A flexible metallic TiC nanofiber/vertical graphene 1D/2D heterostructured as active electrocatalyst for advanced Li–S batteries

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Abstract
The realistic application of lithium–sulfur (Li–S) batteries has been severely hindered by the sluggish conversion kinetics of polysulfides (LiPS) and inhomogeneous deposition of Li₂S at high sulfur loading and low electrolyte/sulfur ratio (E/S). Herein, a flexible Li–S battery architecture based on electrocatalyzed cathodes made of interfacial engineered TiC nanofibers and in situ grown vertical graphene are developed. Integrated 1D/2D heterostructured electrocatalysts are realized to enable highly improved Li⁺ and electron transportation together with significantly enhanced affinity to LiPS, which effectively accelerate the conversion kinetics between sulfur species, and thus induce homogeneous deposition of Li₂S in the catalyzed cathodes. Consequently, highly active electro-electrocatalysts-based cells exhibit remarkable rate capability at 2C with a high specific capacity of 971 mAh g⁻¹. Even at ultra-high sulfur loading and low E/S ratio, the battery still delivers a high areal capacity of 9.1 mAh cm⁻², with a flexible pouch cell being demonstrated to power a LED array at different bending angles with a high capacity over 100 cycles. This work puts forward a novel pathway for the rational design of effective nanofiber electrocatalysts for cathodes of high-performance Li–S batteries.

KEYWORDS
electrocatalysis, electrospinning, interface engineering, nanofiber, vertical graphene
1 | INTRODUCTION

The increasing demand for electrical equipment and devices has been driving the ever-expanding evolution of high-energy-density storage systems, since the performances of current commercial LIBs are approaching their theoretical limitation.1–3 Among potential candidates as next-generation battery systems, Li–S batteries have been regarded as the most promising alternative, owing to their excellent theoretical capacity (1675 mAh g$^{-1}$), the large resource, low cost, and environmental benignity of sulfur.4–8 However, there are still some problematic issues to hamper the commercial implementation of Li–S batteries.9,10 The main drawbacks associated with cathodes are the shuttle effect of the polysulfides (LiPS) and the sluggish reaction kinetics between sulfur and Li$_2$S.11 Moreover, the Li–S chemistry involves complicated liquid–solid phase conversions between LiPS to Li$_2$S, and the notorious problem of inhomogeneous electrodeposition of Li$_2$S is behind severe increase of the mass transfer resistance in battery. The intrinsically high electric insularity of sulfur and Li$_2$S as well as the enormous volume fluctuation in the charge/discharge processes are to lead to insufficient sulfur utilization, rapid capacity decay, and even premature failure of Li–S cells.12–16

Numerous materials have been explored to serve as sulfur hosts or additives to tackle the aforementioned issues, including nonpolar conductive carbon-based materials4,17–19 and polar compounds (oxides, nitrides, and carbides).12,18,20–25 Previous reports proved that nonpolar carbon materials are only able to offer limited affinity with LiPS, due to the rather weak van der Waals force in-between.26–28 Polar transition metal oxides, on the other hand, can provide stronger affinity with LiPS from potential chemical bonding, which is thus more effective in mitigating the shuttle effect. Most of them, however, have poor electronic conductivity, which will result in sluggish reaction kinetics during the charge and discharge cycles.29–35 The sluggish conversion kinetics in a battery cell will cause the accumulation of LiPS in its cathode and consequently gives rise to seriously uneven electrodeposition of Li$_2$S, which in turn results in inhomogeneity in the transfer of electrons, being detrimental to electrochemical processes over charging and discharging.36–38 The electrically insulating Li$_2$S film is also of poor conductivity to Li$^+$ ions, and the formation of uneven Li$_2$S film is therefore considered to be the main factor to greatly aggravates the mass transfer in cells over cycling, which finally leads to termination of the liquid/solid conversion reactions in the discharge/charge processes. However, to date, little effort has been directed toward addressing the problem due to uneven Li$_2$S precipitation and effective schemes are yet to be developed. It is thus envisaged that an excellent sulfur host or cathodes additives should possess the following characteristics: (i) high electric conductivity to support charge transfer during conversion between sulfur-species; (ii) strong affinity with LiPS to suppress the shuttle effect; (iii) high Li$^+$ diffusivity to assist redox kinetics and enhance the utilization of sulfur species; (iv) being able to prevent uneven electrodeposition of Li$_2$S.

