustrates the key process of “synergistic catalyzing effect” targeting promoted Li-S chemistry. The direct PECVD reaction on semiconducting TiO_2 nanotubes at a relatively low temperature (*e.g.*, 500 $^\circ\text{C}$) facilitates the formation of defective graphene coatings, in parallel building a cooperative interface. The presence of ample defective sites would further allow the diffusion of LiPSs onto the surface of TiO_2 . Because of the difference in the work functions between graphene and TiO_2 , abundant interfacial charges could be accumulated at the interface, thereby enhancing the electrical conductivity.^{27,30} In turn, the reduction of Li_2S_8 to $\text{Li}_2\text{S}_6/\text{Li}_2\text{S}_4$ and the subsequent conversion to insoluble Li_2S would be promoted. During the reverse process, the strong interaction between isolated Li^+ ions and the oxygen in TiO_2 is beneficial for lowering the energy barrier of Li_2S decomposition.¹⁰ The graphene overlayers simultaneously allow fast Li^+ -ion and electron migration, which is in favor of the oxidation of Li_2S to S_8 . In addition, the cooperative interface combines the merits of adsorptive TiO_2 and conductive graphene, guaranteeing a high-efficiency LiPS immobilization–diffusion–conversion. Taken together, the direct-PECVD-enabled interface between TiO_2 and graphene realizes the coupling of Li^+ -ion diffusion and electron transfer. Such a “synergistic catalysis” strategy affords a rational guideline for optimizing the sulfur reaction kinetics, which is expected to improve the electrochemical performances of Li-S batteries.

To illustrate the concept of “synergistic catalysis” in our Li-S system, first-principles simulations based on the density

Fig. 1 Schematic illustration of the “synergistic catalyzing effect”: accelerating Li-S chemistry at the cooperative interface between TiO_2 nanotubes and graphene overlayers.

functional theory (DFT) were applied to reveal the enhancement effect on the G-TiO₂ interface. First of all, the stable adsorption configurations of Li were considered for the TiO₂ and G-TiO₂, as respectively shown in Fig. S1 and S2 (ESI†). It can be seen that both systems adopt quite similar configurations. The adsorption energy of Li in the G-TiO₂ (4.49 eV) is higher than that of TiO₂ (3.98 eV); the difference of Li adsorption energies between stable and meta-stable states also shows obvious disparity (0.69 eV for TiO₂ and 0.52 eV for G-TiO₂). These results suggest that the construction of G-TiO₂ enables improved Li capture and facilitates Li entrance to the established interface. Bader charge analysis further indicates that Li realizes more loss of electrons in G-TiO₂ (0.8737 e) than in bare TiO₂ (0.8677 e). According to the difference charge density plots in Fig. 2a and b, it is evident that charge transfer not only takes place on TiO₂ but also on graphene for G-TiO₂, further contributing to the advanced Li accommodation in the G-TiO₂ compound. Secondly, the migration of Li was probed for both systems. As shown in Fig. 2c, the diffusion barrier on G-TiO₂ reaches 0.62 eV, which is lower than that on TiO₂ (0.73 eV). Such accelerated Li diffusion at the G-TiO₂ interface would promote the reversible conversion of LiPSSs. Bader charge analysis again reveals that Li in the transition state loses more electrons at the G-TiO₂ (0.8972 e) when compared to bare TiO₂ (0.8860 e). The difference charge density plots (Fig. S3, ESI†) indicate that graphene acquires more electrons from Li in the transition state than in the stable adsorption state. The migration barrier of Li on graphene is as small as ~0.27 eV (Fig. S4, ESI†). These results again substantiate that the constructed G-TiO₂ interface enables the acceleration of Li diffusion. Finally, the calculated density of states of G-TiO₂ and TiO₂ (Fig. 2d and e) discloses that G-TiO₂ behaves as a metal throughout moving up the Fermi-level of TiO₂ due to charge transfer from graphene to TiO₂. It is also evidenced from difference charge density in Fig. 2f that there is ample charge density present at the G-TiO₂ interface.

