Strong charge polarization effect enabled by surface oxidized titanium nitride for lithium-sulfur batteries

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The commercialization of high-energy-density and low-cost lithium-sulfur batteries has been severely impeded by capacity fading and electrochemical polarization. Here we report a strategy to entrap polysulfides and boost the cathodic redox kinetics by embedding the surface oxidized quantum-dot-size TiN (TiN-O) within the highly ordered mesoporous carbon matrix. While the carbon scaffold offers sufficient electrical contact to the insulate sulfur, benefiting the full usage of sulfur and physical confinement of polysulfides. The surface oxygen renders TiN-O with a strong charge polarization effect for polysulfides via S-O-Ti bond as verified experimentally and theoretically. The suppressed shuttle effect and high lithium ion diffusion coefficient ($7.9 \times 10^{-8}$ cm$^2$ s$^{-1}$) lead to a high capacity of 1264 mA h g$^{-1}$ at 0.2 C with a negligible capacity fading rate of 0.06% per cycle. Additionally, TiN-O based prototype soft-package cells also exhibit excellent cycling stability with flexibility, demonstrating their potential for practical applications.
Lithium–sulfur (Li–S) batteries have been considered as one of the most promising next-generation rechargeable battery systems, which can deliver 5 fold higher energy density (theoretical: 2600 Wh kg\(^{-1}\)) than the current interaction-based lithium-ion batteries\(^3\). In particular, the natural abundance, environmental friendliness and low cost of sulfur make it more competitive for large-scale energy storage applications\(^3\). However, Li–S batteries have suffered from the poor capacity retention and sluggish redox kinetics during the solid–liquid–solid lithiation process. The former mainly arises from the “shuttle effect”, which is caused by the dissolution and diffusion of lithium polysulfides (Li\(_2\)S\(_n\), \(3 \leq n \leq 8\)) through the electrolyte, separator and even the anode. The latter is seriously affected by slow mass and electron transfer process due to the low Li\(^+\) diffusion rate and poor conductivity of S/Li\(_2\)S\(_6\).

Many efforts have been devoted to addressing these issues, including cathode modification\(^7,8\), electrolyte additives\(^9,10\), interlaid separator\(^1,12\), and anode protection\(^11\). In the realm of cathodic structure design, carbonaceous hosts with abundant pores and high pore volume showing the capacity of the physical confinement for lithium polysulfides have attracted extensive attentions\(^14–17\). However, the polysulfides migration driven by concentration diffusion and electrical field cannot be completely prevented, particularly at low rates and over long-term cycling due to the nonpolar feature of the carbon. Therefore, more attentions have been paid on the surface chemistry to strengthen the immobilization and accelerate the redox kinetics of polysulfides. The polar surfaces provided by metal oxides (TiO\(_2\), MnO\(_2\))\(^18,19\), metal nitrides (VN)\(^20\), metal sulfides (Co\(_2\)S\(_3\))\(^21\), metal phosphides (CoP, FeP)\(^22,23\) and metal carbides (MXene)\(^24\) endow strong polar-chemical interactions via dominant chalcogen-lithium binding and minor metal-sulfur binding\(^25\). Along with strong chemisorption, the unique electrocatalytic effect also triggers multistep redox reactions, leading to higher capacity and Coulombic efficiency\(^23,25,26\). Cui’s group has systematically examined the catalytic effect of metal sulfides (Ni\(_3\)S\(_8\), Sn\(_2\)S\(_2\), FeS, CoS\(_2\), VS\(_2\), and TiS) in eliminating the overpotential and activation energy barriers between the polysulfides and sulfur\(^26\). Subsequent research works further explored the catalytically enhanced redox mechanism of metallic Pt particles, \(W_2\)C\(_5\), Mo\(_2\)C, TiC\(_2\), VN\(^20\) and Co\(_2\)C\(^{23}\). Recently, transition metal nitrides such as TiN, have been intensively investigated, owing to their superior conductivity compared to their oxides and sulfides counterparts, have been largely focused in recent years\(^28,29\). They even show metallic characteristic, which would be very beneficial to facilitate the redox reaction kinetics and increase the sulfur utilization efficiency for Li–S batteries. Yet the study of polar and conductive TiN as polysulfide mediator for suppressing shuttle effect and boosting redox kinetics needs further investigation as the surface of TiN usually forms a thin oxidization layer in the ambient condition\(^30\), increasing the complexity of understanding the surface chemistry towards the polysulfides redox reaction. Therefore, it is crucial to study polysulfide mediator down to detailed surface interface level.

