A Lightweight TiO₂/Graphene Interlayer, Applied as a Highly Effective Polysulfide Absorbent for Fast, Long-Life Lithium–Sulfur Batteries

Zhubing Xiao, Zhi Yang,* Lu Wang, Huagui Nie, Mei'e Zhong, Qianqian Lai, Xiangju Xu, Lijie Zhang, and Shaoming Huang*

The development of advanced electrode materials with high energy/power density for energy storage is critical for a sustainable society.^[1,2] Among existing materials, lithium-sulfur (Li-S) batteries show great potential for next-generation electrical energy storage applications. Sulfur cathodes, as well as being cost-effective and environmental friendly, provide a high theoretical capacity of 1675 mA h g⁻¹, a value that is an order of magnitude greater than typical values for conventional lithiated cathodes.^[3] Despite the great promise of Li-S batteries, two main technical challenges must be addressed before they can find practical use. First, the intrinsically poor electronic conductivity of sulfur leads to low use of the active material. Second, the high solubility of the polysulfide's (PS) reaction intermediaries (Li₂S_x, 4 < x < 8), and the action of their notorious "shuttle" mechanism in organic electrolytes, produce a rapid decline in the capacity, and a short cycle life.^[4] To facilitate the development of the Li-S system, it is therefore crucial to improve the conductivity of the sulfur cathode and maintain/ reuse the soluble PS within the cathode structure.^[5]

Impregnating sulfur into porous, nanostructured carbon matrixes,^[3,6] and performing the surface modification of conducting polymers^[7,8] are mainstream approaches that aim to address the above-mentioned issues and to realize a high capacity and an improved cycle life. Although previous studies demonstrated that the use of these approaches resulted in significant improvements in cyclability and capacity, it was noted there was still at least 10-20% loss of sulfur into the electrolyte as PS, especially under conditions with high S loading.^[3,5,7] In addition, the high cost and elaborate procedures required for the synthesis of carbon materials are additional drawbacks for these approaches. The insertion of an interlayer between the cathode and the separator, where the interlayer serves to intercept the migrating PS and reuse the trapped active material, resulted in a significant suppression of the shuttle effect.^[9-15] Manthiram et al. recently developed a bifunctional interlayer

Dr. Z. Xiao, Prof. Z. Yang, Dr. L. Wang, Dr. H. Nie, Dr. Q. Lai, Dr. X. Xu, Dr. L. Zhang, Prof. S. Huang Nanomaterials and Chemistry Key Laboratory Wenzhou University Wenzhou 325027, China E-mail: yang201079@126.com; smhuang@wzu.edu.cn Dr. M. Zhong College of Science Hunan Agriculture University Changsha 410128, China



DOI: 10.1002/adma.201405637

using microporous carbon paper and achieved significant improvements not only in the use of the active material but also in the capacity retention.^[12] More recently, various free-standing carbon interlayers including carbonized paper, a carbonized eggshell membrane, and an acetylene black mesh have been developed for the interception of migrating PS ions.^[13–15] Investigating different categories of carbon interlayers has become a major avenue of current research into the insertion of interlayers. Meanwhile, non-carbon interlayers also appeared on stage. A typical example is that the Li⁺ selective permselective membrane based on a coating layer of Nafion blocks the diffusion of PS anions across the membrane to the Li anode, which greatly suppresses the shuttling of PS.^[16] Since the diffusion of PS was localized on the cathode side, the cycling stability of the Li-S battery can be dramatically improved. Although these carbon and non-carbon interlayers have shown that it is possible to suppress the diffusion of PS and to improve the cycle-ability, some crucial issues remain to be resolved: i) As for these carbon and non-carbon interlayers, the complexity of the processes required for the synthesis of unique interlayers hinders their large-scale application, furthermore, the unsatisfactory thickness/weight of the applied interlayer may lead to a sharp decrease in the overall energy density, which may offset the gains in cell performance; ii) when the carbon interlayer acts only as a physical barrier, its nonpolar nature leads to weak interaction with polar PS anions, greatly reducing their ability to bind and confine these species during cycling. Moreover, the Li⁺ ion transfer may be impeded by the physical barrier; iii) with regard to the non-carbon interlayer, a lower initial discharge capacity compared to the counterpart cathode was arisen likely due to increasing the resistance to some extent. To address shuttling of PS issues, the adjustment of the interlayer components may be a desirable strategy; in theory, an ideal interlayer should be able to selectively control the shuttling of PS anions via strong chemical interactions between them, while not disturbing the Li⁺ ion transfer. Developing a lightweight and chemically selective interlayer carbon is therefore seems to be urgent. Previous reports have demonstrated the successful coupling of mesoporous TiO₂ additives to a C-S composite to improve the cycle life and the capacity retention.^[6,17] It was shown recently that Li-S batteries could achieve 1000 cycles when the sulfur was coated with TiO₂ to create yolk-shell structures.^[18] These results indicated that the mesoporous TiO₂ used in the coating layers promoted the interaction between TiO₂ and S, which was believed to be an electrostatic attraction (S-Ti-O)^[6,19] that improved the surface adsorption of PS on the TiO₂. Inspired by these results, and after comprehensively considering the three