To construct graphene-TiO₂ (G-TiO₂) heterostructures with cooperative interfaces for affording a “synergistic catalyzing

effect”, a multi-step synthetic procedure encompassing assembly, wet-chemistry, and direct PECVD routes is devised in the target (Fig. 3a and S5, ESI†). Through delicate control over precursor concentration and the stirring rate, fine and uniform TiO₂ nanotubes can be readily produced (Fig. 3b). Accordingly, direct PECVD is versatile enough to conformally coat thin layers of graphene on TiO₂ without using any foreign catalyst, facilitating the formation of a cooperative interface bridging the

Fig. 3 Synthesis and microscopic characterization of the G-TiO₂ heterostructure. (a) Schematic illustration of the synthetic procedure of the G-TiO₂ heterostructure involving assembly, wet-chemistry and direct PECVD processes. (b and c) SEM images of TiO₂ and G-TiO₂ nanotubes. (d and e) TEM and high-resolution TEM images corroborating the cooperative interface between TiO₂ nanotubes and graphene overlayers. (f–i) EELS mappings of G-TiO₂ nanotubes. (j) XRD patterns of G-TiO₂ and TiO₂ nanotubes. (k) Raman spectrum of G-TiO₂. (l and m) XPS C 1s and Ti 2p spectra of G-TiO₂.

Fig. 2 Calculated ion and electron transfer at the G-TiO₂ interface. Difference charge density between the Li atom and (a) TiO₂ and (b) G-TiO₂. (c) Plot showing the diffusion barrier of the Li atom on the TiO₂ (101) and G-TiO₂ surfaces; the inset is the diffusion pathway of G-TiO₂. (d and e) Density of states of the TiO₂ (101) and G-TiO₂ surfaces. (f) Difference charge density between graphene and TiO₂ in the G-TiO₂ system. Note that Ti, O, Li, and C atoms are in light grey, red, purple and dark grey, respectively. Cyan and yellow contours with the isosurface value of 0.001 e per bohr³ indicate the reduced and augmented charge density, respectively.

adsorptive TiO_2 and conductive graphene. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations reveal that the thus-derived G- TiO_2 well preserves the tube morphology of pure TiO_2 after the gentle CVD reaction (Fig. 3c, d and S6, ESI†). The high-resolution TEM (HRTEM) images display the co-existence of the TiO_2 (101) plane, uniform graphene overlayers, and the cooperative interface (Fig. 3e and S7, ESI†). The electron energy loss spectroscopy (EELS) mappings again verify the homogeneous wrapping of graphene on the surface of TiO_2 nanotubes by virtue of direct PECVD (Fig. 3f–i). The crystal phases of samples before and after the PECVD process were identified by X-ray diffraction (XRD), as shown in Fig. 3j. Both the G- TiO_2 and bare TiO_2 present mixed anatase and TiO_2 (B) phases. Note that the (101) peak of the anatase phase is dominant, implying its stable state in the as-prepared G- TiO_2 . The structural features of G- TiO_2 were further examined by Raman spectroscopy (Fig. 3k), showing noticeable signals for graphene (D and G bands). The remarkable I_D/I_G intensity ratio also indicates the existence of ample defect sites of direct-PECVD-derived graphene overlayers on TiO_2 nanotubes. X-ray photoelectron spectroscopy (XPS) was employed to inspect the chemical constitution of G- TiO_2 (Fig. 3l, m and S8, ESI†). The high resolution C 1s signal is dominated by the sp^2 C=C bond type (284.7 eV) due to experiencing CVD conditions, indicative of the formation of graphitic carbon (Fig. 3l). As for the Ti 2p spectrum, two main

peaks locating at 464.5 and 458.8 eV can be respectively ascribed to the Ti 2p_{1/2} and Ti 2p_{3/2} signal. The binding energy difference between Ti 2p_{1/2} and Ti 2p_{3/2} is 5.7 eV, substantiating a normal state of Ti^{4+} in G- TiO_2 (Fig. 3m).³⁶ The specific surface areas of G- TiO_2 and TiO_2 were also evaluated by using N_2 adsorption/desorption isotherms (Fig. S9, ESI†), showing calculated Brunauer–Emmett–Teller values of 76.3 and 106.8 $\text{m}^2 \text{g}^{-1}$. In addition, a blue light indicator can continuously work *via* a G- TiO_2 based circuit, revealing favorable electrical conductivity enabled by the PECVD-derived graphene overlayers on the TiO_2 surface (Fig. S10, ESI†).