Herein, we report a rational design on structure and surface chemistry by employing the highly ordered mesoporous carbon (OMC) as matrix and the surface oxidized quantum-dot-size TiN (TiN-O) as polysulfide mediator for suppressing shuttle effect and boosting redox kinetics. The composite with TiN-O embedded in OMC (TiN-O-OMC) not only provides a physical confinement for polysulfides via the narrow-ordered carbon mesoporous channels (with \(\sim 3.5\) nm pore size distribution), but also chemically immobilizes lithium polysulfides due to the polar surface of the embedded TiN. Our density functional theory (DFT) calculations verify the dramatic charge polarization effect between the polysulfides and surface oxidized TiN-O via the S–O–Ti bond as verified by the transfer of 1.67e onto TiN-O. Surprisingly, compared to the pure TiN composite, the surface-oxidized TiN-O-OMC shows a stronger affinity for polysulfides with a higher binding energy of \(-5.51\) eV (vs. \(Li_2S_6\)). Moreover, the superior charge polarization effect could impart an additional driving force propelling the electrons gained from anode into the long-chain polysulfides, and attracting lithium ion onto the TiN surface, giving rise to enhanced electron/charge transfer and thus a faster redox kinetics is achieved. The experimental studies show a good consistency that TiN-O-OMC electrode delivers a superior electrochemical catalytic performance with the lowest overpotential of 271 and 465 mV at 0.2 and 5 C and highest lithium ion diffusion coefficient of \(3.6 \times 10^{-5}\) cm\(^2\) s\(^{-1}\) (Li\(_2\)S\(_6\)\(\rightarrow\)Li\(_2\)S\(_{3}\)). This rationally designed architecture and surface chemistry of TiN-O leads to a high capacity of 1395 mAh g\(^{-1}\) at 0.1 C, a Coulombic efficiency approaching 100% and a high-rate performance of 726 mAh g\(^{-1}\) at 5 C. Furthermore, the as-developed sulfur cathode also exhibits great potential for practical applications as demonstrated by the pouch cell with an initial discharge capacity of 845 mAh g\(^{-1}\) at 0.2 C and stable cycling performance of 634 mAh g\(^{-1}\) after 120 cycles.

**Results**

**Synthesis and material characterization.** Metal nitrides are usually synthesized by using the corrosive and hazardous ammonia gas as nitridizing agent. Herein, we demonstrate a green and facile synthetic approach by using g-C\(_3\)N\(_4\) as N source. As illustrated in Fig. 1a, the highly ordered carbon matrix was first synthesized by a nanocasting process, which employs SBA-15 as the hard template and hexamethylenetetramine (HTM) as the precursor. Then TiO\(_2\) nanoparticles were generated after the hydrolysis of tetrabutyl titanate (Ti(O\(_2\)C\(_{4}\)H\(_9\))\(_4\)) within the OMC. After that, the resultant dark powders were nitrided using g-C\(_3\)N\(_4\) as the upstream N source. Further surface oxidation of TiN was completed by simply exposing the composite in air for 3 days. In addition, control samples carried out without nitriding or natural oxidation process were denoted as TiO\(_2\)-OMC and TiN-OMC, respectively. The transmission electron microscopy (TEM) observations reveal that the as-prepared OMC successfully replicated highly ordered mesoporous structure of SBA-15 with pores size of approximate 3.5 nm and \(-9.9\) nm in the wall thickness (Fig. 1b and c). Meanwhile, the ordered mesoporous structure of OMC was well-reserved by TiN-O-OMC after the nanocoating process, which can be seen from the scanning electron microscopy (SEM) images in Fig. 1d, e. The narrow-ordered channels within carbon matrix is speculated to restrain the growth of TiN-O because a homogeneous distribution of quantum-dot-sized TiN-O nanoparticles (3–5 nm) is observed in the high-resolution TEM images (Fig. 1f, g). Similar results are also found in TiO\(_2\)-OMC and TiN-OMC (Supplementary Fig. 1). Additionally, the non-toxic N-rich g-C\(_3\)N\(_4\) is found to be as effective as NH\(_3\) for the nitridization of TiO\(_2\). After 3 days air-exposing process, the surface of TiN is easily oxidized as confirmed by the elemental mapping (Fig. 1h and Supplementary Fig. 2).

