Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This manuscript reported that identifying the strong charge polarization effect by surface oxidized titanium nitride (TiN-O) for polysulphides via S-O-Ti bond for high performance lithium-sulphur batteries. The results show that the surface oxygen renders TiN-O was shown very good electrochemical performance. Also the pouch cell was fabricated and shown excellent cycling stability with flexibility. It will great potential for the real applications. As this topic is very hot topic, it will be interesting by the reader of CommChem. As it is written and organized well. I strongly recommend to be published in this Journal as it is or minor comments:

1 It is better to give the ratio of TiO2 and TiN in the TiO2(TiN)-O-OMC. It is confused that the results of Figure S5. The lost weight is the sulfur?

2 The fabrication process of pouch cell is not shown in the experimental section.

Reviewer #2 (Remarks to the Author):

This manuscript reports a strategy to entrap polysulphides and boost the cathodic redox kinetics by embedding the surface oxidized quantum-dot-size TiN (TiN-O) within the highly ordered mesoporous carbon matrix. The surface oxygen renders TiN-O with a stronger charge polarization effect for polysulphides via S-O-Ti bond. The suppressed shuttle effect and high lithium ion diffusion coefficient lead to high battery performance. The manuscript is well organized, the electrochemical study has been appropriately carried out, the conclusions are not well-supported by the experimental results. Thus, this work could not be published on Communications chemistry unless some major revisions have to be made.

1. In Supplementary Fig. 6, the SEM elemental mapping of sulfur should be provided to further prove there are no sulfur aggregates.
2. Line 171, the authors claim the voltage hysteresis of TiN-OMC is 1 mV higher than that of TiN-O-OMC at 0.2C, this is inconsistent with the Figure 3C, where the voltage hysteresis of TiN-OMC (270mV) is lower than that of TiN-O-OMC (271 mV). Please give an explanation.
3. For Li-S batteries, high sulfur loading and low electrolyte amount are needed to get high energy density. Why do the authors not use high-sulfur-loading cathodes (4.3 mg cm-2) to assemble the pouch cells since these high-sulfur-loading cathodes in coin cells show good performance? the pouch cell performance is attractive but it is useless since the loading is very low. The flexibility is not an advantage of Li sulfur battery. Any types of battery with a low coating of active materials can be flexible to power a LED.
4. it is well known that the nitrogen doping on carbon has strong chemisorption on both sulfur and polysulfide. it is not clear the role of Ti or N and their contribution in TiN for chemisorption of polysulfide. If it is N playing an important role, the work should provide the difference from the previous work in literature.

Reviewer #3 (Remarks to the Author):

This is a comprehensive study. It may be accepted if these questions are properly addressed.

As for “Then TiO2 nanoparticles were generated after the hydrolysis of tetrabutyl titanate (Ti(OC4H9)4) within the OMC”
The experimental details should be given. What is the mass loading of TiO2 in CMK-3, and is this

infiltration of TiO_2 controllable in terms of the introduced mass of TiO_2? Does the nitridization increase the particle size during conversion from TiO_2 to TiN? From the XRD, the authors should estimate the particle of TiN. Is the oxide layer amorphous on TiN? Can the authors estimate how much of TiN is converted to its oxide?

What is the mechanism of "N" release from g-C_3N_4? Is it N_2? Is C_3N_4 prepared in the authors' lab or purchased? What about the cost of using this material as an N-source?

For the TiN oxidation in air, the humidity would have a large impact. What is the humidity level? To reply on the SEM EDX mapping is not convincing to demonstrate that a significant extent of oxidation has taken place unless such EDX mapping is also done on a controlling sample.

The whole study has been conducted with flooded electrolyte conditions. What about lean electrolytes?

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Line 69: "superconductivity" is mentioned. Do the authors really mean it?

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Response: We thanks the reviewer for the positive comments and kind support. The following is the point-to-point response:

1 It is better to give the ratio of TiO_2 and TiN in the TiO_2 (TiN)-O-OMC. It is confused that the results of Figure S5. The lost weight is the sulfur?

