Mesoporous TiO$_2$ Nanocrystals/Graphene as an Efficient Sulfur Host Material for High-Performance Lithium–Sulfur Batteries

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Supporting Information

ABSTRACT: Rechargeable lithium–sulfur (Li–S) batteries are promising in high-energy storage due to the large specific energy density of about 2600 W h kg$^{-1}$. However, the low conductivity of sulfur and discharge products as well as polysulfide-shuttle effect between the cathode and anode hamper applications of Li–S batteries. Herein, we describe a novel and efficient S host material consisting of mesoporous TiO$_2$ nanocrystals (NCs) fabricated in situ on reduced graphene oxide (rGO) for Li–S batteries. The TiO$_2$@rGO hybrid can be loaded with 72 wt % sulfur. The strong chemisorption ability of the TiO$_2$ NCs toward polysulfide combined with high electrical conductivity of rGO effectively localize the soluble polysulfide species within the cathode and facilitate electron and Li ions transport to/from the cathode materials. The sulfur-incorporated TiO$_2$@rGO hybrid (S/TiO$_2$@rGO) shows large capacities of 1116 and 917 mA h g$^{-1}$ at the current densities of 0.2 and 1 C (1 C = 1675 mA g$^{-1}$) after 100 cycles, respectively. When the current density is increased 20 times from 0.2 to 4 C, 60% capacity is retained, thereby demonstrating good cycling stability and rate capability. The synergistic effects of TiO$_2$ NCs toward effective chemisorption of polysulfides and conductive rGO with high electron mobility make a promising application of S/TiO$_2$@rGO hybrid in high-performance Li–S batteries.

KEYWORDS: TiO$_2$ nanocrystals, reduced graphene oxides, chemisorption, sulfur host material, lithium–sulfur battery

INTRODUCTION

The increasing market for portable electronics, electrical vehicles, and large-scale electrochemical energy storage systems has spurred research of rechargeable lithium-ion batteries (LIBs). However, conventional LIBs based on the LiCoO$_2$/graphite and LiFePO$_4$/graphite systems suffer from small energy densities due to the low specific capacities of the graphite anode and LiCoO$_2$ or LiFeO$_4$ cathodes. Theoretical capacity of a Li–S battery is 1675 mAh g$^{-1}$, and the theoretical specific energy of the Li–S batteries is 2567 Wh kg$^{-1}$ assuming a complete reaction from S to Li$_2$S, and it is 3–5 times bigger than those of LiCoO$_2$/graphite and LiFePO$_4$/graphite. Moreover, S is quite abundant, economical, and nontoxic. Unfortunately, Li–S batteries are plagued by the poor conductivity of sulfur, large volumetric expansion during lithiation (over 80% during the conversion from S to Li$_2$S), and dissolution of the polysulfide intermediates. The poor electron conductivity of sulfur ($\sim$10$^{-30}$ S cm$^{-1}$ at 25 °C) and the discharging products compromises electrochemical utilization, leading to sluggish redox reaction kinetics. Dissolution of long-chain polysulfides (Li$_2$S$_x$, 4 < x < 8) in the electrolyte triggers a polysulfide-shuttle process between the cathode and anode, resulting in loss of active cathode materials, low Coulombic efficiency, and rapid capacity fading.