The sophisticated control of morphology and pore structure was further monitored by small/wide-angle X-ray diffraction (XRD) patterns and \(N_2\) adsorption-desorption isotherms (Fig. 2). A distinct diffraction peak indexed to hexagonal (100) reflection is well preserved by TiN-O-OMC after two nanocoating processes (Fig. 2a), revealing its highly ordered structure\(^{31}\). Additionally, the slight shifts of the (100) peak towards the higher angle of TiN-O-OMC is ascribed to the structure shrinkage after annealing at elevated temperature and the removal of template\(^{32}\). From the wide-angle XRD patterns (Fig. 2b), the typical peaks for both
carbon and TiN can be identified, suggesting the successful nitridization with the assistance of the N-rich g-C3N4. The mesoporous property were further verified by the capillary condensation characterization as shown in Fig. 2c. Similar to SBA-15 and OMC, the N2 adsorption/desorption isotherms of TiN-O-OMC show type IV curve with an H1 hysteresis loop. Additionally, as determined by the Barret-Joyner-Halender (BJH) method, both TiN-O-OMC and OMC demonstrate narrow mesopore size distribution (3.58 and 3.51 nm, respectively), which is consistent with the TEM observation. The control samples, both TiO2-OMC and TiN-OMC also present a consistency of morphology and pore structure (Supplementary Figs. 1, 3–4). Remarkably, the well-designed TiN-O-OMC shows a high Brunauer-Emmett-Teller (BET) surface area of 355.9 m2 g−1 and pore volume of 0.95 cm3 g−1 (Supplementary Table 1), which are critical to providing more active sites and void space to trap and accommodate the sulfur-containing species in Li-S battery.

The chemical composition of the TiN-O-OMC surface was identified by X-ray photoelectron spectroscopy (XPS). The molar ratios of 5.8%, 9.6%, 11.8%, and 72.8% were detected for Ti, N, O and C, respectively (Supplementary Table 2). After the natural oxidization process, two new peaks assigned to O-Ti-O and O-Ti-N are deconvolved at 458.5, 464.4 eV and 457.0, 463.1 eV in the Ti 2p spectrum (Fig. 2d). The oxidized species can also be seen from the N 1s and O 1s spectrum (Supplementary Fig. 5). Based on the different fractions of Ti-containing species (Supplementary Table 3) and previous literature, the chemical structure of surface oxidized TiN is proposed to contain O-Ti-O top layer, followed by O-Ti-N intermediate layer and pure TiN in the bulk (Fig. 2c). Additionally, the molar ratio of TiO2/TiN was calculated to be 12:15, indicating that a high portion of surface TiN has converted to TiO2 owing to the natural oxidization.