Response: Thanks for your valuable suggestion. According to XPS results (**Figure 2d, e and Supplementary Table 3**), the surface oxidized TiN-O-OMC contains three species: TiO_2, Ti-O-N intermediate and TiN. Based on its chemical formula ($Ti_{40}N_{28}O_{37}$), the mole ratio of TiO_2/TiN is calculated to be 12:15. This description is highlighted in XPS section (main text) as:

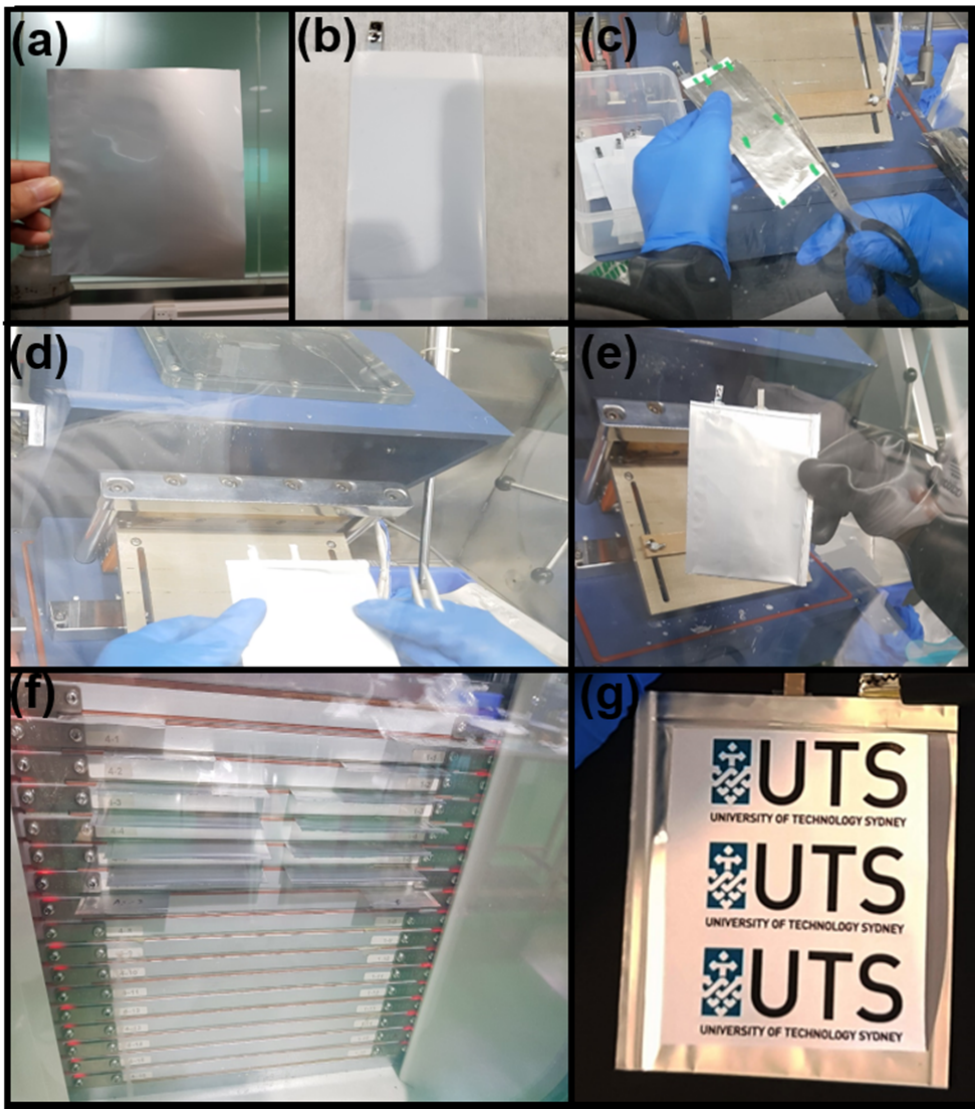
"Additionally, the molar ratio of TiO_2/TiN was calculated to be 12:15, indicating a high portion of surface TiN has been converted to TiO_2 owing to the natural oxidization."