ADVANCED MATERIALS

practical challenges described above, here, we developed an integrated, selective interlayer structure to further mitigate the PS diffusion, simply by coating the surface of a C-S cathode with a graphene/TiO₂ film, which accounted for only \approx 7.8 wt% of the whole cathode. It was found that the application of the graphene/TiO₂ film as an interlayer enabled the porous carbon nanotubes (PCNTs)-S cathode to deliver a reversible specific capacity of \approx 1040 mA h g⁻¹ over 300 cycles at 0.5 C. It was also confirmed that when they were cycled at higher rates, these cathodes exhibited ultrahigh cycling abilities, with a capacity degradation rate of 0.01% and 0.018% per cycle, measured over 1000 cycles at 2 and 3 C, respectively. To the best of our knowledge, such a low capacity degradation rate in the cathodes of advanced Li-S batteries has been reported only rarely. Most importantly, this simple coating approach can be applied for the variety of existing C-S cathodes (e.g., ordered mesoporous carbon materials (CMK-3)/S, porous carbon (PC)/S, carbon black (CB)/S, and carbon fiber/S), which show significantly superior electrochemical performance compared with alternative cathodes.

A schematic illustration of the cell configuration is shown in Figure 1a, and the configuration for a conventional Li-S battery is shown in Figure 1b for comparison. Photographs illustrating the process used to prepare the cathodes are shown in Figure 1c-e, a macroscopically smooth surface was observed after coating with a spreader. In a typical experiment, an interlayer was overlaid on the sulfur cathode simply via coating with a graphene sheet/TiO₂ film, where mesoporous anatase TiO₂ accounted for 3 wt% of the hybrid structure (Figure S1a,b, Supporting Information), this sample is referred to here as PCNTs-S@G/3%T. Figure 1f shows a typical cross-sectional scanning electron microscopy (SEM) image of the PCNTs-S@G/3%T electrode. The thickness of the graphene/TiO2 film and the PCNTs-S cathode were \approx 3 and 30 µm, respectively. The weight of the coating film was determined by weighing the electrode before and after the coating process (some detailed descriptions to measure the weight of cathode layer and interlayer are seen in the Supporting Information); the weight of the graphene/ TiO₂ film and the whole cathode was ≈ 0.15 and 1.80 mg, respectively. That is to say, the graphene/TiO₂ coating film accounted for only ≈7.8 wt% of the whole cathode. The as-obtained graphene/TiO₂ film was lighter than many freestanding interlayers fabricated by other groups.^[9-15] Figure 1g shows typical frontview SEM images of the graphene/TiO₂ film, which exhibit the homogeneous distribution of TiO2 on the interconnected and overlapped graphene sheets. No peaks characteristic of the TiO₂ phase were detected in the X-ray diffraction (XRD) spectra for the graphene/TiO₂ composite (Figure S1c, Supporting Information), which also indicated a uniform distribution of small TiO₂ particles in the graphene/TiO₂ film. As a control experiment, a neat-graphene interlayer was also investigated (Figure 1h, henceforward referred to as the PCNTs-S@G sample). To study the electrochemical properties of this novel Li-S battery, a C/S cathode composite employing PCNTs as a host material that we reported previously was prepared.^[20] After loading with 51.2 wt% (0.51 mg cm⁻²) of S (Figure S2a, Supporting Information), no bulk S particles were found, and the S was uniformly distributed in the PCNTs (Figure S2b-e, Supporting Information). The cell with PCNTs-S showed a much higher specific



capacity and cycle stability than the cell produced using a raw CNTs–S composite (Figure S2f, Supporting Information).