**Electrochemical performance.** To examine the effect of surface oxidized TiN on battery performance, systematic electrochemical measurements were conducted using OMC, TiO2-OMC, TiN-OMC and TiN-O-OMC as cathodes with a sulfur content of 75 wt % (Supplementary Fig. 6). After the sulfur infiltration process, no obvious sulfur aggregates are observed (Supplementary Figs. 7–8), indicating sulfur has penetrated into the highly OMC hosts. Fig. 3a and Supplementary Fig. 9 reveal the typical galvanostatic charge/discharge profiles of the sulfur cathodes at different current densities. Two representative discharge plateaus at around 2.38 and 2.10 V are observed (at 0.1 C current rate, 1 C = 1675 mA g−1), corresponding to the reduction of sulfur to long-chain lithium polysulfides (Li2Sx, 3 ≤ x ≤ 8) and the subsequent formation of short-chain Li2S2/Li2S, respectively. After introducing polar TiO2 and TiN into the OMC matrix, the capacity significantly increases from 710 to 980 and 1264 mA h g−1, respectively (Fig. 3b). Remarkably, TiN-O-OMC electrode delivers the highest specific capacity at different current rates (1395, 1264, 1109, 990, 882, and 727 mA h g−1, respectively, Fig. 3a). Additionally, at a low current rate of 0.2 C, the voltage hysteresis (η) of TiN-O-OMC is only 1 mV lower than that of TiN-O-OMC, indicating their similar redox kinetics for the solid-liquid-solid lithiation process (Fig. 3c, Supplementary Fig. 9).
However, at a high current rate of 5 C, \( \eta \) for TiN-OMC, TiO\(_2\)-OMC and OMC electrodes are 72, 99, and 215 mV higher than TiN-O-OMC, respectively. Thus, the surface oxidized TiN is particularly effective to alleviate the electrochemical polarization at higher current rate. Benefiting from the mesoporous structure and strong trapping affinity with polysulfides, the TiN-O-OMC electrode demonstrates an excellent high-rate performance. As shown in Fig. 3d, the capacity decreases with the increasing current density and can maintain a high capacity up to 718 mA h g\(^{-1}\) at 5 C. Furthermore, the capacity can recover to 1284 mA h g\(^{-1}\) after abruptly switching the current density back to 0.1 C, implying the remarkable robustness and stability of TiN-O-OMC electrode. However, TiN-OMC, TiO\(_2\)-OMC, and OMC cathodes deliver much lower capacities after reversing back to low rates, in decreasing order of 992, 553 and 711 mA h g\(^{-1}\), respectively. For long-term cycling stability at a low current density of 0.2 C (Supplementary Fig. 10), the TiN-O-OMC shows superior cycling stability with a high initial capacity of 1264 mA h g\(^{-1}\) and a fading rate of 0.06 % from the second cycle. While the capacity fading rates of OMC, TiO\(_2\)-OMC and TiN-OMC are 0.14%, 0.17% and 0.13%, respectively. Moreover, at higher current density of 0.5 and 5 C, the capacity of the TiN-O-OMC cathode can maintain at 915 and 612 mA h g\(^{-1}\) with a negligible fading rate of 0.05% over 200 cycles. The high Columbic efficiency (above 98.2%) indicates the dramatically suppressed shuttle effect of polysulfides. Additionally, we further evaluated the long-term cycling stability of TiN-O-OMC with high sulfur loading (4.3 mg cm\(^{-2}\)). It delivers an initial capacity of 645 mA h g\(^{-1}\) and stable cycling to 600 cycles with a capacity fading rate of 0.2 % at a high current density of 5 C (Supplementary Fig. 11). The high capacity retention of TiN-O-OMC cathodes implies the effective immobilization of lithium polysulfides by the well-designed architecture of surface-oxidized polar TiN embedded in the OMC matrix.

**Enhanced redox kinetics.** Once the polysulfide is anchored on the polar material, it is essential to trigger the subsequent liquid-to-solid (Li\(_2\)S\(_n\) to Li\(_2\)S) conversion, which is the key to improve the rate performance, maximum the utilization of sulfur species and extending the battery lifespan. To this end, cycling voltammogram (CV) scanning, electrochemical impedance spectroscopy (EIS) and Li\(_2\)S nucleation experiments were conducted to study how the surface-oxidized TiN affects the electrochemical process (Fig. 4). As shown in Fig. 4a, TiN-O-OMC electrode shows two cathodic peaks at 2.32 (C1) and 2.04 V (C2) and two anodic peaks at 2.31 (A1) and 2.38 V (A2) at a scan rate of 0.1 mV s\(^{-1}\), which is consistent with the Galvanostatic charge/discharge profiles. Additionally, C1, C2 peaks locate at higher potential positions than those of OMC, TiO\(_2\)-OMC, and TiN-OMC electrodes, whereas A1 and A2 show an opposite tendency (Supplementary Fig. 12), which is in good agreement with the \( \eta \) results (Fig. 3c). The mitigated electrochemical polarization of the TiN-O-OMC electrode is also manifested from the well-separated cathodic/anodic peaks with approximately double the current density than other electrodes. Furthermore, the Li\(^+\) diffusion coefficient (\( D_{Li^+} \), a good descriptor to evaluate the redox kinetics) was measured by CV under different scanning rates from 0.1 to 0.5 mV s\(^{-1}\). As seen in Fig. 4b, the cathodic and anodic peaks (\( I_p \)) of all the electrodes exhibited a good linear relationship with the square root of scanning rates (\( \sqrt{v} \)), indicating a diffusion-controlled process. Based on the classical Randles-Sevcik Eq. (1):\(^{26}\)

\[
I_p = 268600 \; n^2 \; A \; D_{Li^+} \; C \; \sqrt{v}
\]  