For the TGA figure, the lost weight is the sulphur and the new caption has been corrected to: "**Supplementary Figure 6 | Sulphur compositions.** TGA curves of OMC@S, TiO_2-OMC@S, TiN-O-OMC@S and TiN-OMC@S measured under N_2 atmosphere with a heating rate of 10 □ min^{-1} from room temperature to 500 □."

2 The fabrication process of pouch cell is not shown in the experimental section.

Response: Thanks for your constructive suggestion. The details have been added to the revised Supplementary Information (**Supplementary Figure 15**) and listed as follows:

"Supplementary Method | The laminate film with 16 * 20 cm size was first half-folded and sealed by the hot-sealing machine as the shell of pouch cell (**Supplementary Figure 15a**). 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*8 cm. The Al tab was welded onto the cathode electrode. Then, the cathode was sticked the Celgard 2300 separator by the anti-electrolyte-tape (**Supplementary Figure 15b**). Afterwards, the Li foil anode was pasted on the separator with anti-electrolyte-tape in glovebox with welded Ni tap (**Supplementary Figure 15c**). Then both the cathode and Li foil anode were put in the laminate film package and side sealed by the hot-sealing machine (**Supplementary Figure 15d**). 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 (**Supplementary Figure 15e**). After standby for 1 day, the pouch cell was pressed by formation machine and activated by discharging and charging to 1.7 V and 2.8 V at a low current density of 0.2 C (**Supplementary Figure 15f**). After for another 12 h, the pouch cell was electrochemically tested using the Land Workstation (**Supplementary Figure 15g**)."



Supplementary Figure 15 | Fabrication of pouch cell. (a) Half-sealed laminate film. **(b)** Separator coated cathode. **(c)** Li foil coated separator along with cathode. **(d)** Side-sealed laminate film. **(e)** Pouch cell after injection of electrolyte and full-sealing. **(f)** Stabilization, cold press and formation of pouch cell. **(g)** Pouch cell ready for testing.

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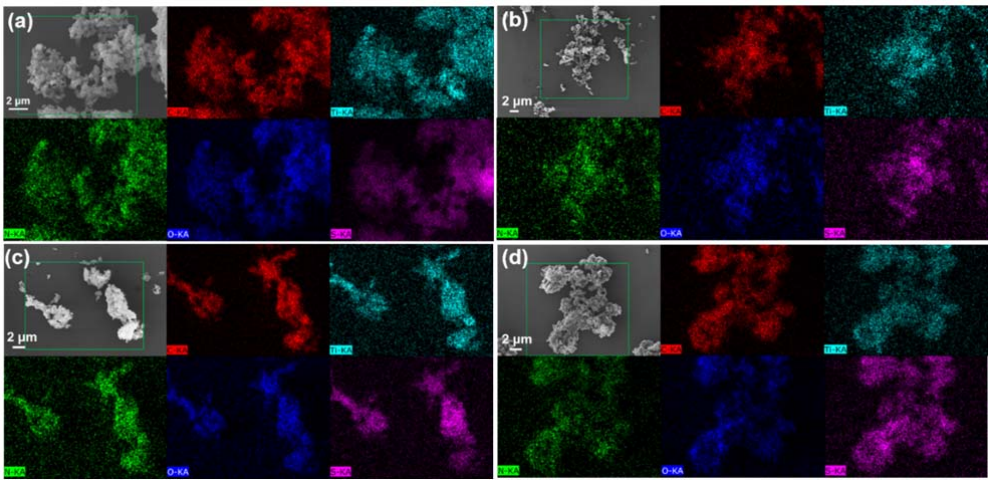
Response: We thanks the reviewer for the constructive comments. The following is the point-to-point response:

1. In Supplementary Fig. 6, the SEM elemental mapping of sulfur should be provided to further prove there are no sulfur aggregates.

Response: Thanks for your good suggestion. The SEM elemental mapping of OMC@S, TiO_2-OMC@S, TiN-O-OMC@S and TiN-OMC@S have been measured.