Figure 2a shows cyclic voltammetry (CV) plots for the PCNTs-S@G/3%T cathode, for the initial four cycles. In the first cathodic scan, two pronounced peaks at ≈2.35 and 2.02 V were observed. The former corresponded to the transition from elemental S to long-chain PS (Li_2S_x , 4 < x < 8), and the latter was related to the further reduction of low-order PS to Li₂S₂ and Li₂S. In the subsequent anodic scan, a strong, broader peak, and a shoulder peak were observed at \approx 2.38 and 2.42 V; these peaks were associated with the reverse reactions in the charging stage that occurred with the conversion from Li₂S to PS, and from PS to elemental S.^[21] The variation in the anodic peaks between the first and second cycles was ascribed to the rearrangement of active sulfur from its original positions to more energetically stable sites.^[20] No significant changes were detected for either of the anodic/cathodic peaks in the subsequent three cycles, indicating a high electrochemical stability. Interestingly, in the CV plots of PCNTs-S cathode (Figure S3a, Supporting Information), a weak and broader cathodic peak at 1.76 V was visible in the first cycle, but this peak disappeared in the next scans. This may be due to the irreversible reduction of LiNO₃, which only occurred in the first cathodic scanning.^[22] In contrast, for PCNTs–S@G/3%T cathode (Figure 2a), a cathodic current peak at 1.72 V could be detected during all the initial four cycles. Compared with these results, we therefore speculated that the broader cathodic current peak at 1.72 V was ascribed to the lithiation of anatase TiO2, which was in agreement with previous researches.^[19,23,24] More interestingly, no delithiation peak for anatase TiO₂ was observed in Figure 2a, which was in contrast with the expected peak at ≈ 2.15 V.^[19,23,24] We speculated that this missing peak was obscured by the delithiation process of S. Because the potentials of delithiation process for Li_xTiO₂ and Li₂S are close, the chemical absorption between TiO₂ and S may have resulted in the overlapping of the chemical processes and the non-detection of different charge plateaus. It is also interesting that the PCNTs-S@G/3%T cathode exhibited a higher peak location compared with the other two samples (Figure 2b). It is speculated here that the lithiation of sulfur may have resulted in an improved interphase electronic contact between the particles, derived from the electrostatic attraction between the TiO₂ and the PS. In addition, it is worth emphasizing that the collection coefficient (the ratio of the area of the peak associated with the formation of Li₂S, at \approx 2.0 V, to that of the peak for the formation of PS, at ≈ 2.4 V) for the dissolved PS at the cathode was 2.4, 2.7, and 3.2 for the PCNTs-S, PCNTs-S@G, and PCNTs-S@G/3%T samples, respectively (Figure 2b); these results showed the same trend as the ratio of the capacity for the low plateau and the capacity for the high plateau (Figure 2c). Moreover, the PCNTs-S@G/3%T sample also exhibited the lowest voltage hysteresis (ΔV), compared with PCNTs-S and PCNTs-S@G (Figure 2c); these results suggested a highly facile electrochemical redox reaction and low resistance for the PCNTs-S@G/3%T cathode.^[10] These results further indicated that the existence of TiO₂ in the graphene/TiO₂ film chemically influenced the electrochemical reaction mechanism of the cathode, which benefited the electrochemical performance. The performance of the PCNTs-S@G/3%T cathode at various current rates (0.2-3 C) is illustrated in the charge-discharge curves





Figure 1. Schematic of electrode configuration for Li–S battery with a graphene/TiO₂ coating film (a) and conventional Li–S battery (b); c–f) typical photographs of the coating process: as-prepared raw cathode (c); cathode coated with graphene/TiO₂ film (d,e); typical cross-sectional SEM images of fresh cathode with graphene/TiO₂ coating film (f); g,h) typical front-view SEM images of graphene/TiO₂ coating film (g), and neat graphene coating film (h).

in Figure 2d. Consistent with the CV curves, these discharge voltage profiles displayed the typical two-plateau behavior of an Li–S system; the flat lower discharge plateau indicated a slight electrochemical kinetic barrier.^[19] Specific capacity values of 1221, 1050, and 881 mA h g⁻¹ (determined by measuring the mass of S) were measured at 0.2, 0.5, and 1 C (0.86 mA cm⁻²),

respectively, values which were all superior to those of the PCNTs–S and PCNTs–S@G samples. Importantly, a reversible capacity of 1048 mA h g⁻¹ was retained when the current was abruptly switched back to 0.5 C (Figure S4, Supporting Information), indicating a highly reversible rate performance. The cycling stability was measured at a low current rate (0.5 C),