\( I_p \) (cm\(^2\) s\(^{-1}\)) can be calculated from the slope of the curve (\( I_p/\sqrt{v} \)) as the \( n \) (number of electrons transferred in the redox reaction), A (electrode area, cm\(^2\)), and C (concentration of Li\(^+\) in the cathode, mol cm\(^{-3}\)) are unchanged (Fig. 4c). For TiN-O-
OMC cathode, $D^{\text{Tin}}_{Li^+} = 1.8 \times 10^{-8}$, $D^{\text{OMC}}_{Li^+} = 3.6 \times 10^{-8}$, $D^{\text{TiO}_2}_{Li^+} = 8.9 \times 10^{-8}$, and $D^{\text{TiN}}_{Li^+} = 7.9 \times 10^{-8}$ cm$^2$s$^{-1}$ are obtained, which are 1–3 times higher than the values for OMC, TiO$_2$-OMC, and TiN-OMC. Without any embedded particles, OMC demonstrated the lowest Li$^+$ diffusivity, indicating its limited surface activity towards the redox reaction. The inferior performance of TiO$_2$-OMC electrode could be ascribed to its large charge transfer resistance confirmed by the EIS result ($R_{ct}$, 90.8 $\Omega$, Fig. 4d and Supplementary Table 4). Surprisingly, although a higher $R_{ct}$ is observed for TiN-OMC than TiN-OMC (59.9 $\Omega$ vs. 27.3 $\Omega$), the TiN-OMC presents higher $D^{\text{Li^+}}_{Tin}$ diffusion coefficient than TiN-OMC, which originates from the oxidation layer of TiN. To probe the electrochemical conversion of lithium polysulfides at the electrode/electrolyte interface, symmetric cells employing two identical carbon paper as electrodes (mass loading of 0.4 mg cm$^{-2}$, without sulfur) and Li$_2$S$_6$ as electrolyte (40 $\mu$L of 0.4 M) were assembled$^{23}$. The enhanced current density observed in Fig. 4e proves the fastest lithium polysulfides redox conversion by TiN-OMC electrode due to the strong affinity for polysulfides and facilitated ion/electron transport, which has been validated by the adsorption and Li$^+$ diffusion experiments. The EIS spectra further validate the significantly improved conductivity of TiN-containing electrodes (Supplementary Fig. 13).

To further study the favorable effect of the surface oxidized TiN on the polysulfide redox reaction at the liquid-solid boundary, Li$_2$S precipitation experiments on the surface of OMC, TiO$_2$-OMC, TiN-OMC, and TiN-OMC were performed$^{36}$. The deposition was studied under galvanostatic discharge to 2.06 V at a constant current of 0.112 mA, which aims to consume most of the long-chain lithium polysulfides$^{37}$. Then, the potentiostatic conditions were applied to maintain an overpotential of 10 mA at 2.05 V till the current fell below 0.01 mA. The 10 mA of overpotential is necessary to provide the driving force for the nucleation of Li$_2$S since a surface energy barrier must be overcome$^{36}$. According to the previous report$^{36,37}$, the precipitation of Li$_2$S begins with the nucleation and is then followed by the growth of impingement, as illustrated by the current peak in Fig. 4f and Supplementary Fig. 14. The potentiostatic curves deliver three important data: (i) the current peak increases in the order of OMC < TiO$_2$-OMC < TiN-OMC < TiN-OMC, (ii) whereas the corresponding disposition time (at current peak) witnesses an opposite tendency of 7489 > 5160 > 5151 > 2709 s, and (iii) the calculated capacities of Li$_2$S precipitation (yellow section) of 45 < 59 < 68 < 95 mA h g$_{sulf}$$^{-1}$ in the same order. The former two values indicate that the fast conversion rate
of Li$_2$S nucleation process and the last one reveals the enhanced Li$_2$S deposition process. Therefore, these results clearly elucidate the enhanced electrochemical catalytical property of the naturally oxidized layer of TiN for Li$_2$S conversion than the pure TiN phase.