Very recently, Nazar et al. have reported ordered mesoporous carbon encapsulated with sulfur as promising...
cathodes in Li–S batteries. The sulfur/carbon (S/C) nano-composite coated with an additional thin layer polymer delivers an initial reversible capacity as high as 1320 mAh g\(^{-1}\) and good cyclability. Other types of carbon materials such as meso-/microporous carbon, carbon nanotubes, carbon fibers, and graphene have also been used to prepare S/C composites to confine sulfur within the cathode and reduce the shuttling effect of polysulfide. Despite recent advances, the S/C composites still suffer from insufficient cycle stability as a result of the poor affinity between the nonpolar hydrophobic carbonaceous materials and polar hydrophilic lithium polysulfide species, leading to weak confinement of the intermediate polysulfide. It has been shown that polar metal oxides such as MnO\(_2\), \(\text{Ti}_4\text{O}_7\), \(\text{MoO}_2\), \(\text{TiO}_2\), \(\text{Al}_2\text{O}_3\), can be effective adsorbents to capture the soluble polysulfides by taking advantage of the chemisorption effect toward polar polysulfide species. In particular, \(\text{TiO}_2\) is a promising host for polysulfides due to the high chemical absorption ability. However, the intrinsically low electrical conductivity of metal oxide causes poor electrochemical utilization and rate capability of the active sulfur species due to the poor electron mobility. In addition, most of the reported S-based cathodes with high capacity and/or long cycle life have been achieved only with a relatively low S mass loading (<60 wt %). Abreuña et al. have demonstrated that the sulfur content in S-based composites is crucial to the energy density of Li–S batteries and the volumetric energy density of Li–S batteries can exceed current LIBs of \(\text{LiCoO}_2\)/graphite only if the S mass absorption ability. However, the intrinsically low electrical conductivity of \(\text{TiO}_2\) promotes host for polysulfides due to the high chemical absorption ability. Therefore, the intrinsically low electrical conductivity of metal oxide causes poor electrochemical utilization and rate capability of the active sulfur species due to the poor electron mobility. In addition, most of the reported S-based cathodes with high capacity and/or long cycle life have been achieved only with a relatively low S mass loading (<60 wt %). Abreuña et al. have demonstrated that the sulfur content in S-based composites is crucial to the energy density of Li–S batteries and the volumetric energy density of Li–S batteries can exceed current LIBs of \(\text{LiCoO}_2\)/graphite only if the S mass loading is higher than 70 wt %. It is thus important to design novel S-based materials that can not only effectively tether soluble polysulfide intermediates on the cathode, but also be loaded with a large mass loading of S, and provide high conductivity simultaneously.

Herein, we report a novel and efficient S host material consisting of mesoporous \(\text{TiO}_2\) nanocrystals (NCs) fabricated in situ on reduced graphene oxide (rGO) for Li–S batteries. Ultradispersed mesoporous anatase \(\text{TiO}_2\) NCs with dimensions of 10–20 nm are prepared in situ on highly conductive rGO by a one-pot hydrothermal technique using glucose as the dispersing agent and linker. The \(\text{TiO}_2\)/rGO nanohybrids can be loaded with 72 wt % S. The \(\text{TiO}_2\) NCs on rGO nanosheets can effectively capture the polysulfide intermediates via strong chemical binding, and the two-dimensional (2D) rGO provides a large surface area and high electrical conductivity for efficient electron and ion transport. The sulfur-incorporated \(\text{TiO}_2\)/rGO hybrid (S/\(\text{TiO}_2\)/rGO) shows large capacities of 1116 and 831 mA h g\(^{-1}\) at the current densities of 0.2 and 1 C (1 C = 1675 mA g\(^{-1}\) after 100 and 200 cycles, respectively. When the current density is increased from 0.2 to 4 C, 60% of the capacity is preserved. The S/\(\text{TiO}_2\)/rGO hybrid electrode suggests a two-in-one approach to improve the electrochemical properties of sulfur-based cathodes by combining the advantages of the polar \(\text{TiO}_2\) NCs and highly conductive 2D rGO and has great potential in Li–S batteries.

**Experimental Section**

**Preparation of Mesoporous \(\text{TiO}_2\)/rGO Hybrid.** The graphite oxide (GO) was obtained from Six Element Materials Technology Co., Ltd. (Changzhou), and the other chemical reagents (AR) were purchased from Sinopharm Chemical Reagents Co., Ltd., which were used without further purification. In a typical synthesis, the GO was first dispersed in distilled water at a concentration of 2 mg/mL ultrasonically. Next, 0.84 g of \(\text{Ti(SO}_4\))\(_2\) was dissolved in 70 mL of the GO solution under magnetic stirring for 10 min, and 0.07 g of glucose was subsequently added into the solution. After being stirred for 30 min, the solution was transferred to a 100 mL Teflon-sealed stainless steel autoclave and maintained at 180 °C for 12 h. After freeze-drying, the \(\text{TiO}_2\)/rGO nanocomposite was obtained. The rGO nanosheets were produced by the same method without addition of \(\text{Ti(SO}_4\))\(_2\). 