To experimentally probe the interactions between G- TiO_2 and LiPSs, visualized adsorption tests (Fig. 4a) were carried out in parallel by dosing the same amount (25 mg) of G- TiO_2 or bare TiO_2 into a prepared Li_2S_4 solution (7 mmol L^{-1}). The choice of Li_2S_4 mainly stems from the fact that it could serve as a direct precursor for Li_2S nucleation. It is hence necessary to explore the adsorption behavior of Li_2S_4 . As shown in Fig. 4b, after adding both the materials for 24 h, the originally orange-colored Li_2S_4 solution becomes colorless, in sharp contrast to the control solution, indicating the strong affinity between G- TiO_2 and polysulfides. In addition, STEM imaging combined with elemental mapping was employed to examine the sulfur distribution on G- TiO_2 after the Li_2S_4 adsorption test. The elemental maps disclose a homogeneous distribution of sulfur (Fig. 4c), corroborating favorable anchoring of sulfur species by

Fig. 4 Experimental measurements and theoretical simulation on the anchoring ability of G- TiO_2 nanotubes for sulfur species. (a and b) Visualized adsorption measurements of G- TiO_2 and TiO_2 with Li_2S_4 . (c) TEM image and corresponding C, T, O, and S maps of G- TiO_2 after Li_2S_4 adsorption for 24 h. (d and e) Optimal configurations and related binding energies of sulfur species with the (101) facet of TiO_2 . (f) Operando Raman spectra based on the S/G- TiO_2 cathode collected during the first cycle at 0.2C.

the G-TiO₂ host. The experimental observation also implies that the direct coating of ultrathin graphene overlayers over TiO₂ sustains the adsorption ability of TiO₂. To systematically evaluate the bindings between G-TiO₂ and sulfur species, DFT calculations were further used. The (101) facet of TiO₂ was selected as the examined surface owing to its stable and dominant state. The graphene surface was also included for comparison purposes. As plotted in Fig. 4d and S11 (ESI[†]), the binding energies between the TiO₂ (101) with Li₂S, Li₂S₂, Li₂S₄, Li₂S₆, Li₂S₈, and S₈ species are calculated to be 4.48, 3.74, 3.17, 3.41, 3.09, and 0.87 eV, respectively. These values are much higher than those pertaining to pure graphene (Fig. 4e), revealing strong binding between TiO₂ and sulfur species. Such an advanced anchoring effect *via* the G-TiO₂ host is beneficial for mitigating the LiPS dissolution into the electrolyte during the electrochemical process. In response, Fig. 4f and S12 (ESI[†]) show the *operando* Raman spectra of the electrolyte collected in the first cycle at 0.2C using S/G-TiO₂ as the cathode, manifesting a gradual disappearance of Li₂S₈ (279 and 396 cm⁻¹) and Li₂S₆ (178 and 458 cm⁻¹) signals upon discharge and the signal regeneration upon charge.

The sulfur reaction encompasses multi-step LiPS evolutions with the company of Li⁺-ion and electron migration. To unravel the synergistic catalyzing effect of G-TiO₂ nanotubes for Li-S chemistry, Li⁺-ion diffusion and LiPS conversion processes were systematically probed. The CV curves collected at different scan rates from 0.1–0.5 mV s⁻¹ were employed to identify the

electrode kinetics pertaining to the Li⁺-ion diffusion coefficient (Fig. S13, ESI[†]). As displayed in Fig. 5a–c, all the cathodic and anodic peak currents for the tested G-TiO₂ and TiO₂ electrodes exhibit a linear relationship against the square root of scan rates. This accordingly fits well with the classical Randles–Sevcik equation: $I_p = (2.69 \times 10^5)n^{1.5}AD^{0.5}C_{Li}\nu^{0.5}$, where I_p is the peak current, n is the charge transfer number, A is the geometric area of the active electrode, D is the Li⁺-ion diffusion coefficient, C_{Li} is the Li⁺-ion concentration in the electrode, and ν is the scan rate. The slope of the curve ($I_p/\nu^{0.5}$) reflects the Li⁺-ion diffusion rate owing to the unchanged n , A and C_{Li} in a certain system. It can be clearly observed that the S/G-TiO₂ electrode presents much faster Li⁺-ion diffusion compared to S/TiO₂ through the whole sulfur redox, demonstrating that the “synergistic catalysis” helps to accelerate the electrode reaction kinetics.