Recent research interests have mainly been centered upon designing active electrocatalysts with high electric conductivity and chemisorption capability, in order to mitigate the insulating problem associated with sulfur and Li$_2$S, to suppress the shuttle effect and to enhance the sulfur redox reaction kinetics. For example, nitrogen-doped Ti$_3$C$_2$ MXene41,42 MoN12 IT$^+$-ReS$_2$20 and nitrogen-doped CoSe$_2$39 have been utilized as active electrocatalysts to help deliver the aforementioned characteristics (i)–(iii), demonstrating effectively improved specific capacity, cycle stability, and sulfur utilization.27 Among these active electrocatalysts, the electrically conductive TiC ($10^4$ S cm$^{-1}$) is endowed as a promising candidate with a strong affinity for LiPS.27,29,44 However, the problem due to uneven deposition of the insulative Li$_2$S film is yet to be addressed, which looms large in the way for delivering practical Li–S batteries when high S loading and low E/S ratio are essential requests.45 A way forward lies in significant enlargement in the specific interfacial area with electrocatalysts, so that Li$_2$S could be spread over a large surface to reduce overall film thickness and avoid local aggregation. Conducting two-dimensional (2D) materials such as low-defect graphene would be an additive material of choice, so that its effective coupling with nanoelectrocatalysts could enable the best use of the surficial area of the catalysts while providing an electric highway for charge and ion transportation.17,46–50

In this work, we report in situ interfacial engineering via chemical vapor deposition (CVD) of vertical graphene on TiC nanofiber (denoted as VG/TiC), as highly active electrocatalysts for cathodes of Li–S batteries. A novel method was developed for in situ growth of vertical graphene with the simultaneous conversion of the substrate TiO$_2$ nanofibers into TiC ones, and the well-interconnected interfaces within the metallic VG/TiC 1D/2D heterostructured electrocatalyst provided a large specific interfacial area with a strong affinity to LiPS and transportation highway to enable fast redox kinetics essential for Li–S cells. As a result, nanostructured VG/TiC cathodes were capable of delivering remarkable electrocatalytic performance at high S-loading and low E/S ratio, owing to remarkably improved chemisorption, even distribution of S-containing species and hence effective suppression of the shuttle effect, and highly
improved redox kinetics over charge/discharge. At high sulfur content of 85.7% in the cathode, the Li–S cell exhibited impressive rate ability and delivered a high capacity of 971 mAh g\(^{-1}\) at 2C. Even with the high sulfur loading of 8 mg cm\(^{-2}\) and low E/S ratio of 6:1, the cell was able to provide a high areal capacity of 9.1 mAh cm\(^{-2}\) at 0.1C, and a high specific capacity of 600 mAh g\(^{-1}\) at 0.5C was maintained over 800 cycles. Encouragingly, a flexible 12 cm\(^{2}\) pouch cell was assembled to deliver a total initial capacity of 10.5 mAh and maintained a capacity of 8 mAh over 100 cycles. This work offers a novel avenue for in situ fabrication of high-performance cathode critical to practical high-energy-density Li–S batteries.

2 RESULT AND DISCUSSION

The VG/TiC heterostructured electrocatalysts were prepared by electrospinning coupled with the CVD growth of VG petals, as shown in Figure 1 with details given in the experimental part. First, the PVP/Ti nanofibers were fabricated by electrospinning the PVP and TBOT precursor, followed by heating the PVP/Ti nanofibers at 600°C in air to remove PVP and obtain TiO\(_2\) nanofibers. The application of a low heat treatment temperature of 600°C led to structure relaxation, facilitating the formation of flexible TiO\(_2\) nanofibers, which could still maintain the flexibility in the subsequent process. The resultant films of TiO\(_2\) nanofibers were then subjected to CVD as substrates to grow vertical graphene upon. During the graphene growth process, the TiO\(_2\) nanofibers were transformed in situ to TiC nanofibers due to the strongly reducing atmosphere of CH\(_4\) and H\(_2\), resulting in the VG/TiC electrocatalysts. The catalysts were then loaded with sulfur by mechanical mixing for cathode slurry.