These S mapping figures are similar to those of Ti, N, O and C. There is no obvious aggregates, indicating homogenous distribution of sulphur within OMC matrix. The results have been added to the revised Supplementary Information (**Supplementary Figure 8**).



Supplementary Figure 8 | Elemental mapping. SEM elemental mapping images of **(a)** OMC@S, **(b)** TiN-O-OMC@S, **(c)** TiO_2-OMC@S and **(d)** TiN-OMC@S.

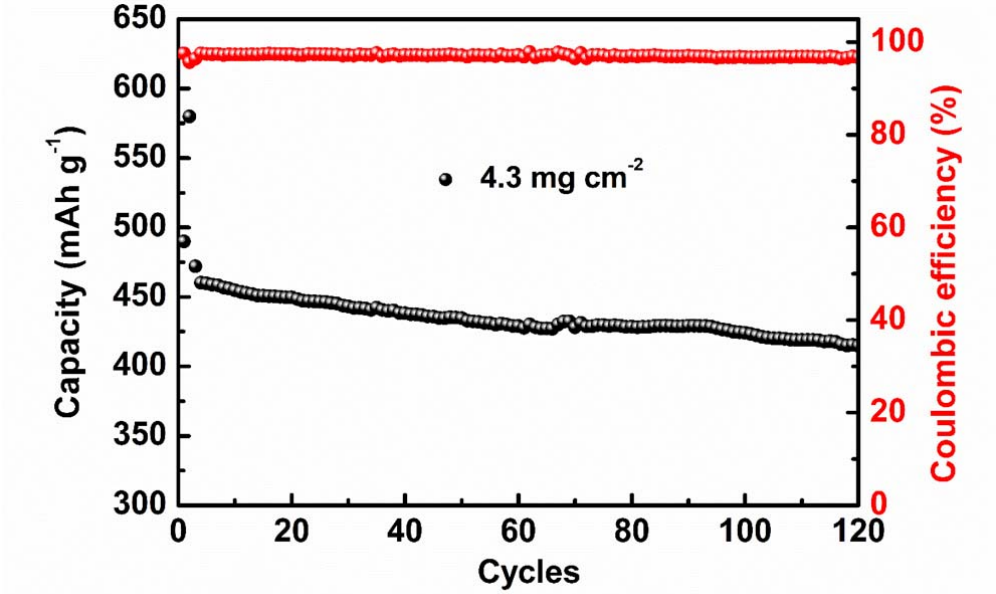
2. Line 171, the authors claim the voltage hysteresis of TiN-OMC is 1 mV higher than that of TiN-O-OMC at 0.2 C, this is inconsistent with the Figure 3C, where the voltage hysteresis of TiN-OMC (270mV) is lower than that of TiN-O-OMC (271 mV). Please give an explanation.

Response: Thanks for the reviewer's valuable comment. We are sorry for the inconsistent description. The correction has been made in revised manuscript as follows:

"Additionally, at a low current rate of 0.2 C, the voltage hysteresis (η) of TiN-OMC is only 1 mV lower than that of TiN-O-OMC, indicating their similar redox kinetics for the solid-liquid-solid lithiation process (**Figure 3c, Supplementary Figure 9**). However, at a high current rate of 5 C, η 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."

3. For Li-S batteries, high sulfur loading and low electrolyte amount are needed to get high energy density. Why do the authors not use high-sulfur-loading cathodes (4.3 mg cm^{-2}) to assemble the pouch cells since these high-sulfur-loading cathodes in coin cells show good performance? The pouch cell performance is attractive but it is useless since the loading is very low. The flexibility is not an advantage of Li sulfur battery. Any types of battery with a low coating of active materials can be flexible to power a LED.

Response: Thanks for your valuable suggestion. We have assembled the pouch cell with a high sulphur loading of ~4.3 mg cm^{-2} and the result is shown in **Supplementary Figure 17**. Because the higher sulphur content would impede the diffusion of electrolyte and increase the charge transfer resistance. As a result, the utilization of sulphur was lower and the redox kinetics was more sluggish. Therefore, after 120 cycles, the capacity is 210 mA h g^{-1} lower than that at a lower sulphur loading of 1.4 mg cm^{-2} (**Figure 6e**). However, the cycling performance at such high sulphur loading is still good with a fading rate of 0.06% after the third cycle.