To further reveal the advanced electrocatalytic effect of the interface, LiPS evolution was examined by a suite of reaction kinetics characterization experiments. With respect to the LiPS diffusion, note that non-conducting TiO₂ limits the direct conversion of Li₂S₄ on its surface owing to suppressed redox charge transfer; hence Li₂S₄ has to diffuse from TiO₂ to nearby conductive media to complete the conversion process. Our DFT simulation manifests that the Li₂S₄ diffusion barrier on the TiO₂ (101) plane remains as low as 1.20 eV (Fig. 5d), guiding a fast migration from TiO₂ to the cooperative interface. In turn, Li₂S nucleation tests were carried out to explore the Li₂S₄

Fig. 5 Sulfur redox kinetics characterization. (a–c) Plots of CV peak current for the first cathodic reduction, second cathodic reduction and the anodic oxidation process *versus* the square root of the scan rates. (d) Energy profile for Li₂S₄ diffusion on the facet (101) of TiO₂. (e and f) Potentiostatic discharge curves of Li₂S₈/tetralyme solution on CP-G-TiO₂ and CP-TiO₂ at 2.05 V. (h and g) SEM images of the Li₂S deposit on CP-G-TiO₂ and CP-TiO₂. (i) Tafel plots for the corresponding Li₂S₄ conversion reaction of S/G-TiO₂ and S/TiO₂.

conversion kinetics by potentiostatically discharging Li_2S_8 /tetraglyme solution at 2.05 V on different surfaces, involving G-TiO₂ and TiO₂ loaded commercial carbon papers (denoted as CP-G-TiO₂ and CP-TiO₂, respectively). As shown in Fig. 5e and f, the capacities of Li_2S deposition on CP-G-TiO₂ and CP-TiO₂ are calculated to be 104.2 and 54.7 mA h g⁻¹, respectively. In addition, post-mortem SEM observation after Li_2S nucleation displays that the CP-G-TiO₂ surface is fully covered by Li_2S precipitation (Fig. 5g and S14, ESI[†]), whereas CP-TiO₂ presents a relatively low Li_2S coverage (Fig. 5h). The observation of less LiPS residuals on the separator pertaining to CP-G-TiO₂ further corroborates the superior LiPS conversion ability of G-TiO₂ (Fig. S15, ESI[†]). These results verify a remarkable electrocatalytic activity of the *in situ* built interface *via* G-TiO₂ toward Li_2S_4 conversion. The Tafel plots with respect to Li_2S_4 conversion in Fig. 5i present a lower Tafel slope value (36.6 mV dec⁻¹) of S/G-TiO₂ in stark contrast to that of S/TiO₂ (85.1 mV dec⁻¹). The small Tafel slope value of S/G-TiO₂ further substantiates enhanced Li_2S nucleation.

On the basis of the theoretical and experimental results, the synergistic catalyzing effect can be depicted as follows: (i) the direct PECVD-derived graphene overlayers possess ample defects to allow smooth LiPS adsorption, ensuring sufficient precursor supply for the subsequent Li_2S nucleation; (ii) the difference in the work functions between graphene and TiO₂ is in favor of abundant interfacial charge storage at the interface, enhancing the electrical conductivity of the interface and

thereby accelerating the LiPS conversion; (iii) the cooperative interface realizes the comprehensive management of LiPS, hence propelling the Li_2S nucleation; (iv) the strong interaction between isolated Li⁺ ions and the oxygen in TiO₂ is beneficial for lowering the energy barrier of Li_2S decomposition; (v) the graphene overlayers simultaneously allow for fast Li⁺-ion and electron migration, benefiting the oxidation of Li_2S back to S₈.