**Preparation of S/\(\text{TiO}_2\)/rGO and S/rGO Composites.** The S/\(\text{TiO}_2\)/rGO and S/rGO composites were prepared by conventional meltdiffusion melting. In brief, the sublimed sulfur was mixed with the \(\text{TiO}_2\)/rGO (or rGO) and then ground in an agate mortar at a weight ratio of 3:1. The mixture was sealed in vacuum glass tubes and heated to 155 °C for 12 h. To remove adsorbed sulfur from the surface, the S/\(\text{TiO}_2\)/rGO and S/rGO were heated to 300 °C for 2 h.

**Materials Characterization.** The morphology, structure, and composition of the samples were characterized by field-emission scanning electron microscopy (FE-SEM), nano SEM 450, Tecnai G20, transmission electron microscopy (TEM, Tecnai G20), high-resolution TEM (HR-TEM, Tecnai G20), energy dispersive X-ray spectroscopy (EDS, Oxford INCA 200), X-ray diffraction (XRD, GAXRD, Philips X’Pert Pro), X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W), and Raman scattering (HR RamLab). The nitrogen adsorption–desorption isotherms and pore size distribution were determined by Brunauer–Emmett–Teller (BET, Micrometrics, ASAP2010) at 77 K. The S contents in S/\(\text{TiO}_2\)/rGO and S/rGO were determined by thermogravimetric (TG) analysis (TGA, NETZSCH, TG 209 F3).

**Electrochemical Assessment.** To prepare the working electrodes, the S/\(\text{TiO}_2\)/rGO or S/rGO was mixed with carbon black and polyvinylidene fluoride (PVDF) at a ratio of 7:2:1, and N-methylpyrrolidinone (NMP) was added to form a slurry. The homogeneous slurry was cast onto aluminum current collectors (15 μm thick) by the blade doctor method, vacuum-dried at 60 °C for 12 h, and punched into rounded disks to form the cathodes. The average sulfur concentration was 1.3 mg cm\(^{-2}\). The S/\(\text{TiO}_2\)/rGO composite has a sulfur content of 72 wt % and the prepared cathode has a sulfur content of 50.4 wt %. For comparison, the S/rGO cathode was prepared by the same procedures. The CR2025-type coin cells were assembled in an argon-filled glovebox under water and oxygen below 0.1 ppm. The lithium metal was the counter electrode, and the polypropylene membrane (Celgard 2400) served as the separator. The electrolyte was 1 M bis(trifluoromethane)sulfonylimide lithium (LITFSI) with 1% LiNO\(_3\) as the additive dissolved in dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 by volume) (Beijing Institute of Chemistry, Beijing, China). Cyclic voltammetry (CV) was performed on an electrochemical workstaton (CHI 600E, Shanghai, China) at a scanning rate of 0.1 mV s\(^{-1}\) between 1.7 and 2.8 V versus Li+/Li. Electrical impedance spectroscopy (EIS) was conducted on the same instrument at frequencies between 100 kHz and 0.01 Hz with an amplitude of 5 mV. The galvanostatic charging–discharging (GCD) tests were carried out on the Xinwei instrument (Shenzhen, China), and the cutoff voltage was controlled from 1.7 to 2.8 V versus Li+/Li. The specific capacity values were calculated on the basis of the mass loading of the active sulfur, and all of the electrochemical tests were performed at room temperature.