Figure 2. a) CV profiles of the PCNTs-S@G/3%T cathode; b) CV profiles of PCNTs-S, PCNTs-S@G, PCNTs-S@G/3%T cathode; c) galvanostatic charge-discharge profiles of the PCNTs-S, PCNTs-S@G, PCNTs-S@G/3%T cathodes at 0.2 C; d) galvanostatic charge-discharge profiles of the PCNTs-S@G/3%T cathode at various current rate; e) cycling stability of PCNTs-S, PCNTs-S@G, PCNTs-S@G/3%T cathodes at 0.5 C, the current density of 0.86 mA cm⁻².

as illustrated in Figure 2e. The discharge capacity started at 1050 mA h g⁻¹, and displayed a gradual increase for the first 20 cycles. An electrochemical activation step occurred during the first few cycles, due to the electrolyte diffusion through the coating film and the porous structure of the PCNTs.^[23] Most importantly, capacity of ~1040 mA h g⁻¹ was achieved over 300 cycles; in sharp contrast, the PCNT–S and PCNTs–S@G samples retained capacities of only 430 and 750 mA h g⁻¹, respectively. The improved cycling stability of the PCNTs–S@G/3%T sample was also reflected in the charge–discharge curves (Figure S5, Supporting Information). The higher discharge plateaus ($Q_{\rm H}$) corresponding to the formation of highly soluble PS were retained well, suggesting that the outward migration of dissolved PS and the loss of active material were

greatly suppressed by the graphene/TiO₂ coating film.^[14] In addition, electrochemical impedance spectra (Figure S6, Supporting Information) showed that both the PCNTs–S and the PCNTs@G–S sample exhibited two semicircles after 300 cycles. This behavior may be associated with the presence of a passivation film in the high-frequency region and charge-transfer resistance (R_{ct}) in the medium-to-low frequency region. These results suggested dissolution of PS followed by their deposition onto the electrodes.^[10,25] In contrast, the appearance of only one semicircle for the PCNTs–S@G/3%T samples with a decreased R_{ct} value, indicated a low resistance caused by the entrapment of the dissolved PS^[10] and good electrolyte infiltration as well as good charge transport.^[25] The corrosion of lithium piece and the formation of a Li₂S/Li₂S₂ deposition layer on the lithium were

www.advmat.de





Figure 3. a) Cycling stability of PCNTs–S@G/3%T cathode at 2 and 3 C; b) cycling stability of PCNTs–S and PCNTs–S@G/3%T cathodes with S loading of 82% at 0.5 C. c) Typical galvanostatic charge–discharge profiles of the PCNTs–S@G/3%T cathode with S loading of 82% at 0.5 C, the current density of 0.86 mA cm⁻² for 1 C.

therefore largely mitigated. These results agreed well with the observations from the voltage profiles (Figure 2c). These superior properties demonstrated that the graphene/TiO₂ coating film not only suppressed the detachment of S and PS but also reduced the resistance of the cathode, because of the enhanced interactions at the TiO₂/electrolyte/carbon junction.^[17,26]

The long-term cycling stability of the PCNTs-S@G/3%T cathode was also tested at high current densities of 2 and 3 C (Figure 3a). After 1000 cycles, the discharge capacity of the cells approached 630 and 535 mA h g^{-1} at 2 and 3 C, with capacity degradation rates of 0.01% and 0.018% per cycle, respectively. In addition, the Coulombic efficiency also increased from 96.2% at 2 C to 99.8% at 3 C. In comparison, the cells based on PCNTs-S and PCNTs-S@G suffered from a rapid decrease in the capacity, achieving only 200 and 400 cycles, respectively (Figure S7, Supporting Information); these results indicated a greater degree of dissolution of the PS into the electrolyte. It is noteworthy that the Cui and Cairns groups reported prolonged cycling performance over 1000 and 1500 cycles at 0.5 C, with a decay rate of 0.033% and 0.039%, respectively.^[18,27] Certainly, it also need to point out here that capacity degradation might be severe if the current rate was lowered or the sulfur loading amounts were increased, due to the PS dissolution in the electrolyte and their diffusion as well as reaction with the anode.^[28] Meanwhile, high currents could also increase the Coulombic efficiency and the cycling stability, since the diffusion of PS to the anode was slower than the total electrochemical reaction time.^[28] Even so, to the best of our knowledge, such an