**Enhanced chemical interactions.** Ultraviolet–visible (UV–vis) absorption spectroscopy was carried out after immersing the cathode host materials in 5 mM Li$_2$S$_6$ solution to check the trapping effect of lithium polysulphide on oxidized TiN. As shown in Fig. 5a, TiN-OMC, followed by TiN-OMC, displays the lowest adsorption intensity and completely purify the Li$_2$S$_6$ solution, exhibiting the strongest adsorption affinity for Li$_2$S$_6$. Because of the lower polysulphide binding energy of TiO$_2$ than that of TiN, TiO$_2$-OMC shows lower chemisorption ability with much darker color in Li$_2$S$_6$ solution. In contrast, OMC shows the weakest affinity to Li$_2$S$_6$ owing to the limited binding effect towards Li$_2$S$_6$. Moreover, the strong chemical interaction between the surface oxidized TiN-OMC and polysulphide was further confirmed by the XPS spectra after vacuuming the solvent used in adsorption experiment. As verified in Fig. 5b, c, the Ti 2p and O 1s spectra show a significant 0.2 ~ 1.0 eV shift to the lower binding energy. The enhanced XPS intensity around 456.5 eV might indicate the formation of S-O-Ti binding. To gain more insights into the oxidation effect of TiN, DFT calculations were performed to study the absorption of typical lithium polysulphide, Li$_2$S$_6$, on the TiN (200) crystal facet as reported previously. For a comparison, the binding behavior and chemical interaction of Li$_2$S$_6$ with the pristine TiN was also studied. As shown in Fig. 5d, the terminal S site of Li$_2$S$_6$ tends to locate above the Ti atom while Li atom tends to interact with N atom with the binding lengths of 2.43 and 1.98 Å, respectively. Whereas, for the oxidized TiN, S sites preferentially stand away from the surface while Li atom shows a shorter binding length of 1.89 Å to O atom, predicting a stronger binding affinity. This is further confirmed by the higher binding energy ($E_b$) of surface oxidized TiN (~5.51 eV) than that of pure TiN (~5.39 eV), which is consistent with the existing experimental observations. Moreover, the O atoms are favorable in the charge polarization effect due to the larger electronegativity of oxygen, which is widely studied in the field of hetero-atom doping. As depicted from the charge density difference diagrams (Fig. 5f, g), the olive and cyan iso-surfaces represent the...
region of net electron accumulation and deficit, respectively. In details, a limited 0.1 e is transferred from the long-chain Li$_2$S$_6$ to pure TiN, whereas 1.67 e is transferred to the surface oxidized TiN. The significant polarization of electronic density is also in good accordance with the negative shifting (0.2~1 eV) of Ti 2p and O 1s XPS spectra (Fig. 5b–c). It can be inferred that in the discharge process, the enhanced electronic polarization effect could provide an additional driving facilitate to profit the electrons transfer from anode to polysulfides, attract Li$^+$ onto the surface of TiN-O-OMC and accelerate charge/electron transport (as illustrated in Fig. 5h, i).

Motivated by the urgent demand for developing flexible future energy storage devices, herein we manufactured prototype pouch cells, employing the as-prepared TiN-O-OMC as the cathode material with a sulfur loading of ~1.4 mg cm$^{-2}$ and a size of 60 mm × 80 mm (Fig. 6a and Supplementary Fig. 15). This unique pouch cell demonstrates superior flexibility by adapting to different folding movements from 0 to 180° (Fig. 6b, Supplementary Movie 1). Benefiting from the enhanced physiochemical adsorption ability for lithium polysulfides and fast redox kinetics, the TiN-O-OMC in pouch cells also shows a high specific capacity of 884, 788, 727, 650, and 550 mA h g$^{-1}$ at 0.1, 0.2, 0.5, 1, and 2 C, respectively, and a low η of 239 mV at 0.2 C (Fig. 6c and Supplementary Fig. 16). In addition, the TiN-O-OMC pouch cell exhibits an excellent rate performance that the capacity can recover to 790 mA h g$^{-1}$ after decreasing the current density from...
Discussion
In summary, we successfully developed a technique by employing the highly OMC as matrix and the surface oxidized quantum-dot-size TiN-O as polysulfide mediator to suppress shuttle effect and boost redox kinetics of Li-S batteries. Both the physical confinement and chemical adsorption for the polysulfides of the as-prepared materials facilitate the redox reaction between sulfur and polysulfides. Especially, the surface oxidized TiN-O is more effective in alleviating the polysulfides shuttle effect and boosting the overall redox kinetics, which has been confirmed by both experimental and theoretical studies. The DFT calculations further verified that the surface oxygen renders a charge polarization effect for imparting additional “driving force” to propel both the electrons and Li\(^+\) transportation. Benefiting from the synergetic effects of mesoporous architecture and oxidized surface chemistry, the TiN-O-OMC cathode exhibits significant enhancement on the charge transfer process, lower polarization (271 mV), high lithium ion diffusion coefficient (7.9 × 10\(^{-8}\) cm\(^2\) s\(^{-1}\)) and Li\(_2\)S nucleation/deposition conversion. Thus, the TiN-O-OMC electrode achieves high specific capacities of 1395 and 726 mA h g\(^{-1}\) at 0.1 and 0.5 C and high Coulombic efficiencies (~100%). The cathode material also delivers excellent rate performance and cycling stability. When assembling to the prototype pouch cells, the as-prepared materials show a superior flexibility with high capacity of 890 mA h g\(^{-1}\) at 0.2 C and stable cycling performance of 634 mA h g\(^{-1}\) after 120 cycles, indicating great potential for practical applications.