SEM images in Figure 2(A–D) show the morphology of VG/TiC nanofibers, which could serve as the flexible cathode as active electrocatalysts in Li–S batteries, revealing a core–shell structure with the core of TiC and the shell of vertical graphene. As shown in Figure S1, Supporting Information the prior TiO\(_2\) nanofibers are of a uniform morphology with an average diameter of 200 nm. Figure S2 shows the SEM images of commercial TiC particles with an average diameter of 5 μm for comparison. Figure 2(E–G) shows the TEM images of VG/TiC composite, which exhibits few-layer graphene vertically grown on the fibers, with an HRTEM image resolving the typical few-layer characteristics. Figure 2H shows the HRTEM image of VG/TiC nanofiber, confirming the lattice spacings of 0.21 and 0.23 nm corresponding to (200) and (111) of TiC, respectively. Figure 2(I) shows the elemental mapping of VG/TiC, showing even distribution of Ti and C over the fiber surface owing to the high population of VG. The overall phase structures were characterized by XRD (Figure 2(J)) with the strong diffraction peaks of the TiO\(_2\) nanofibers being assigned to the anatase phase (PDF: 01-070-7348). The peaks located at 36.3°, 42.3°, 61.4°, 73.4°, and 77.4° in the XRD patterns can be indexed to (111), (200), (220), (311), and (222) planes of TiC (PDF: 65-0242), respectively. The hillock peak of VG/TiC located at about 25° corresponds to the (002) lattice plane, with significant peak broadening being typical for few-layered graphene (since the size of diffraction maxima from the reciprocal space is inversely proportional to the corresponding crystal size in the real space). Figure 2(K) shows the Raman spectroscopy of TiO\(_2\) and VG/TiC nanofibers. The Raman peaks located at 142, 395, 514, and 639 cm\(^{-1}\) are indexed to the vibrational model of \(E_g^{(1)}, B_{1g}, A_{1g}, \text{and } E_g^{(3)}\) from the anatase TiO\(_2\),\(^{44,51,52}\) and the peaks located at 264, 402, and 600 cm\(^{-1}\) are assigned to TiC,\(^{53,54}\) while the peaks located at 1330, 1567, and 2680 cm\(^{-1}\) correspond to the primary D, G, and 2D peaks of graphene. The significantly lowered D peak intensity than that of G peak with the well-defined 2D peak also indicates good crystallinity of the graphene phase. These results confirm the successful fabrication of VG/TiC nanofibers using the current in situ growth process.

Figure S4 shows the Ti 2p XPS spectrum from TiO\(_2\) and the VG/TiC nanofiber.\(^{55,56}\) The Ti 2p spectrum of TiO\(_2\) nanofiber reveals a typical double peak corresponding to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) of Ti–O bond, located at 458.6 and 464.0 eV, respectively. The Ti 2p spectrum of VG/TiC nanofiber shows not only the Ti–C bond located at 455.4 and 461.5 eV, but also other doublet peaks close to the positions of the Ti–O bond, which are attributed to the surface passivation of TiC.\(^{57,58}\) This is consistent with the Raman spectra of VG/TiC nanofiber, where a very weak peak of VG/TiC Raman spectrum located at 142 cm\(^{-1}\) corresponds to the major anatase TiO\(_2\) vibrational model of \(E_g^{(1)}\).

The overall adsorption capability of an electrocatalyst is very important for a Li–S battery. Therefore, the \(N_2\) adsorption–desorption isotherms were characterized to assess the BET surface area and pore size distributions, as shown in Figures 2(L) and S5. VG/TiC nanofiber reveals a much large BET surface area of 145.4 m\(^2\) g\(^{-1}\), many times that of the TiO\(_2\) nanoparticle (18.4 m\(^2\) g\(^{-1}\)). For comparison, the BET surface area and pore size distributions of commercial TiC particles were also assessed (Figure S6), which reveals a very low BET surface area of 1.5 m\(^2\) g\(^{-1}\). This is suggestive of highly enhanced adsorption power owing to much larger specific surface areas in the nanostructured VG/TiC electrocatalyst.

Computational simulations based on the density functional theory (DFT) were carried out to investigate
the interaction of the VG/TiC surfaces with Li and S-containing species. The stable structural configurations of the TiC and VG/TiC were established, as shown in Figures 3(A–C) and S7, with vertical graphene being assembled upon the TiC (002) surface via geometric relaxation. Figures S8 and S9 show the stable adsorption configurations of Li atoms on TiC and VG/TiC surface. The difference charge density diagrams on TiC and VG/TiC surface (Figures 3(D,E) and S10) reveal potential charge transfer between Li and the substrates, either the TiC surface or the VG grown on TiC, being consistent with the stronger adsorption of Li on the VG/TiC than on TiC (−2.34 vs. −2.06 eV). The calculated densities of states (DOS) for TiC and VG/TiC (Figure 3(F)) suggest that the VG/TiC coupling leads to enhanced DOS at the Fermi-level due to charge screening between the two phases. These simulation results confirm the accelerated Li$^+$ diffusion and improved Li compatibility with VG/TiC, which are desirable characteristics in an electrochemical Li–S system. UPS spectroscopy was carried out to determine the work function and Fermi level of VG/TiC and TiO$_2$, as shown in Figure 3 (G,H). From the energy cutoff edges, we derived the work function of VG/TiC and TiO$_2$ to be 4.22 and 4.52 eV, respectively. The Fermi level of VG/TiC is consistent with that of the instrumental reference, and in comparison, the valence edge of TiO$_2$ is 2.2 eV lower (at higher binding energy), typical for a wide gap semiconductor. The UPS results are consistent with the DFT predicted metallic nature of both phases in the VG/TiC electrocatalyst, which is fundamentally much more electrically conductive than the semiconductor TiO$_2$.