ultrahigh cycling stability at 2 C (3.4 g^{-1} , 1.7 mA cm^{-2}) and 3 C (5 A g^{-1} , 2.6 mA cm^{-2}) has been reported only rarely for Li–S batteries so far. The reasons may be ascribed to two aspects: i) the porous structure in PCNTs may be an important factor because of their intrinsic capability to trap soluble intermediate PS, and to accommodate volume variations of the S cathode, to efficiently convey Li⁺ ions in the electrolyte; ii) the resulting low resistance and high efficient entrapment for the dissolved PS rooted in the introduction of the TiO₂/graphene interlayer should be another important reason for the ultrahigh stability at high current rate. The developed Li–S battery based on TiO₂/graphene interlayer shows great potential for future energy storage devices ranging from portable electronics and consumer devices to electric vehicles and large-scale grid energy storage.

Recently, some groups proposed the concept of "two lows,"^[29,30] they pointed out that low sulfur content in the cathode and a low areal loading were not suitable for a practical application. To solve the "two lows" issue, some groups reported prolonged cycling performance with high S loading at low current rate conditions.^[31,32] Taking the relatively low areal loading (0.51 mg cm⁻²) of S in the PCNTs–S@G/3%T cathode into consideration, the effects of high loading of sulfur were therefore investigated when coating the graphene/TiO₂ film. As shown in Figure 3b, when the sulfur loading on the electrode was as high as 82 wt% (1.2 mg cm⁻²) (Figure S2a, Supporting Information), instead of the rapid initial decay generally observed for typical PCNTs–S cathodes, the first few cycles showed a





Figure 4. a) Typical colors of electrolyte for the PCNTs-S@G/3%T (1) and PCNTs-S (2) cathodes after 300 cycles in sealed vials. b,c) UV–vis absorption spectra of the solution obtained by soaking the cycled PCNTs-S@G/3%T (b) and PCNTs-S (c) cathodes in a mixture of DOL/DME (1:1, vol). d) The 1st and 300th cycles of UV–vis absorption spectra of the cycled PCNTs–S@G/3%T and PCNTs-S cathodes. e,f) EDX spectra for the cycled (e) and fresh (f) PCNTs-S@G/3%T cathode, unit: keV. The weak fluorine signal results from the polyvinylidene fluoride (PVDF).

slight increase in specific capacity from 802 to 835 mA h g⁻¹, corresponding to the kinetic activation mentioned above. Surprisingly, subsequent cycles showed very stable performance, with a coulombic efficiency of ~97%, and a capacity retention of over 82% over 250 cycles. It is interesting to note that both the PCNTs–S@G/3%T cathode and the PCNTs–S cathode showed a similar $Q_{\rm H}$ capacity (Figure S8, Supporting Information). The discrepancy in the capacity at the lower plateaus corresponding to the formation of L₂S₂ or L₂S was likely due to the diffusion-blocking of soluble short-chain PS, which was indicative of a better cycling stability. Furthermore, the overlapping $Q_{\rm H}$ (Figure 3c) also highlighted the abilities of the graphene/TiO₂ film in intercepting S and soluble PS.

UV–vis absorption spectra were measured to obtain further insight into the electrode coated with the graphene/ TiO_2 film. The solutions were obtained by soaking the various cycled

cathodes (discharge state) in a mixture of 1,3-dioxolane/1,2dimethoxyethane (DOL/DME, 1:1, vol). As shown in Figure 4a, the color of the solvent exhibited only slight variations for the PCNTs-S@G/3%T cathode, even after 300 cycles (Figure S9, Supporting Information). In striking contrast, the solvent changed to a dark gold color for the PCNTs-S sample (Figure S10, Supporting Information). In addition, the distortion and deformation caused by the corrosion of aluminum and the exfoliation of the active materials was clearly visible for the PCNTs-S cathode piece. The PCNTs-S@G/3%T sample maintained a good appearance, without any distinct deformation, suggesting a facile electrochemical reaction kinetic for the cell. Figure 4b shows UV-vis absorption spectra for the PCNTs-S@G/3%T electrode. The PS contents in the electrolyte were only subtly different, even after 300 cycles, as revealed by the similar peak and peak intensities; these results indicated low