The electrochemical performances were systematically evaluated by assembling standard CR2032-type coin cells with Li metal as a counter electrode and S/G-TiO₂ as a cathode. The S/TiO₂ cathode and pure sulfur cathode were also fabricated for a better comparison. Fig. 6a presents the cyclic voltammetry (CV) profiles of S/G-TiO₂ and S/TiO₂ cathodes with an identical sulfur loading of 1.4 mg cm⁻² at a scanning rate of 0.05 mV s⁻¹. It is evident that both CV curves exhibit featured cathodic/anodic signals of sulfur electrodes. Note that the S/G-TiO₂ cathode shows apparent positive shifts to a higher potential in dual reduction peaks and a negative shift to a lower potential in the single oxidation peak, as well as augmented peak intensities as compared to those of the S/TiO₂ cathode, indicating improved sulfur redox kinetics. This is in good agreement with the foregoing analysis. As shown in Fig. 6b, the cycling performances of S/G-TiO₂, S/TiO₂, and pure S cathodes were examined at a low current density of 0.5C (1C = 1672 mA g⁻¹). The S/G-TiO₂ cathode manages to deliver an initial discharge capacity of 1096 mA h g⁻¹ and maintains a stable cycling performance after 100 cycles (955 mA h g⁻¹). It is worth mentioning that the

Fig. 6 Electrochemical performances of S/G-TiO₂ cathodes. (a) CV curves at a scan rate of 0.05 mV. (b) Cycling performance at a current density of 0.5C. (c and d) Rate capability of Li-S batteries. (e) Galvanostatic discharge-charge curves at various current densities. (f) Long-term cycling performance at a current density of 2.0C.

coulombic efficiency of such a cathode after 100 cycles is close to 100%. The S/TiO₂ cathode harvests an initial discharge capacity of 1034 mA h g⁻¹ and a lower capacity of 797 mA h g⁻¹ after 100 cycles. In contrast, the pure S cathode delivers a far inferior initial capacity of 717 mA h g⁻¹, which fades rapidly upon cycling with a low capacity retention of only 65.8%. In further contexts, the performances of our S/G-TiO₂ cathode enabled by the “synergistic catalysis” compare favorably with those of reported Ti-based hosts (Table S1, ESI†).

Fig. 6c shows the comparison between the rate capabilities of S/G-TiO₂, S/TiO₂, and pure S cathodes at various current densities from 0.2 to 3.0C and further back to 0.2C, with the average reversible capacities correspondingly plotted in Fig. 6d. Obviously, our S/G-TiO₂ cathode demonstrates a superior rate performance, manifesting average capacities of 1316, 1044, 845, 727, and 640 mA h g⁻¹ at a rate of 0.2, 0.5, 1.0, 2.0, and 3.0C, respectively. When the current density is returned to 0.2C, the capacity can recover to a high capacity of 1083 mA h g⁻¹. In response, Fig. 6e shows the galvanostatic discharge/charge profiles of the S/G-TiO₂ cathode at the current densities ranging from 0.2 to 3.0C. Two discharge plateaus at around 2.36 and 2.05 V and one charge plateau between 2.2 and 2.4 V can be witnessed, which accords well with the CV results. Detailed comparison with the pure S cathode indicates smaller voltage polarizations and hence advanced reaction kinetics of the S/G-TiO₂ cathode (Fig. S16, ESI†). Further, the cycling stability of the S/G-TiO₂ cathode was investigated at a high rate of 2.0C for 1000 cycles. As shown in Fig. 6f, the initial discharge capacity reaches 810 mA h g⁻¹. Benefiting from the synergistic catalyzing effect, the capacity remains remarkably stable for 1000 cycles, achieving a capacity decay per cycle of only 0.052%. Note that the measured capacity of the bare G-TiO₂ cathode is quite low

and thus has negligible contribution to the entire capacity of Li-S batteries (Fig. S17, ESI†). The electrochemical impedance spectroscopy (EIS) tests of fresh and cycled cathodes (200 cycles at 1.0C) highlight the advancement of graphene incorporation, facilitating the superior electrochemical performance of the S/G-TiO₂ cathode (Fig. S18, ESI†).

Visual examination of cathodes and separators after 200 cycles at 1.0C was further carried out. Almost no LiPS can be observed to dissolve in the DME solution for the S/G-TiO₂ cathode (Fig. S19, ESI†). Post-mortem SEM inspections reveal that the morphologies of the S/G-TiO₂ cathode can be well-maintained after 200 cycles at 1.0C (Fig. S20, ESI†). Furthermore, XPS Ti 2p and S 2p spectra of the cycled S/G-TiO₂ cathode not only reflect good electrochemical stability of G-TiO₂ but also verify the formation of Ti-S bonds (Fig. S21, ESI†).