**Results and Discussion**

Figure 1a illustrates the synthesis of the \(\text{TiO}_2\)/rGO nanohybrid. Uniform \(\text{TiO}_2\) NCs are prepared in situ on the rGO nanosheets by a simple one-pot hydrothermal technique using glucose as the dispersing agent and linker and Ti(SO\(_4\))\(_2\) as the Ti precursor. \(^{21\text{–}22}\) During the hydrothermal process, Ti(SO\(_4\))\(_2\) was dissolved in the solution to produce \(\text{TiO}_2\) crystal seeds, which were fixed on the surface of GO by the glucose molecules, whereas GO is reduced to rGO. The hydroxyl groups of glucose on one end of the glucose molecular are in contact with the \(\text{TiO}_2\) facets, whereas the hydroxyl groups on the other end connect with rGO, enabling in situ production of \(\text{TiO}_2\) NCs on both sides of the rGO during the hydrothermal process forming.
Figure 1. (a) Schematic diagram illustrating the synthesis procedure of TiO2@rGO composite; (b) transmission electron microscope (TEM) image of rGO; (c and d) TEM images of TiO2@rGO composite; and (e) high-resolution TEM image of TiO2@rGO composite.

Figure 2. (a) Field emission scanning electron microscope (FESEM) image of TiO2@rGO composite; (b and c) FESEM image of S/TiO2@rGO composite and their corresponding EDX mappings; and (d) X-ray diffraction (XRD) pattern of sublimed sulfur and S/TiO2@rGO composite.
Figure 3. (a) Thermogravimetric plot of S/TiO$_2$@rGO composite in Ar atmosphere with the heating rate of 5 °C/min from room temperature to 800 °C; (b) Raman spectra of sublimed sulfur, TiO$_2$@rGO, and S/TiO$_2$@rGO composite; and (c and d) nitrogen adsorption–desorption isotherms and their corresponding pore size distribution of rGO, TiO$_2$@rGO, and S/TiO$_2$@rGO composite.

Figure 4. Wide spectrum and high-resolution X-ray photoelectron spectroscopy (XPS) spectra of S/TiO$_2$@rGO composites: (a) wide spectrum; (b–d) high-resolution spectra of C 1s, Ti 2p, and S 2p, respectively.
the other peaks at 170.40 and 169.05 eV reflect sulfate and C−S bonds. The strong chemical absorption ability of TiO$_2$ NCs toward S or polysulfide is further confirmed by the simple adsorption experiment shown in Figure 5. The 3 mL of orange Li$_2$S$_6$ solution (10 mM) is first prepared, and then 30 mg of rGO or TiO$_2$@rGO is added into the solution. After the TiO$_2$@rGO powders were added, the color of the polysulfide solution changes from orange to colorless, but the color of polysulfide solution does not change after adding rGO powders. When the polysulfide solution is placed inside a glovebox for 3 days and the polysulfide solution containing the rGO powders turns white yellow from orange, the polysulfide solution containing TiO$_2$@rGO is still colorless. These experimental results confirm that the TiO$_2$@rGO nanohybrid has stronger and faster adsorption ability toward polysulfide than rGO. The enhanced chemical absorption ability can be attributed to the TiO$_2$ NCs on the rGO, which could effectively tether soluble polysulfide intermediates within the cathode.

