Hierarchical TiO$_2$ spheres as highly efficient polysulfide host for lithium-sulfur batteries


Hierarchical TiO$_2$ micron spheres assembled by nano-plates were prepared through a facile hydrothermal route. Chemical tuning of the TiO$_2$ through hydrogen reduction (H-TiO$_2$) is shown to increase oxygen-vacancy density and thereby modifies the electronic properties. H-TiO$_2$ spheres with a polar surface serve as the surface-bound intermediates for strong polysulfides binding. Under the restricting and recapturing effect, the sulfur cathode could deliver a high reversible capacity of 928.1 mA h g$^{-1}$ after 50 charge-discharge cycles at a current density of 200 mA g$^{-1}$. The H-TiO$_2$ additive developed here is practical for restricting and recapturing the polysulfide from the electrolyte.

Results and Discussion

Figure 2a shows a typical scanning electron microscopy (SEM) image of the TiO$_2$. Interestingly, the hierarchical TiO$_2$ micromspheres are composed of TiO$_2$ nano-plates. The nano-plates are arranged in spatial divergence form, which can be directly elucidated from the collapsed spheres (Fig. 2b). Highly ordered nano-plates are located in the core and arranged along the radial orientation to the outer surface. Hollow interior structure of as-obtained TiO$_2$ spheres are also observed by TEM, as shown in Fig. 2c. Therefore, the hierarchically porous and hollow structure provide high surface area to adsorb the polysulfide dispersed in electrolyte. The TEM image of nano-plates in Fig. 1d further reveals that the component unit was fan-shaped plates with the diameter of about
The electrical conductivity of TiO$_2$ can be substantially enhanced, after annealing in a reducing gas atmosphere$^{9,28}$. The anatase TiO$_2$ and hydrogen reduced TiO$_2$ were characterized by XRD (Fig. 3a). The identified peaks are indexed as anatase TiO$_2$ (JCPDS card No. 84–1285), and no observable structural differences are observed.
between TiO$_2$ and H-TiO$_2$. There were also no obvious morphological and structure changes observed for H-TiO$_2$ upon hydrogen treatment (Figure S1). To further probe the electronic and chemical environment, X-ray photoelectron spectroscopy (XPS) analysis was performed. Both spectra were calibrated with respect to the C 1s peak at 284.5 eV for clear comparison. Figure 3b (insets) illustrates the Ti 2p core level spectra for anatase TiO$_2$ and H-TiO$_2$. The anatase TiO$_2$ sample shows two predominant peaks at 464.3 and 458.6 eV, which are attributed to the characteristic Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ peaks of Ti$^{4+}$. In comparison to anatase TiO$_2$, the peaks of the H–TiO$_2$ sample show a red shift in binding energy, suggesting that they have different bonding environments. By subtracting the normalized Ti 2p spectra of H–TiO$_2$ with TiO$_2$ sample, there are two extra peaks centered at ca. 463.4 and 458.1 eV (Fig. 3b). These two peaks are within the range of published Ti$^{3+}$ binding energy.9,28–30. The result suggests that oxygen vacancies (Ti$^{3+}$ sites) are created in H–TiO$_2$ sample during hydrogenation. It has been reported that the less positively charged Ti$^{3+}$ nuclei leads to an increment in electron density and therefore a weaker binding effect.9

Restricting and recapturing of polysulfide diffusion from additive H-TiO$_2$ were clearly demonstrated through an in-situ visual–electrochemical study. The designed S and S$^\text{−}$ cathodes are cycled in sealed vials against Li anodes with the same electrolyte as used in coin cells. As shown in the photograph in Fig. 4a–c, the electrolyte with S cathode changed from colourless to bright yellow during 250 cycles under the scan rate of 1 mV s$^{-1}$. The colour change indicated that the polysulfides diffuse out of the cathode and dissolve in the electrolyte. However, the electrolyte with S + H-TiO$_2$ cathode showed no obvious change, demonstrating the restriction of polysulfide diffusion from the H-TiO$_2$ component. After 250 CV cycles, H-TiO$_2$ was added to the bottle with pure S cathode and shook for several seconds. After resting for 2 hours, the turbid electrolyte turned clear as H-TiO$_2$ precipitated, and its yellow color faded simultaneously. This demonstrates that the H-TiO$_2$ additive in these cathodes also shows efficient adsorption properties for the escaped polysulfide.

To further demonstrate the interaction of polysulfide and H-TiO$_2$, we studied the precipitate from the sealed vial (shown as Fig. 4e). On the basis of the energy-dispersive X-ray spectroscopy (EDS) mappings (Fig. 5a–d), various sulfur bonds can be observed, which also confirmed the existence of S. The peak at 166–170 eV is related to the electrolyte. As reported in previous studies, the peak in the range of 162–163 eV can be assigned to Li$_3$S$_2$ species.9 Therefore, we confirmed that the H-TiO$_2$ spheres were efficient in adsorption of polysulfide and deposition of S species. The S + H-TiO$_2$ cathode after 25 cycles (Fig. 5f) shows little precipitation of insoluble products on the surface of the H-TiO$_2$ particles.