To investigate the role of “synergistic catalysis” in the realm of practical Li-S systems, S/G-TiO₂ cathodes with high-sulfur-loadings were further fabricated. Fig. 7a present the cycling performances of S/G-TiO₂ with areal sulfur loadings at 3.3, 4.3, 5.1 and 6.9 mg cm⁻² at 0.2C, managing to deliver initial areal capacities of 3.7, 4.3, 4.8 and 6.1 mA h cm⁻², respectively. Upon cycling, the corresponding capacity retentions harvest 75.7%, 74.4%, 75.0% and 68.9%. Moreover, increasing the areal sulfur loadings to 7.4 and 9.4 mg cm⁻², high initial capacities of 7.4 and 8.7 mA h cm⁻² can still be respectively achieved at 0.1C (Fig. 7b). Note that such high-sulfur-loaded cathodes maintain high areal capacities of 5.0 and 4.2 mA h cm⁻² even after 60 cycles, which are readily superior to the standard for commercial lithium-ion batteries (4.0 mA h cm⁻²). The element distributions within S/G-TiO₂ with a sulfur loading of 9.4 mg cm⁻² were mapped out in a cross-sectional SEM identification, showing the homogeneous distributions of sulfur, titanium,

Fig. 7 Electrochemical performance of high-load S/G-TiO₂ cathodes. (a and b) Stable operation of S/G-TiO₂ cathodes with a range of sulfur loadings from 3.3 to 6.9 mg cm⁻² at 0.2C and 7.4 to 9.4 mg cm⁻² at 0.1C. (c) Cross-sectional SEM image of the S/G-TiO₂ cathode with a sulfur loading of 9.4 mg cm⁻² and corresponding elemental maps. (d) EIS profiles of S/G-TiO₂ cathodes with a range of sulfur loadings from 3.1 to 8.5 mg cm⁻². (e) Areal capacity of high-load S/G-TiO₂ cathodes in comparison with other reported sulfur hosts.

oxygen and carbon elements with a measured thickness of 310 μm (Fig. 7c). EIS measurements were performed to explore the charge-transfer feature of the high-sulfur-loading S/G-TiO₂ cathodes. As depicted in Fig. 7d, the charge-transfer resistances of S/G-TiO₂ with areal sulfur loadings at 3.1, 4.4, 6.1 and 8.5 mg cm^{-2} are 13.4, 14.5, 23.0 and 28.2 Ω , respectively, demonstrating favorable electrochemical kinetics. Fig. 7e shows the performance comparison between this work and others on high-sulfur-loading cathodes. Our work is one of the best results reported by far.^{15,37–42} The direct-PECVD-enabled interface between TiO₂ and graphene realizes the coupling of Li⁺-ion diffusion and electron transport for full LiPS utilization, thereby resulting in accelerated sulfur reaction kinetics and a suppressed shuttle effect. Impressively, the “synergistic catalysis” strategy could still well adapt to optimizing Li-S systems even with high sulfur loadings, holding promise for practical and scale-up sulfur host fabrication.

Conclusion

In summary, we have elaborated that the graphene coated TiO₂ nanotubes can accelerate the Li-S chemistry reaction kinetics on the basis of practical experimentations and theoretical calculations. Such a “synergistic catalysis” strategy lies in the following aspects: (i) the introduction of the direct-PECVD route endows the graphene overlayers with tunable defect density, allowing smooth LiPS migration onto the surface of TiO₂; (ii) the ample charge storage at the interface due to the difference in the work functions between graphene and TiO₂ can enhance the electrical conductivity of the interface; (iii) the cooperative interface combines the merits of highly adsorptive ability and smooth carrier transfer, facilitating the LiPS conversion and Li₂S decomposition. Therefore, the S/G-TiO₂ cathode delivers favorable rate capability and cycling lifespan even at high sulfur loadings. Our work is anticipated to offer a new solution for rationalizing the electrocatalysis of Li-S chemistry toward the design of advanced sulfur cathodes.

Conflicts of interest

There are no conflicts to declare.

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