S and PS mobilities. In contrast, a large boost in peak intensities revealed the severe detachment of PS from the PCNTs-S cathode (Figure 4c). The sharp peak located at 280 nm was attributed to S_8 and S_6^{2-} species, the shoulder peak at 310 nm was attributed to S_6^{2-} or S_4^{2-} species, and the peak at 420 nm was attributed to S_4^{2-} species.^[33,34] When focusing on the 1st and 300th curves for the PCNTs-S and PCNTs-S@G/3%T samples (Figure 4d), a new, emerging band at 330 nm, and a redshift at 420 nm for the S_4^{2-} species, were discernible for PCNTs-S cathode, suggesting greater PS dissolution and a subsequent disproportionation reaction.[35,36] The cycled electrodes were further studied using SEM and energy-dispersive X-ray (EDX) spectroscopy. SEM images of the cathodes showed that for the PCNTs-S@G/3%T cathode, even after 300 cycles at 3 C the TiO₂ was uniformly distributed in the graphene sheets, and the overall morphology and structure of the electrode were well preserved (Figure S11a). Conversely, a rough surface and particle aggregation were clearly observed for the PCNTs-S cathode (Figure S12, Supporting Information). EDX analysis revealed a richer distribution of sulfur in the cycled PCNTs-S@G/3%T cathode (Figure 4e) compared with the fresh cathode (Figure 4f), indicating that the diffusion of S and PS anions was greatly inhibited by the graphene/TiO₂ film. In addition, the uniform distribution of S, C, and Ti suggested that the trapped S did not form agglomerates (Figure S11b-e, Supporting Information), which is conductive to decreasing the cell resistance. It is noteworthy that the carbon signals in the EDX results shown in Figure 4e,f were still conspicuous after longterm cycling, reconfirming that the trapped S and PS active materials did not agglomerate, but continuously reactivated, and benefited the cycling stability.^[13] For the cycled PCNTs-S cathode (Figure S12, Supporting Information), a much lower sulfur concentration was found in the elemental maps after long-term cycling (Figure S13, Supporting Information), compared with a fresh cathode (Figure S2c-e, Supporting Information), indicating the extensive dissolution of S and PS anions in the electrolyte. The SEM images, coupled with the EDX and elemental map results, indicated that the uniformly distributed TiO₂ did not block the porous Li⁺/electrolyte channels in the graphene sheet, but continuously captured and reactivated the dissolved PS/active material. This could be ascribed to two possible mechanisms: On one hand, the interconnected and overlapped graphene provided rapid electron transfer to reactivate the trapped active materials, restraining the formation of inactive precipitates.^[11] On the other hand, the homogeneous distribution of TiO₂ interacted favorably at the three-phase TiO₂/ electrolyte/carbon junction, leading to the stabilization of the runaway active materials and PS in the TiO2/graphene barrier.^[17] Such an optimized electrochemical environment therefore ensured a significant contribution to the overall capacity, and a ultralow decay rate per cycle.

To probe the electronic and chemical environment of the TiO₂ in the cycled PCNT–S@G/3%T cathode, X-ray photoelectron spectroscopy (XPS) analysis was performed, as illustrated in Figure S14, Supporting Information. Compared with the control TiO₂ sample, the Ti $2p_{1/2}$ XPS peak at 465 eV was found to be broader, which may be ascribe to the existing of Ti–S bond.^[17–19] The enhancement of the electrochemical properties of the PCNTs–S@G/3%T cathode (compared with

those of the PCNTs–S@G cathode) may therefore be explained as the result of a synergistic effect between the weak chemical adsorption on the surface of the TiO_2 and the physical entrapment by the graphene coating film, which together inhibited the loss of PS into the electrolyte.