The electrochemical properties of the S/TiO$_2$@rGO cathode are evaluated using the CR2025 coin cells. Figure 6a shows the cyclic voltammetry (CV) profiles in the voltage window of 1.7−2.8 V (vs Li/Li$^+$) at a scanning rate of 0.1 mV s$^{-1}$. The cathodic peaks at 2.30 and 2.02 V are attributed to the formation of long-chain lithium polysulfide (Li$_2$S$_n$) and short-chain insoluble lithium sulfide (Li$_2$S$_2$ or Li$_2$S). The anodic peaks at 2.35 and 2.40 V reveal two oxidation processes from lithium sulfide to long-chain lithium polysulfide and sulfur. From second to fifth, the peak positions of the S/TiO$_2$@rGO nanocomposite are...
nearly unchanged, implying good reversibility. The integrated CV areas of the S/TiO2@rGO gradually increase from first to fifth, suggesting gradual electrochemical activation of S/TiO2@rGO during lithiation and delithiation.16,37 The CV curves of the S/rGO cathode are depicted in Figure S3. The cathodic peaks and anodic peaks are located at 2.30, 1.99 V and 2.36, 2.42 V, respectively, implying slightly larger polarization in comparison with the S/TiO2@rGO cathode. The discharging–charging curves of the S/TiO2@rGO cathode at a rate of 0.2 C (1 C = 1675 mA/g) are displayed in Figure 6b. The two plateaus in the discharging curves correspond to a two-step reaction of sulfur with lithium, and the two plateaus in the charging curves show the reverse reactions from lithium sulfide to polysulfide and finally sulfur. The discharging plateau of the S/rGO cathode at 2.05 V becomes smaller from the second to 100th cycles (Figure S3b). However, the S/TiO2@rGO nanocomposite exhibits a large and stable discharge plateau at 2.05 V from the second to 100th cycles, implying a higher S utilization ratio as well as reversible and stable reaction of sulfur to Li2S due to strong chemical absorption of TiO2@rGO toward polysulfide. Figure 6c shows the long-term cycle stability test results of the S/rGO and S/TiO2@rGO cathodes. The capacity of S/TiO2@rGO increases initially during the first 10 cycles, which can be attributed to the delayed electrolyte infiltration into S/TiO2@rGO structure and gradually increased activation of S8 participation in the electrochemical reaction during the charge–discharge process. These electrochemical activation processes are also observed in the reported references.12,35–39 From the 10th to 100th cycles, the S/TiO2@rGO reaches a stable capacity of 1116 mA h g–1 with Coulombic efficiency (CE) reaching almost 100%. Different from the S/TiO2@rGO cathode, the discharging capacity of the S/rGO cathode decreases gradually with cycle, and the capacity is only 745 mA h g–1 after 100 cycles, which is 63.7% of the initial discharge capacity. These results indicate that incorporation of TiO2 NCs onto rGO effectively immobilizes polysulfide within the cathode and improves the electrochemical stability of the S/TiO2@rGO cathode.

Figure 6d discloses the rate capability of the S/rGO and S/TiO2@rGO cathodes at different current densities. The S/TiO2@rGO cathode is superior to the S/rGO cathode in terms of capacity at all measured current densities. At a large current density of 4 C, the discharging capacity of S/TiO2@rGO is 680 mA h g–1, which is twice that of S/rGO (300 mA h g–1). The discharging–charging curves of the S/rGO and S/TiO2@rGO cathodes at different current densities are displayed in Figure S4. The S/rGO cathode exhibits larger polarization than the S/TiO2@rGO cathode with increasing current densities. The long-term cycling performance of S/TiO2@rGO at a rate of 1 C is illustrated in Figure S5. After 200 cycles, the discharging capacity remains at 831 mA h/g with the capacity retention ratio of 94.8%, which is larger than those of previously reported S-based cathodes.40–43 The cycling properties of the S/TiO2@rGO cathode with different areal sulfur loading at a current density of 1 C were also presented in Figure S5. The S/TiO2@rGO cathode with sulfur loading of 2.1 mg cm–2 exhibited excellent cycle stability with the capacity retention ratio of 98.8% after 200 cycles. When the areal mass loading of S is increased to 3.2 and 3.9 mg cm–2, the S/TiO2@rGO cathodes still exhibited high capacity of 618 and 550 mA h g–1 after 200 cycles with 0.18% and 0.19% decay per cycle, respectively. The EIS profiles of the Li–S batteries based on S/rGO and S/TiO2@rGO cathodes before and after 100 cycles are shown in Figure 6e, and the corresponding equivalent circuit is presented in Figure S6. The semicircle at high frequencies represents the charge transfer resistance at the electrode–electrolyte interface (Rct). The charge transfer resistance of S/TiO2@rGO electrode is smaller than that of S/rGO cathode, indicative of better rate performance. Moreover, Rct becomes smaller after cycling due to better electrolyte infiltration, suggesting faster charge transport.12