Figure 6 depicts the typical cyclic voltammetry (CV) curves at a constant scan rate of 0.1 mV/s in the voltage range of 1.5–3.0 V. During the first cycle, two pronounced cathodic peaks at approximately 2.29 and 1.98 V are observed. According to the previously reported mechanism, the peak at 2.29 V corresponds to the transition from elemental sulfur to long-chain lithium polysulfides (Li$_n$S$_{2n}$, 4 < n < 8).9,30 The peak at 1.98 V is related to the further reduction of low-order lithium polysulfides to Li$_2$S and Li$_3$S. The oxidation peak at about 2.52 V is associated with the reverse reactions in the charging stage. In the second CV scan, the cathodic peak at 1.98 V of the initial cathodic peak shifts to the position at about 2.01 V, and the current of the corresponding peak decreases to a low value. In the subsequent anodic cycle (3–6th cycles), the oxidation peaks shift to the position at 2.49 V, which are believed to be attributed to the complete conversion of Li$_2$S into elemental S the formation of Li$_2$S$_2$ (n > 2).9,31

Peaks located at 1.72 V and 2.03 V reveal the lithiation and delithiation of anatase TiO$_2$.

To further study the electrochemical properties, galvanostatic cycling was performed at a current density of 200 mA g$^{-1}$. The S + TiO$_2$ and S + H-TiO$_2$ electrodes delivered an initial discharge capacities of 1339.4 and 1301.9 mA h g$^{-1}$, respectively. Among them, the S + H-TiO$_2$ electrode exhibited the best capacity retention, as shown in Fig. 7a. After 50 cycles, it still has a capacity of 928.1 mA h g$^{-1}$, corresponding to a capacity retention of 71%. After 100 cycles at a current density of 1 A g$^{-1}$, it still has a capacity of 407 mA h g$^{-1}$ (Fig. 2s). The S + TiO$_2$...
The S + H-TiO₂ cathode showed relatively poor cycling stability, but much better than that of the pure sulfur electrode. The best performance of the S + H-TiO₂ electrode also demonstrated that the critical role of H-TiO₂ additive in mitigating the polysulfide dissolution into the electrolyte.

Figure 7b displays the charge–discharge curves of the S + H-TiO₂ electrode cathode. Two well-defined discharge plateaus were observed, which could be assigned to the two-step reaction of sulfur with lithium. The first plateau, centered around 2.35 V, was generally attributed to the reduction of the S₈ ring and the formation of S₈²⁻. The discharge plateau at 2.08 V was ascribed to the further reduction of the higher polysulfides (Li₂Sn, 4 ≤ n ≤ 8) to the lower polysulfides (Li₂Sn, n ≤ 3). There exhibited two plateaus in the charge process at about 2.37 and 2.47 V, respectively. Peaks at the beginning charging profile can be attributed to H-TiO₂. The positions of the plateaus were in accordance with the typical peaks of the S + H-TiO₂ electrode in the CV profiles. Within the first 20 cycles, the plateaus were well preserved. In longer cycling, the capacity only dropped from 1081.3 to 928.1 mA h g⁻¹, indicating that the H-TiO₂ additive was effective in preventing the long-term loss of sulfur into the electrolyte during the redox processes. These behaviors of the S + H-TiO₂ electrode in the coin cells were consistent with what was observed in the sealed vials, where the H-TiO₂ additive showed effective polysulfide restricting and recapturing ability.

The S + H-TiO₂ cathodes also show excellent cycling stability under continuously varying current densities, as shown in Fig. 8a. A reversible high and stable capacity of 850.8 mA h g⁻¹ was retained after 5 cycles at a current rate of 0.4 A g⁻¹. At a high current rate of 0.6 A g⁻¹, the S + H-TiO₂ electrode can give a reversible capacity of 650 mA h g⁻¹. When the current was further increased to 1.2 A g⁻¹, a high capacity of 466.4 mA h g⁻¹ can still be achieved, indicating fast reaction kinetics. It is worth mentioning that when the current was abruptly switched from 1.2 A g⁻¹ to 0.4 A g⁻¹ again, the capacity were recovered to 650.6 mA h g⁻¹, indicating the superior robustness and reversibility of the S + H-TiO₂ electrode. The electrochemical impedance spectroscopy (EIS) was also performed to study internal resistance of the S + H-TiO₂ and the corresponding Nyquist plots are shown in Fig. 8b. All the impedance plots for charged to 3.0 V are composed of a semicircle in the high-frequency region relating to the charge transfer resistance of the cathode and a sloping, straight line in the low-frequency region corresponding to the Li-ion diffusion within the cathode. The intersection of the semicircle on the real axis provides an approximate indication of the charge transfer resistance (Rct). This indicates that the slow accumulation of Li₂S on the surface of the S + H-TiO₂ cathode slightly caused the increase of Rct and the capacity degradation with cycle processing.