To further test the general applicability of the simple graphene/TiO₂ coating process, other typical carbon materials (Figure S15, Supporting Information), including CMK-3, PC, CB, and vapor-grown carbon fiber (VGCF) were used to fabricate Li-S batteries. Figure S16, Supporting Information shows results for the cycle stability of the various carbon materials cathode, measured at 1 C. Taking CMK-3-S as an exemplary case (Figure S16a, Supporting Information), the cathode coated with graphene/TiO2 (CMK-3-S@G/3%T) exhibited a capacity of 560 mA h g⁻¹ after 200 cycles, compared with the maximum 650 mA h g⁻¹ after the fifth cycle. In contrast, the cathode without TiO₂ (CMK-3–S@G) and the raw cathode (CMK-3–S) retained a capacity of only 420 and 295 mA h g⁻¹, respectively. Figure S16b, Supporting Information shows that the commercial CB, when applied as a conductive matrix, exhibited a severe, rapid reduction in capacity. After coating with graphene/TiO₂, the CB-S cathodes showed distinct improvements in capacity and cyclability. Furthermore, considering Figure S16c,d, Supporting Information, it is interesting to note that the VGCF-S and PC-S cathodes also displayed enhanced electrochemical performance when coated with a graphene/TiO₂ film. These results demonstrated that this graphene/TiO₂ coating film was effective in enhancing the performance for Li-S batteries.

In summary, we successfully obtained an integrated selective interlayer simply by coating the surface of a C-S cathode with a commercial graphene/TiO2 film, which accounted for only ≈7.8 wt% of the whole cathode. In this rational design, the porous graphene afforded an additional electrically conductive network, and physically trapped S and PS; as an added bonus, the TiO₂ in graphene/TiO₂ barrier film further chemically suppressed the dissolution of PS, and alleviated the undesirable shuttle effect. The PCNTs-S cathode coated with a graphene/TiO₂ film delivered a reversible specific capacity of ≈ 1040 mA h g⁻¹ over 300 cycles at 0.5 C. Ultralow capacity degradation rates of 0.01% and 0.018% per cycle were achieved at 2 and 3 C, respectively, over 1000 cycles. Most importantly, this simple coating approach can be further extended to various C-S cathodes, including CMK-3-S, CB-S, PC-S, and VGCF-S cathodes. This graphene/TiO₂ approach opens a new avenue for the construction of interlayers that act as a barrier between a sulfur cathode and a separator.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work was supported in part by grants from the National Science Foundation of China (NSFC, Grant Nos. 21273163, 51002106, 21475096, and 51420105002), NSFC for Distinguished Young Scholars (Grant No. 51025207) and the National Science Foundation of Zhejiang

www.advmat.de



www.MaterialsViews.com

Province (NSFZJ, Grant No. LY13B050002), and Xinmiao talent project of Zhejiang Province (Grant No. 2013R424061).

Received: December 10, 2014 Revised: March 2, 2015 Published online: March 26, 2015

- Q. Pang, D. Kundu, M. Cuisinier, L. F. Narzar, Nat. Commun. 2014, 5, 4759.
- [2] H. B. Yao, G. Y. Zheng, P. C. Hsu, D. S. Kong, J. J. Cha, W. Y. Li, Z. W. Seh, M. T. McDowell, K. Yan, Z. Liang, V. K. Narasimhan, Y. Cui, *Nat. Commun.* **2014**, *5*, 3943.
- [3] X. Ji, K. T. Lee, L. F. Nazar, Nat. Mater. 2009, 8, 500.
- [4] C. Zhang, H. Wu, C. Yuan, Z. Guo, X. Lou, Angew. Chem. Int. Ed. 2012, 51, 9592.
- [5] X. Tao, J. Wang, Z. Ying, Q. Cai, G. Zheng, Y. Gan, H. Huang, Y. Xia, C. Liang, W. Zhang, Y. Cui, *Nano Lett.* **2014**, *14*, 5288.
- [6] J. Schuster, G. He, B. Mandlmeier, T. Yim, K. T. Lee, T. Bein, L. F. Nazar, Angew. Chem. Int. Ed. 2012, 51, 3591.
- [7] L. F. Xiao, Y. L. Cao, J. Xiao, B. Schwenzer, M. H. Engelhard, L. V. Saraf, Z. M. Nie, G. J. Exarhos, J. Liu, *Adv. Mater.* **2012**, *24*, 1176.
- [8] B. B. Wu, X. Y. Jiang, L. F. Xiao, W. H. Zhang, J. X. Pan, X. P. Ai, H. X. Yang, Y. L. Cao, *Electrochim. Acta* 2014, *135*, 108.
- [9] S. Dorfler, M. Hagen, H. Althues, J. Tubke, S. Kaskel, M. J. Hoffmann, *Chem. Commun.* 2012, 48, 4097.
- [10] G. M. Zhou, S. F. Pei, L. Li, D. W. Wang, S. G. Wang, K. Huang, L. C. Yin, F. Li, H. M. Cheng, Adv. Mater. 2013, 26, 4.
- [11] S. H. Chung, A. Manthiram, Adv. Mater. 2014, 26, 1360.
- [12] Y. S. Su, A. Manthiram, Nat. Commun. 2012, 3, 1166.
- [13] S. H. Chung, A. Manthiram, Chem. Commun. 2014, 50, 4184.
- [14] Y. S. Su, Y. Z. Fu, B. K. Guo, S. Dai, A. Manthiram, Chem. Eur. J. 2013, 19, 8621.
- [15] T. G. Jeong, Y. H. Moon, H.-H. Chun, H. S. Kim, B. W. Cho, Y.-T. Kim, Chem. Commun. 2013, 49, 11107.