The above-mentioned results indicate that the S/TiO2@rGO cathode has improved electrochemical properties in comparison with the S/rGO cathode. To further understand the role of TiO2 NCs in S/TiO2@rGO cathodes, the separators and electrodes of Li–S batteries based on S/rGO and S/TiO2@rGO cathodes after cycling are characterized. As shown in Figure S7, the surface of the separator based on the S/rGO cathode has a yellow substance after 100 cycles at 0.2 C, and the yellow color is deeper than that of the S/TiO2@rGO cathode, suggesting that polysulfide shuttling is suppressed on S/TiO2@rGO. After 100 cycles, the morphology of the S/TiO2@rGO cathode is the same as that of the pristine S/TiO2@rGO, but the S/rGO cathode is covered by a polysulfide layer as shown by Figure S8. The obvious absorption difference of rGO and TiO2@rGO toward polar polysulfide is confirmed by Figure 5. Thus, it is safe to conclude that the large capacity and good rate capability of the S/TiO2@rGO cathode arise from the synergistic effects of TiO2 NCs toward effective chemisorption of polysulfides and high conductivity rendered by the 2D rGO nanosheets. The conductivity of TiO2 and TiO2/rGO was measured by the four-point probes resistivity measurement system. As shown in Table S1, the average sheet resistance of TiO2/rGO electrode is 1082 mΩ/□, which is 10 times lower than that of TiO2 electrode (10 356 mΩ/□). These results indicate that the conductivity of TiO2@rGO hybrid TiO2 NCs is much improved in comparison with TiO2 NCs. Because of the strong chemical absorption between the polar TiO2 NCs and polar polysulfide, the polysulfide intermediates are effectively restricted on the surface of S/TiO2@rGO cathode as schematically shown in Figure 7a. On the contrary, the liquid polysulfide can easily diffuse into the electrolyte from S/rGO cathode due to the weak physical adsorption between the polar polysulfide and rGO during the discharging process (Figure 7b). Consequently, S/TiO2@rGO shows much improved electrochemical reversibility and stability in comparison with S/rGO. A comparison of the capacity and rate performance of the S/TiO2@rGO (the current work) with previously reported S cathodes based on metal oxides is shown in Table 1. It can be seen that the S/TiO2@rGO composite has
Table 1. Performance Comparison of S/TiO$_2$@rGO Nanocomposite with Other Oxide Matrices for Application in Li–S Batteries