As to the chemical interaction between the LiPS and the VG/TiC, DFT simulation identified geometrically stable configurations of Li$_2$S$_4$-graphene, Li$_2$S$_6$-graphene, Li$_2$S$_4$-VG/TiC, and Li$_2$S$_6$-VG/TiC shown in Figures 4(A–D) and S11. These results reveal that both S and Li species in LiPS such as Li$_2$S$_4$ or Li$_2$S$_6$ are more strongly bonded to the TiC surface, with a much larger binding energy of −3.77 eV (Li$_2$S$_4$) and −4.01 eV (Li$_2$S$_6$) for bond formation with the TiC surface, which is behind higher adsorption capability of the VG/TiC than graphene alone.

A series of electrochemistry tests were then performed to assess the electrocatalytic capability of the VG/TiC nanocomposite versus that from a single compound of TiC or TiO$_2$. Figure 4(E) shows the CV curves of the VG/TiC, TiC, and TiO$_2$-based sulfur cathode. The CV profiles from the VG/TiC electrocatalyst reveals two pairs of typical sulfur redox peaks, corresponding to the reduction process of solid S$_8$ to soluble Li$_2$S$_8$, Li$_2$S$_6$, and Li$_2$S$_4$ and finally to insoluble Li$_2$S$_2$/Li$_2$S and the oxidation process of Li$_2$S$_2$/Li$_2$S to S$_8$. In comparison, the CV curves from the TiC and TiO$_2$ electrocatalysts show much larger voltage changes over the redox processes at lower current densities, which elaborates apparently faster redox kinetics for the VG/TiC catalyst. Furthermore, symmetric cells were assembled to assess the electrocatalysis of the three electrocatalysts on the Li$_2$S$_6$ redox process, as shown in Figure 4(F). Both VG/TiC and TiC reveal two pairs of redox peaks, with the former showing lesser voltage
polarization at a larger current density. The TiO$_2$, however, only displays a broad peak in the CV curves, indicating poorer catalytic performance due to inadequate electric conductivity. In comparison, the two pairs of redox peaks of VG/TiC are assigned to reduction peaks of A and B and oxidation peaks C and D, which are located at 0.07, −0.13, −0.07, and 0.13 V, correspondingly. The reduction peak of A is derived from the transform of S$_8$ to Li$_2$S$_6$ and peak B corresponds to the reduction of Li$_2$S$_6$ to Li$_2$S. The oxidation peaks of C and D are assigned to the reverse process of A and B to the reaction of Li$_2$S to Li$_2$S$_6$ and then to S$_8$. Obviously, the VG/TiC-based cell demonstrates a much bigger peak current density with weak voltage polarization, suggesting highly active electrocatalysis toward the fast redox kinetics during the conversions between sulfur species. The VG/TiC is thus confirmed to be the best catalyst candidate to facilitate remarkably enhanced electrochemical reversibility.