- [16] J.-Q. Huang, Q. Zhang, H.-J. Peng, X.-Y. Liu, W.-Z. Qian, F. Wei, Energy Environ. Sci. 2014, 7, 347
- [17] S. Evers, T Yim, L. F. Nazar, J. Phys. Chem. C 2012, 116, 19653.
- [18] Z. W. Seh, W. Y. Li, J. J. Cha, G. Y. Zheng, Y. Yang, M. T. McDowell, P. C. Hsu, Y. Cui, *Nat. Commun.* **2013**, *4*, 1331.
- [19] Z. Liang, G. Zheng, W. Li, Z. W. Seh, H. Yao, K. Yan, D. Kong, Y. Cui, ACS Nano 2014, 8, 5249.
- [20] Z. B. Xiao, Z. Yang, H. G. Nie, Y. Q. Lu, K. Q. Yang, S. M. Huang, J. Mater. Chem. A 2014, 2, 8683.
- [21] H. J. Peng, J. Q. Huang, M. Q. Zhao, Q. Zhang, X. B. Cheng, X. Y. Liu, W. Z. Qian, F. Wei, Adv. Funct. Mater. 2014, 24, 2772.
- [22] S. S. Zhang, J. Electrochem. Soc. 2012, 151, A920.
- [23] N. Li, G. Liu, C. Zhen, F. Li, L. Zhang, H. M. Cheng, Adv. Funct. Mater. 2011, 21, 1717.
- [24] Z. Wang, X. W. Lou, Adv. Mater. 2012, 24, 4124.
- [25] Z. F. Deng, Z. Zhang, Y. Q. Lai, J. Liu, J. Li, Y. X. Liu, J. Electrochem. Soc. 2013, 160, A553.
- [26] M. Bailey, S. Donne, J. Electrochem. Soc. 2011, 158, A802.
- [27] M.-K. Song, Y. G. Zhang, E. J. Cairns, Nono Lett. 2013, 13, 5891.
- [28] Y. V. Mikhaylik, J. R. Akridge, J. Electrochem. Soc. 2004, 151, A1969.
- [29] L. X. Miao, W. K. Wang, A. B. Wang, K. G. Yuan, Y. S. Yang, J. Mater. Chem. A 2013, 1, 11659.
- [30] M. Wang, W. Wang, A. Wang, K. Yuan, L. Miao, X. Zhang, Y. Huang, Z. Yu, J. Qiu, Chem. Commun. 2013, 49, 10263.
- [31] L. Zhu, H. Peng, J. Liang, J. Q Huang, C. M Chen, X. Guo, W. Zhua, P. Li, Q. Zhang, *Nano Energy* **2015**, *11*, 746.
- [32] G. Zhou, L. Li, C. Ma, S. Wang, Y. Shi, N. Koratkar, W. Ren, F. Li, H. Cheng, *Nano Energy* **2015**, *11*, 356.
- [33] Y. J. Li, H. Zhan, S. Q. Liu, K. L. Huang, Y. H. Zhou, J. Power Sources 2010, 195, 2945.
- [34] C. Barchasz, F. Molton, C. Duboc, J. C. Leprêtre, S. Patoux, F. Alloin, Anal. Chem. 2012, 84, 3973.
- [35] D. H. Han, B. S. Kim, S. J. Choi, Y. J. Jung, J. Kwak, S. M. Park, J. Electrochem. Soc. 2004, 151, E283.
- [36] M. M. Patel, R. Demir-Cakan, M. Morcrette, J. M. Tarascon, M. Gaberscek, R. Dominko, *ChemSusChem* 2013, 6, 1177.