<table>
<thead>
<tr>
<th>material</th>
<th>S content in composite (wt %)</th>
<th>S content in electrode (wt %)</th>
<th>areal S mass loading (mg cm$^{-2}$)</th>
<th>cycling stability</th>
<th>rate capability</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/TiO$_2$@rGO (this work)</td>
<td>72%</td>
<td>50.4%</td>
<td>1.3</td>
<td>1116 mA h g$^{-1}$ after 100 cycles at 0.2 C</td>
<td>917 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/MnO$_2$@HCF$^{15}$</td>
<td>71%</td>
<td>49.7%</td>
<td>2.1</td>
<td>912 mA h g$^{-1}$ after 100 cycles at 1 C</td>
<td>690 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/Ti$_2$O$_2$$^{17}$</td>
<td>64.2%</td>
<td>51.36%</td>
<td>3.2</td>
<td>758 mA h g$^{-1}$ after 100 cycles at 1 C</td>
<td>527 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/MoO$_2$$^{19}$</td>
<td>38%</td>
<td>30.4%</td>
<td>3.9</td>
<td>673 mA h g$^{-1}$ after 100 cycles at 1 C</td>
<td>705 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/β-MnO$_2$$^{40}$</td>
<td>40%</td>
<td>28%</td>
<td>3.5</td>
<td>900 mA h g$^{-1}$ after 100 cycles at 0.2 C</td>
<td>780 mA h g$^{-1}$ after 100 cycles at 0.05 mA cm$^{-2}$</td>
</tr>
<tr>
<td>S/TiO$_2$ rods$^{41}$</td>
<td>57.5%</td>
<td>40.25%</td>
<td>0.7</td>
<td>1033 mA h g$^{-1}$ after 100 cycles at 0.1 C</td>
<td>357 mA h g$^{-1}$ at 0.6 C</td>
</tr>
<tr>
<td>S/MnO$_2$ sheets$^{16}$</td>
<td>75%</td>
<td>56.25%</td>
<td>0.75</td>
<td>1030 mA h g$^{-1}$ after 200 cycles at 0.2 C</td>
<td>950 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/Ti$_2$O$_2$$^{18}$</td>
<td>60%</td>
<td>48%</td>
<td>0.75</td>
<td>950 mA h g$^{-1}$ after 100 cycles at 0.2 C</td>
<td>830 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/TiO$_2$@CNT$^{20}$</td>
<td>56%</td>
<td>44.8%</td>
<td>1.8</td>
<td>1040 mA h g$^{-1}$ after 100 cycles at 1 C</td>
<td>931 mA h g$^{-1}$ at 5 C</td>
</tr>
<tr>
<td>S/Ti$_2$O$_2$ yolk-shell$^{22}$</td>
<td>71%</td>
<td>53.25%</td>
<td>0.4</td>
<td>906 mA h g$^{-1}$ after 100 cycles at 0.5 C</td>
<td>725 mA h g$^{-1}$ at 1 C</td>
</tr>
<tr>
<td>S/TiO$_2$@HCNF$^{43}$</td>
<td>67.5%</td>
<td>54%</td>
<td>1.6</td>
<td>650 mA h g$^{-1}$ after 200 cycles at 0.5 C</td>
<td>630 mA h g$^{-1}$ at 1 C</td>
</tr>
</tbody>
</table>

Distinct advantages as compared to previously reported S-based cathodes based on oxides host materials for Li–S batteries in rate capability and capacity. The large capacity and high rate capability of S/TiO$_2$@rGO cathode stem from the relatively large S mass loading (72 wt %), strong chemical absorption of TiO$_2$ NCs toward polysulfide, and high conductivity of the TiO$_2$@rGO nanosheets.

**CONCLUSION**

Mesoporous TiO$_2$ anocrystals are prepared in situ on reduced graphene oxide (rGO) by a one-step hydrothermal method and serve as the super host material to incorporate a large amount of sulfur for Li–S batteries. The TiO$_2$@rGO, which can be loaded with 72 wt % S, and the S/TiO$_2$@rGO cathode show a high capacity of 1116 mA h g$^{-1}$ at a 0.2 C after 100 cycles and 831 mA h g$^{-1}$ at 1 C after 200 cycles. When the current density is increased 20 times from 0.2 to 4 C, 60% capacity is retained. As compared to S/rGO, S/TiO$_2$@rGO cathode material delivers larger capacity, better rate capability, and cycle stability. The excellent electrochemical properties of the S/TiO$_2$@rGO cathode are ascribed to strong chemical adsorption of polysulfide by the mesoporous TiO$_2$ nanocrystals and high conductivity of the 2D rGO nanosheets. The S/TiO$_2$@rGO cathode provides a two-in-one approach to improve the electrochemical properties of sulfur-based cathodes and has great potential in high-performance Li–S batteries.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b09479.

Preparation of the polysulfide solution, adsorption experiment of polysulfide, and disassembly of cells (experimental sections); Figures S1 and S2, characterization of TiO$_2$@rGO composite; Figures S3–S8, electrochemical tests and characterizations of S/rGO and S/TiO$_2$@rGO cathodes; Table S1, conductivity measurement of TiO$_2$ and TiO$_2$@rGO electrodes (PDF)

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**Notes**

The authors declare no competing financial interest.