Galvanostatic intermittent titration technique (GITT) was used to assess the redox kinetics of sulfur species based on the three different electrocatalysts, as shown in Figure 4(G). Generally, except for the effect from passivation at ohmic contacts, the extent in voltage rise in the discharge process and drop in the charge process results from polarization due to electrochemical products over the redox processes. In the upper discharge voltage plateau, the voltage rise in the GITT profile is attributed to
the sluggish conversion kinetics of LiPS, such that the cell with fast LiPS conversion kinetics exhibits the lowest voltage rise in the first discharge plateau. The voltage rise in the second discharge voltage plateau is mainly associated with the insoluble electrodeposition of Li$_2$S/Li$_2$S on the cathode surface, with the three catalysts having nearly the same voltage values. The extent of the voltage rise increases with discharge depth, indicating that the voltage rise is positively correlated to surficial passivation due to the formation of the insulating Li$_2$S film. The solid Li$_2$S film deposited on the cathode surface results in resistance to both ionic and electric transportation, at the final stage of discharging when the conversion to Li$_2$S is stopped. The cutoff capacity in the second discharge plateau corresponds to the end of discharging, so that cells with larger surficial areas and hence thinner Li$_2$S films demonstrate bigger cutoff capacities. One can understand that any irreversible recovery of Li$_2$S over sequential discharging cycles would lead to loss of sulfur and capacity, worsened polarization, aggravated internal resistance, and premature failure of the battery cell in the end. The same phenomenon associated with polarization can be found in the charging process, so that the cell with a larger voltage rise in the GITT curves during discharging corresponds to a bigger voltage drop over charging, especially at the commencement of the charging state. The overpotential experienced at the commencement of the charging curve is typical due to slower
kinetics for conversion of solid Li$_2$S into soluble LiPS. The fast transition kinetics for the VG/TiC was behind quicker recovery toward equilibrium voltage at the initial stage of charging, followed by gradual voltage rise toward the later stage of charging. Being consistent with the GITT curves from the discharging process, the cutoff capacity for the VG/TiC-based cell was also significantly larger than the other two cells.

As to cell performance, the battery cells based on the three electrocatalysts exhibited similar voltage and delivered nearly the same specific capacity of 400 mAh g$^{-1}$ at the end of the upper discharge plateau in the GITT curves, since this voltage plateau originated from the same electrochemical reaction from Li$_2$S$_8$ to Li$_2$S$_4$. The main difference was in the cutoff capacities of the second discharge voltage plateaus, when the VG/TiC electrocatalyst provided the highest capacity of 1200 mAh g$^{-1}$, compared to those with TiO$_2$ (1050 mAh g$^{-1}$) and TiC (650 mAh g$^{-1}$) based cells. These confirm again that thicker Li$_2$S film in the cathode is responsible for incomplete Li$_2$S$_4$ conversion to Li$_2$S due to difficulty in electron and ion transportation. The largest surficial area from the highly conductive VG/TiC electrocatalyst led to even deposition of insoluble sulfide species, resulting in thinner film and fast discharging kinetics and remarkable utilization of the sulfur source.

In situ EIS of VG/TiC electrode was performed to study the kinetics of LiPS conversion and cathode surface passivation due to Li$_2$S precipitation, as shown in Figure S12. Figure S13 shows the simulated circuit of EIS curves. The first intersection of an EIS curve on the $Z'$-axis is attributed to the ohmic resistance ($R_e$) between electrodes and electrolyte, which experienced rather slight change over the whole redox process.
The interfacial resistance between cathode materials and electrolyte (fitted as $R_2$) is associated with the semicircle in the high-frequency region, which was smaller for discharging and became bigger during subsequent charging. The second semicircle in the lower frequency region (fitted as $R_3$) is attributed to slowed electron and mass transportation due to passivation from Li$_2$S precipitation, which was behind the irreversible recovery of sulfur from insulating sulfides when film thickness got too big. Such Li$_2$S-related resistance increased with the discharge depth related to the second voltage plateau, reaching maximum at the end of discharge. In the recharging process, the $R_3$ declined rapidly at the beginning of charging and lowered to the minimum at the end of charging. Such observation is consistent with the GITT tests, affirming that the evolution of the Li$_2$S film does play an important role in the conversion efficiency between soluble and solid S-containing species over the redox process in Li-S batteries.

For comparison, EIS curves from the cells based on the three electrocatalysts are shown in Figure 4(H,I) for tests before discharging and after half discharging (when the discharge capacity reaches the half amount of the last cycle), respectively. The outcome data are summarized in Tables S1 and S2, respectively. Apparently, the $R_2$ for the VG/TiC-based cell before discharge was only slightly lower than that based on the TiC or TiO$_2$ electrocatalyst, when interfacial reactions were not involved. At the half discharge state, the VG/TiC showed more pronounced benefit in having the lowest $R_2$ and $R_3$, with the overall benefit of best electric conductivity owing to VG, effective mass.
transportation and charge transfer across interfaces of cathode materials, and thinner Li$_2$S films associated to larger specific surface areas.