Methods
Synthesis of OMC. In a typical synthesis, 1 g SBA-15\(^{32}\) and 10 g of HTM (Sigma-Aldrich, 99.0%) were well-dispersed in 20 mL of deionized water. The solution was then vacuumed at room temperature for 2 h and stirred for another 3 h. After centrifugation (9000 rpm, 3 min), the collected paste was further heated at 60°C for 12 h and annealed at 750°C for 6 h under Ar stream with a heating rate of 3°C min\(^{-1}\). Finally, the black carbonaceous product was obtained after a 5% HF (Sigma-Aldrich, 40–45%) solution etching process.

Synthesis of titanium nitride/oxide-carbon composites. Specifically, 100 mg of OMC was added to 4 mL of ethanol (Sigma-Aldrich, 99.8%)/tetrabutyl titanate

2 to 0.2 C (Fig. 6d). Notably, the cathode displays a stable cycling performance with a high capacity retention of 634 mA h g\(^{-1}\) (at a low fading rate of 0.16% per cycle) and high Coulombic efficiency of 98.5% at 0.2 C (Fig. 6c). When tested at a high sulfur loading of ~4.3 mg cm\(^{-2}\), the pouch cell shows a capacity of 552 mA h g\(^{-1}\) and a good cycling stability with a fading rate of 0.06% after the third cycle (Supplementary Fig. 17). The state-of-art pouch cells with TiN-O-OMC as cathode material can drive a mini electric car as demonstrated in Supplementary Movie 2, further indicating the potential for practical application.

Fig. 6 Pouch cell performance of TiN-O-OMC@S cathode. a Schematic of the basic configuration of a proof-of-concept Li-S pouch cell. b Flexibility test with folding angles from 0 to 180°of the as-prepared TiN-O-OMC pouch cell. c Galvanostatic charge/discharge profiles at low rates of 0.1, 0.2, and 0.5 C. d Rate performance and Coulombic efficiency at different current densities. e Cycling stability and Coulombic efficiency at 0.2 C with a sulfur loading of 1.4 mg cm\(^{-2}\).
Synthesis of TiN-O-OMC cathodes. In this work, sulfur was loaded by a multi-
diffusion strategy. Typically, 25 wt% of TiN-O-OMC and 75 wt% of sulfur (Sigma-
Aldrich, 99.5%) was ground together till the mixture show a good color uniformity.
The solid was transferred to a small glass tube sealed with polyethylene wrap and
(Aldrich, 97%) (1:1, volume ratio) solution, followed by a sonication for 30 min.
While TiO2-OMC was prepared via the similar procedure as that of TiN-O-OMC except for the absence of g-C3N4 as N source in the annealing process.

Material characterization. Field-emission SEM (Zeiss Supra 55VP) and TEM
(JEM-2100) were applied to record the morphologies of the samples. XRD patterns
(Bruker D8 Discover) and N2 adsorption and desorption isotherms (Micro-
meritics 3 Flex) were obtained to analyse the ordered structure. XPS (ESCA-
LAB250Xi) with a monochromatic Al Kα source and elements mapping were used to probe the chemical compositions of the cathodes. The thermogravimetric analysis
(TGA, SII DT2960) was carried out on simultaneous thermal-gravimetry and dif-
ferential thermal analysis with a heating rate of 5 °C min⁻¹ under N2 atmosphere.
UV–vis adsorption spectral analysis (Cary 60) was performed to study the adsorption of Li2S6.