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Supporting Information

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**Preparation of the polysulfide solution**

To prepare the polysulfide solution, appropriate amounts of commercial sublimed sulfur powders and lithium sulfide (Li$_2$S) were added to 50 mL of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, V/V) to form a 10 mM Li$_2$S$_6$ solution under stirring for 24 h. The chemical reaction is: $5S + Li_2S = Li_2S_6$. 3 mL polysulfide solution was then introduced to 5 mL glass bottles for subsequent experiments.

**Adsorption experiment of Polysulfide**

30 mg rGO and 30 mg TiO$_2$@rGO powders were added into different bottles containing 3 mL Li$_2$S$_6$ solution and mixed vigorously for one minute. After precipitation for 1 h and 3 days, photographs were taken by a camera.

**Disassembly of cells**

The coin cells were disassembled in an argon-filled glove box under water and oxygen below 0.1 ppm. The electrodes were rinsed with DME and DOL at least 3 times and dried prior to examination by SEM. The separators were taken out without rinsing for photographic comparison.
Figure S1. Thermogravimetric curve of TiO$_2$@rGO in Ar and O$_2$ hybrid gas with the heating rate of 5 °C/min from room temperature to 800 °C.

Figure S2. X-ray diffraction (XRD) patterns of TiO$_2$@rGO composite.
Figure S3. (a) Cyclic voltammetry (CV) plots of S/rGO cathodes with a scan rate of 0.1 mV/s; (b) Discharge-charge profiles of S/rGO cathodes at 0.2 C.

Figure S4. Discharge-charge curves of S/rGO (a) and S/TiO$_2$@rGO (b) cathodes at different current densities.
Figure S5. Cyclic properties of S/TiO$_2$@rGO cathode with different areal sulfur mass loading at a 1 C rate.

![Graph showing cyclic properties of S/TiO$_2$@rGO cathode](image)

Figure S6. The equivalent circuit of S/TiO$_2$@rGO cathode.

![Equivalent circuit](image)

Figure S7. The optical photograph of separators before and after 100 cycles at 0.2 C with S/rGO and S/TiO$_2$@rGO cathode materials. (a) Pristine separator; (b) cycled separator with S/rGO cathode; (c) cycled separator with S/TiO$_2$@rGO cathode.
Figure S8. FESEM images of the surfaces of S/rGO (a and b) and S/TiO$_2@$rGO (c and d) cathode before and after 100 cycles at a 0.2 C rate.

Table S1. The conductivity measurement of Al foil, TiO$_2$ and TiO$_2@$rGO electrodes by the 4-point probes resistivity measurement system.

<table>
<thead>
<tr>
<th></th>
<th>TiO$_2$ electrode</th>
<th>TiO$_2$/rGO electrode</th>
<th>Al foil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average sheet resistance (mΩ/□)</td>
<td>10356</td>
<td>1082</td>
<td>5</td>
</tr>
</tbody>
</table>

The TiO$_2$ or TiO$_2$/rGO powder was mixed with conductive agent (carbon black) and binder (polyvinylidene fluoride, PVDF) at a ratio of 7:2:1 with the N-2-methyl pyrrolidinone (NMP) as a solvent to form homogeneous slurry. The slurry was cast onto aluminum current collectors by the blade doctor method, vacuum dried at 60 °C for 12 h, and punched into rounded disks to form the electrode slices. The conductivity was measured by the 4-point probes resistivity measurement system (RTS-8, Guangzhou, China) and evaluated by the value of average sheet resistance.
As shown in Table S1, the average sheet resistance of TiO$_2$/rGO electrode is 1082 mΩ/□, which is ten times lower than that of TiO$_2$ electrode (10356 mΩ/□). These results indicate that the conductivity of TiO$_2$ NCs is much improved by cooperating with rGO to form TiO$_2$@rGO hybrid.