Figure 4(J) compares the chronoamperometric evolution of Li$_2$S in the Li$_2$S$_6$ electrolyte with the cathodes based on the three electrocatalysts, under a constant over potential of 2.08 V using the potentiostatic electrochemical technique. Apparently, the VG/TiC electrocatalyst-based cell exhibited the highest electrodeposition capacity with early occurrence of a current peak. This provides further evidence that the fastest liquid to solid conversion kinetics was enabled owing to the VG/TiC electrocatalyst. Furthermore, the resultant Li$_2$S films were examined by SEM, after the cells were fully discharged. As shown in Figure S14, the VG/TiC-based cathode reveals thin and smooth morphology of Li$_2$S film, and in contrast, TiC and TiO$_2$-based cathode show rather uneven Li$_2$S coverage with much rougher surfaces due to aggregated local deposition, which is detrimental to reversible redox processes.

Moving on to the battery performance, electrochemical assessments were carried out for Li–S cells based on the three electrocatalysts as sulfur host in cathodes. Figure 5(A) compares the rate performance of the Li–S cells. Even at the high current density of 2C, the VG/TiC-based cell still delivered a high capacity of 885 mAh g$^{-1}$, compared with TiC (699 mAh g$^{-1}$) and TiO$_2$ (421 mAh g$^{-1}$) based cells. Besides, the VG/TiC-based cell was able to deliver an even higher capacity of 1069 mAh g$^{-1}$ after the current density was lowered from 2C to 0.5C. This is suggestive of the effective reversibility of redox processes. Figure 5(B) shows the charge/discharge curves of the VG/TiC-based cell at 0.1C to 2C, with all exhibiting the typical two discharge voltage plateaus and one charge voltage plateau event at the high current density of 2C, which is consistent with effective electrocatalysis and remarkable capability in anchoring LiPS, thus reducing the shuttle effect and loss of sulfur in dead electrochemical products.

As is well-recognized by now, high sulfur loading is essential to practical Li–S batteries with high energy...
dynamics. Figure 5(C) compares the performance of cells at a fairly high sulfur loading of 4 mg cm\(^{-2}\) in the cathodes. Encouragingly, the VG/TiC-based cell delivered a high initial area capacity of 6.3 mAh cm\(^{-2}\) and maintained 4.6 mAh cm\(^{-2}\) after 50 cycles, much higher than cells based on TiC and TiO\(_2\) electrocatalysts. At even higher sulfur loading of 4.7, 6.0, and 7.3 mg cm\(^{-2}\), VG/TiC-based cells were still able to deliver a high areal capacity of 8.7 mAh cm\(^{-2}\) at the sulfur loading 7.3 mg cm\(^{-2}\) (Figure 5(D)). In terms of prolonged cycle performance, as shown in Figure 5(E), after activation at 0.1C the VG/TiC-based cell delivered a significantly higher specific capacity of 1099 mAh g\(^{-1}\) with 1000 mAh g\(^{-1}\) still maintained after 300 cycles, which is significantly better than the control cells using the other two electrocatalysts.

In addition to sulfur loading, high sulfur content in the slurry is another necessary request to evaluate the electrochemistry performance of Li-S batteries. Therefore, cathode slurry with a high sulfur content of 85.7 wt % was prepared by ball milling the VG/TiC and sulfur with a PVDF-in-NMP solution. Figure S15(A) shows the XRD pattern of the ball-milled composite of VG/TiC and sulfur (denoted as VG/TiC/S), which proves homogenous mixing of the two materials. XPS spectra from the VG/TiC/S composite are shown in Figure S15(B,C). The Ti-O/S and the S-Ti bonded states were detected in the Ti 2p and S 2p spectra, confirming good chemical bonding with loaded sulfur. Figure S16(A–E) shows the SEM images and EDS mapping from the VG/TiC/S composite, which reveal a homogeneous morphology and uniform distribution of Ti, C, and S.