Electrochemical measurements. To evaluate the electrochemical performance of TiN-OMC, 2030-type coin cells were assembled using lithium metal as anode and reference electrode, and Celgard 2300 as the separator. The cells were assembled in an Ar-filled glove box (Unilab, Mbraun, Germany) with low levels of both H2O and O2 (0.1 ppm). A freshly prepared solution containing 1 M lithium bis-(tri-
fluoromethanesulfonyl) imide (LiTFSI, 99.95%) and 1 wt% LiNO3 in DOL/DME
(volume ratio 1:1) was used as electrolyte. The cells were operated in a voltage range of 1.7–2.8 V. Neware battery tester. Cyclic voltammetry was recorded on a Bio-Logic VMP3 electrochemical workstation in the voltage range of 1.7–2.8 V. EIS was tested in the frequency range between 0.01 Hz and 100 kHz.

Li2S8 adsorption test. The Li2S8 solution (5 mM) was prepared by dissolving Li2S
and sulfur at a molar ratio of 1:7 in tetraglyme in the glovebox. The Li2S8 catholyte was
1.6 mg cm⁻². For the 2030-type coin cells assembly, 20
5 mm catholyte was injected into the package and side
rolled out for the UV-visible adsorption test.

Assembly of Li2S8 symmetric cells and measurement. Two identical carbon paper
films (1.2 cm in diameter) were used as current collectors to load the as-prepared
Li2S8 catholyte. The well-sonicated suspension of the catholyte was added to the
Li2S8 solution, followed by a soaking, standing process. Finally, 3 mL of the
clear upper solution was taken out for the UV-visible adsorption test.

Li2S8 nucleation measurements. The 0.4 M Li2S catholyte was firstly synthesized by stirring the Li2S with sulfur at a molar ratio of 1:7 in tetraglyme in the glovebox
for 8 h at room temperature.29 Accordingly, the cathodes were the same with those
as mentioned in the symmetric cells experiment while lithium foils were used as
anodes. For the 2030-type coin cells assembly, 20 μL Li2S catholyte was firstly added to the cathode, followed by a Celgard 2000 separator and a 20 μL Li-S
electrolyte on the top. The batteries were galvanostatically discharged to 2.0 V
under 0.12 mA and then held at voltage 2.05 V until the current was below 0.01 mA.
Based on Faraday’s law, the nucleation/growth of Li2S can be evaluated via the
fitting of current-time curves after the second potentiostatically discharge stage.

Assembly of pouch cells. The laminated film with 16 x 20 cm size was first halffolded and sealed by the hot-sealing machine as the shell of pouch cell. The pouch
cell cathode electrodes were prepared with the same procedures as those electrodes
prepared for coin cells but with a larger size of 6 x 8 cm. The Al tab was welded
onto the cathode electrode. Then, the cathode was stuck the Celgard 2300 separator by the anti-electrolyte-tape. Afterwards, the Li foil anode was pasted on the separator with anti-electrolyte-tape in glovebox with welded Ni tap. Then both the cathode and Li foil anode were put in the laminate film package and side sealed by the hot-sealing machine. Then 1.2 g of Li-S electrolyte was injected into the package through the unsealed side. After that, the package was vacuumed and sealed via the vacuum sealing machine. After standby for 1 day, the pouch cell was waisted by formation machine and activated by discharging and charging to 1.7 and 2.8 V at a low current density of 0.2 C. After for another 12 h, the pouch cell was electrochemically tested using the Land Workstation (see Supplementary Fig. 15a–g).

DFT calculations. The first principle calculations were conducted using spin-
polarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional by
Vienna Ab initio Simulation Package (VASP).45 The Grimme DFT-D2 method was
applied to treat the van der Waals force between Li2S6 and TiN-TiN-O. There are
more than 100 atoms in TiN-O structure with relaxed lattice constants 8.488 Å, and the vacuum gap is more than 20 Å. For the initial structure, many possible stacking patterns and distances between Li2S6 and TiN were tested to obtain the stable configuration. The kinetic cutoff energy is set 400 eV, while the Γ-centered Monkhorst–Pack grid is 2 x 2 x 1. The convergence of force of each atom was 0.05 eV Å⁻¹. The binding energy (E_b) is calculated using Eq. (2):

\[ E_b = E_{(Li_2S_6 + TiN-O)} - E_{(Li_2S_6)} - E_{(TiN-O)} \]

where the E (Li2S6 + TiN-O) presents the total energy for optimized configuration of Li2S6 and TiN-O complex, and the E (Li2S6) and E (TiN-O) present the energies for optimized isolated Li2S6 and TiN-O structures, respectively. All the crystal structures and charge density plots were drawn using ESTA.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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