Figure 4. Visual confirmation of restricting and recapturing polysulfide. (a–c) Sealed vials with S and S + H-TiO₂ cathodes under CV cycles from 1.7–3.0 V; Sealed vial with S cathode after 250 CV cycles after H-TiO₂ added and rested for (d) 0 hour and (e) 2 hours.
Figure 5. (a–d) SEM image, EDX elemental mapping of Ti, O, S, and (e) S 2p XPS spectra of the precipitation gathered from the sealed vial in Fig. 3e. (e) SEM images of S + H–TiO₂ cathode after the 25th charge.

Figure 6. Cyclic voltammetry of the sulfur with hydrogen reduced TiO₂ cathode obtained at 0.1 mV s⁻¹.
Figure 7. (a) Cycling performance of sulfur, sulfur with TiO$_2$ and sulfur with hydrogen reduced TiO$_2$ cathodes at 200 mA g$^{-1}$. (b) Typical charge/discharge profiles of sulfur with hydrogen reduced TiO$_2$ cathode at 200 mA g$^{-1}$.

Figure 8. (a) Rate performance of the sulfur with hydrogen reduced TiO$_2$ cathode at different current density from 0.4 A g$^{-1}$ to 1.2 A g$^{-1}$; (b) impedance plots of the battery at different cycles under completely charged state.
Conclusions
Hierarchical TiO₂ spheres consisting of nano-plates reduced through hydrogen provide polysulfides host material as a cathode additive. The reduced TiO₂ spheres with a polar surface serve as the surface-bound intermediates for strong polysulfides binding. After 50 cycles, it still has a capacity of 928.1 mAh g⁻¹, corresponding to the capacity retention of 71%. The fine performances from S+H-TiO₂ electrodes also confirm that the critical role of H-TiO₂ additive in restricting and recapturing the polysulfide from the electrolyte.

Methods
Preparation of Cathode Composites. In a typical synthesis, 1 mL of titanium tetrachloride and hydrofluoric acid were added to 40 mL of ethyl alcohol. After stirring for a few minutes, the solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 6 h. The autoclave was then taken out of the oven and left to cool naturally to room temperature. The white precipitate was harvested via centrifugation, washed thoroughly with ethanol, and dried at 60 °C overnight. Hydrogen treatment of TiO₂ was performed by a thermal annealing process in an Ar (with H₂ 10%) gas flow. The temperature was increased from room temperature at a rate of 2 °C /min and held at 500 °C for 3 h. The TiO₂ or H-TiO₂ additive (80 mg) and sulfur (160 mg) were ground together for 15 min.

Materials Characterization. The crystalline phase of TiO₂ and H-TiO₂ was identified by X-ray diffraction (XRD, Dmax/2500PC, Rigaku, Japan) with Cu Kα radiation (λ = 1.5406 Å). Morphology and structure of the samples were characterized by a transmission electron microscope (TEM, JEM-2100F, 200 kV), and a field emission scanning electron microscope (SEM, JSM-6700F/Japan or FEIXL-30/USA with genesis 2000 energy-dispersive X-ray spectroscopy attachment). X-ray photo-electron spectrometry with an ESCALAB250 analyzer (XPS) were employed to characterize the obtained samples. Thermal gravimetric analysis (SDT Q600, TA Instruments Inc. USA) was carried out to estimate the amount of sulfur under Ar flow (100 mL min⁻¹) at a heating rate of 10°C min⁻¹.

Electrochemical Measurements. The TiO₂-additive and sulfur mixtures were mixed with Super-P carbon black and PVDF binder, with a mass ratio of 60:20:20, in N-methyl-2-pyrrolidone to produce electrode slurries. The resulting slurries were then casted on carbon fiber paper (15 g m⁻², Jiangsu China) with a laboratory doctor blade. The prepared electrode sheets were dried at 60 °C for 12 h in a vacuum oven. The typical areal density loading of active S was 0.8−1.3 mg/cm². CR2025-type half-coin cells were assembled in an argon-filled glove box with the H₂O and O₂ contents below 1 ppm. Metallic lithium foil was used as the counter and reference electrode. Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) in cosolvent of 1,3-dioxolane and 1,2-dimethoxyethane (volume ratio 1:1) was used as electrolyte. Charge-discharge performances were evaluated by a LAND CT2001A battery instrument at a constant current.

References

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Author Contributions
Z.Y. and H.W. conceived the work. Z.Y., L.L., C.W. and X.Z. performed the experiments. Z.Y., H.W., J.W. and Q.J. analyzed the data and prepared the manuscript. All authors discussed the results and commented on the manuscript.

Additional Information
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