Figure 6(A) shows the rate ability of VG/TiC/S cells, which delivered a large capacity of 971 mAh g\(^{-1}\) at 2C, at a high sulfur loading of 8 mg cm\(^{-2}\) and low E/S ratio of 6:1, and the cell was able to achieve a high areal capacity of 9.1 mAh cm\(^{-2}\) at 0.1C (Figure 6(B)). As is shown in Figure 6(C), a high specific capacity of 600 mAh g\(^{-1}\) at 0.5C was maintained after 800 cycles, which is very impressive to think that, at such high sulfur loading and low E/S, only bare lithium was used as anode without any surficial protection. More encouragingly, a flexible pouch cell with a size of 12 cm\(^2\) was assembled, which delivered a high total capacity of 10.5 mAh with a capacity of 8 mAh being maintained after 100 cycles (Figure 6(D)). Figure 6(E) demonstrates the flexibility test of a pouch cell, showing sustaining lighting of an LED array while being bent to various angles. As an essential part of the Li–S battery, lithium plays an irreplaceable role in the electrochemical system, and the status of the lithium anode plays a critical role in the performing cell. To probe the change of surficial morphologies of the lithium anode after cycling, we disassembled the VG/TiC/S-based cell after 200 cycles. As shown in Figure S17, the lithium anode exhibits a dense and smooth surface morphology. This demonstrates that the VG/TiC was indeed able to suppress the LiPS shuttle to the anode, and thereby restricted the reaction of LiPS with lithium to enabling the significantly improved cell stability over service. In addition, Figure S18 compares the electrochemical performances between this work and reported data from high sulfur loading cathodes in Li–S batteries, which shows that the outcome from this work delivered the best areal capacity attractive to high-energy-density Li–S batteries.

3 | CONCLUSION

In summary, we have devised a highly active electrocatalyst for Li-S batteries, by in situ growth of vertical graphene with simultaneous conversion of the substrate TiO\(_2\) nanofibers into TiC ones.

Such an active VG/TiC electrocatalyst was successfully used as a sulfur host to enabled highly improved redox kinetics owing to the following desirable advantages: (a) high conductivity to both electrons and lithium ions; (b) remarkable affinity to sulfur-containing species, leading to effective alleviation of the shuttling of poly-sulfides; (c) large surficial area as a superb substrate to accommodate even deposition of solid sulfides, thus preventing their aggregation and limiting their thickness over discharging; (d) evenly distributed solid sulfides in turn helping reduce polarization to benefit charge transfer and ion transportation; and (e) effectively enhanced utilization of sulfur owing to reversible reactions over prolonged redox cycles.

The highly improved redox kinetics resulted in significantly improved performance for Li–S cells at large sulfur loading and low electrolyte to sulfur ratios. The current work offers a novel pathway toward rational design of highly active electrocatalysts to enable flexible Li–S batteries with high energy density.

4 | EXPERIMENTAL

4.1 | Materials

Lithium metal plates with a diameter of 15.6 mm and thickness of 400 μm were purchased from China Energy Lithium Co., Ltd. The carbonate-based electrolyte was commercially available from Nanjing Mojiesi Energy Technology Co., Ltd. Tetrabutyl titanate (TBOT) and titanium (IV) carbide powder (99%, 2–4 μm) were purchased from the Shanghai Macklin Biochemical Co., Ltd.
Polyvinylidene fluoride (PVDF) was obtained from Arkema. Sublimed sulfur (S) and N-methyl-2-pyrrrolidone (NMP) were obtained from Aladdin. All materials were of analytical grade and were used without further purification.

4.2 | Synthesis

4.2.1 | Preparation of the TiO$_2$ nanofibers and vertically aligned graphene and TiC composite

First, 1.1 g of polyvinylpyrrolidone (PVP Mw = 1 300 000, Sigma–Aldrich) and 3 mL tetrabutyl titanate (TBOT) were dissolved in a mixed solution of ethyl alcohol and acetic acid to prepare faint yellow precursor under mechanical stirring. The electrospinning method was then applied using the above precursor to fabricate nanofibers, which were then subjected to heat treatment at 600°C in air for 3 h to obtain TiO$_2$ nanofibers. The TiO$_2$ nanofibers were then utilized as substrates to grow vertical graphene by chemical vapor deposition (CVD) at 1100°C for 2 h, using CH$_4$ and H$_2$ as the carbon source under a reducing atmosphere. The H$_2$ and CH$_4$ and gases were introduced to the preheated CVD chamber with a flow rate of 160 and 20 mL min$^{-1}$, respectively. At the same time, the substrate TiO$_2$ fibers were in situ reduced into TiC during the CVD process.

4.2.2 | Preparation of Li$_2$S$_6$ solution

Li$_2$S$_6$ solution was chosen as an analogue to soluble LiPS with the concentration of 0.2 M. Li$_2$S and S powders in stoichiometric amounts were dissolved in 1,2-dimethoxyethane (DOL)/1,3-diamethoxyethane (DME) with 1 M lithium bis(trifluoromethanesulfonylimide) (LITFSI) under continuous magnetic stirring for 12 h.

4.3 | Materials characterization

Scanning electron microscopy (SEM) images were acquired using a field-emission gun ZEISS SIGMA 500 at 5.0 kV. Transmission electron microscopy (TEM) was performed using a field-emission gun FEI Tecnai G20 at 120.0 kV. Element mapping was carried out using the energy dispersive spectroscopy (EDS) unit interfaced to the TEM facility. X-ray diffraction (XRD) was performed using a Rigaku Ultima IV system. Raman spectroscopy was carried out using a LabRAM HR Evolution instrument with a 532 nm laser excitation. X-ray photoemission spectroscopy (XPS) and ultra-violet photoemission spectroscopy (UPS) were performed by an AXIS Supra facility. The pore size distributions and Brunauer–Emmett–Teller (BET) surface area of the samples were conducted by an ASAP 2460 system (Micromeritics).

4.4 | Electrochemical characterization

CR2025 type coin cells were used to evaluate the electrochemical performances of composites. The coin and pouch cells were assembled in an argon-filled glove box with moisture and oxygen levels below 0.1 ppm. The usual sulfur cathode was prepared by mechanical grinding to mixing sulfur, VG/TiC and carbon black with a ratio of 6:1.5:1.5 in a mortar for 30 min (denote as VG/TiC/S), for the convenience to compare with control samples using TiO$_2$ and TiC. Then the VG/TiC/S and poly(vinylidene fluoride) (PVDF) were dissolved in N-methyl-2-pyrrrolidinone (NMP) with a ratio of 9:1 to prepare the slurry. Finally, the slurry was directly coated on the film of carbon nanofibers (CNFs) as cathode after dried at 60°C for 12 h. The cathode preparation using TiO$_2$ nanofiber and commercial TiC particles (Sigma–Aldrich) was the same as the above for the VG/TiC electrocatalyst.

For the high 85.7% sulfur content cathode, VG/TiC and sulfur with a ratio of 1:6 without carbon black were directly mixed by ball milling to fabricate the active material slurry coupled with PVDF in NMP solution. The sulfur loading of cells for the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and long cycle measurement is 1.2–1.5 mg cm$^{-2}$ and the mass of CNF film is 4 mg cm$^{-2}$. Lithium metal was used as the anode, and 1,2-dimethoxyethane (DOL)/1,3-diamethoxyethane (DME) with 1 M lithium bis(trifluoromethanesulfonyl) imide (LITFSI) plus 1 wt% LiNO$_3$ was employed as the electrolyte. A microporous polypropylene membrane (Celgard 2500) was used as the separator. The symmetrical cells were fabricated using identical working and counter electrodes, with 40 μL electrolyte containing 0.1 mol L$^{-1}$ Li$_2$S$_6$ being applied.

Galvanostatic charge–discharge tests were conducted through a Land CT2001A battery analyzer within a voltage window of 1.7–2.7 V. The EIS, CV curves, and symmetrical cell tests were achieved using a CHI 660D electrochemical workstation. The EIS test was conducted in the frequency range between 0.01 Hz and 200 kHz with a perturbation amplitude of 5 mV. The CV test was performed in a voltage range of 1.7–2.7 V at 0.1 mV s$^{-1}$.

4.4.1 | Li$_2$S evolution via nucleation and growth

VG/TiC, commercial TiC particles, and TiO$_2$ nanofiber were coated on CNFs as the working electrodes, with 40 μL Li$_2$S$_6$ catholyte being dropped onto the electrode
with 1.0 M LiTFSI (DME/DOL, volume ratio was 1:1). The whole process to assemble the CR2025 coin cell was in an Ar-filled glovebox. The cell was first discharged to 2.1 V by a Land CT2001A battery analyzer with a current of 0.2 mA and then kept potentiostatically at 2.08 V to assess Li$_2$S evolution by CHI 600D electrochemical workstation.

Galvanostatic intermittent titration test (GITT) test was performed by a Land CT2001A battery analyzer. The cells were discharged at 0.1 mA current for 20 min, followed by a 20 min rest.

### 4.4.2 DFT calculations

The calculations were performed based on the DFT, using the Vienna ab initio simulation package (VASP). The Perdew–Burke–Ernzerhof (PBE) functionals for exchange correlation and the Grimme’s semiempirical DFT-D3 scheme was employed to describe the long-rang interaction necessary for 2D phases. The plane wave cutoff was set to be 450 eV. For the geometrical optimization, the Hellmann–Feynman forces convergence criterion on the atoms was set as 0.02 eV Å$^{-1}$, and the energy convergence criterion was $10^{-5}$ eV. Summation over the Brillouin zone was performed with a $3 \times 3 \times 1$ k-point mesh.

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### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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