Supplementary Figure 17 | Cycling stability of pouch cell. Cycling performance and Coulombic efficiency at 0.2 C with a sulphur loading of 4.3 mg cm^{-2}.

4. It is well known that the nitrogen doping on carbon has strong chemisorption on both sulfur and polysulfide. It is not clear the role of Ti or N and their contribution in TiN for chemisorption of polysulfide. If it is N playing an important role, the work should provide the difference from the previous work in literature.

Response: Thanks for your valuable advice on the role of N-doping. In this work, OMC is actually an N-doped carbon as its precursor (hexamethylenetetramine, HTM) is an organic compound with a high N concentration of 40 wt%. These N dopants can be confirmed by N 1s spectra (**Supplementary Figure 5**) and the higher N concentration (9.62%) compared with Ti (5.79%) (**Supplementary Table 2**).

Compared to the N-doped OMC, TiO_2-OMC, TiN-OMC and TiN-OMC all show an improved binding energy to polysulphides (**Figure 5**). Moreover, the enhanced electrochemical catalytic capacity of TiN-O-OMC has been demonstrated by our electrochemical measurement as shown in **Figure 4**. Therefore, it is verified that N-doping does not play a critical role to boost the Li-S batteries but the surface oxidization plays the crucial effect in binding and catalytic performance.

Reviewer #3 (Remarks to the Author):

This is a comprehensive study. It may be accepted if these questions are properly addressed.

Response: We appreciate the reviewer's positive comments and kind support on this work. The following is the point-to-point response:

1. As for "Then TiO_2 nanoparticles were generated after the hydrolysis of tetrabutyl titanate ($Ti(OC_4H_9)_4$) within the OMC. The experimental details should be given. What is the mass loading of TiO_2 in CMK-3, and is this infiltration of TiO_2 controllable in terms of the introduced mass of TiO_2? Does the nitridization increase the particle size during conversion from TiO_2 to TiN? From the XRD, the authors should estimate the particle of TiN. Is the oxide layer amorphous on TiN? Can the authors estimate how much of TiN is converted to its oxide?

Response: Thanks for the reviewer's constructive suggestion.

1) The experimental details are described as follows: "Specifically, 100 mg of OMC was added to 4 mL of ethanol (Sigma-Aldrich, 99.8%)/tetrabutyl titanate (Aldrich, 97%) (1:1, volume ratio) solution, followed by a sonication for 30 mins. The suspension was then vacuumed for 20 mins to allow a complete infiltration of tetrabutyl titanate. After centrifugation (9,000 rpm, 3 mins), the black paste was spread on a petri dish and exposed to air for 1 day to allow a completed hydrolysis of tetrabutyl titanate within OMC matrix."
2) The mass loading of TiO_2 in OMC was about 40 wt% by weighting OMC and its hydrolysis composite.
3) The controllable infiltration and mass loading of TiO_2 is controllable because the concentration of tetrabutyl titanate can be adjusted by the amount of ethanol.[1] In our case, the ratio of tetrabutyl titanate/ethanol is controlled at 1:1 (by volume).
4) Based on Debye-Scherrer Equation, the average crystalline size of TiN and TiO_2 was calculated to be 5.4 and 29.2 nm respectively. The nitridization does not cause an increase in the crystalline size.
5) As TiN is easily oxidized in ambient environment in the absence of H_2O via the following reaction:[2]

$$\mathrm{TiN} + O_2 \rightarrow TiO_2 + N_2$$

The surface oxidized crystallised TiO_2 is amorphous phase because no XRD peaks were detected in TiN-O-OMC (**Figure 2b**).

6) For the conversion ratio from TiN to TiO_2, the description is shown as follows: According to XPS results (**Figure 2d-e** and **Supplementary Table 3**), the surface oxidized TiN-O-OMC consists of three species: TiO_2, Ti-O-N and TiN. Based on its chemical formula of $Ti_{40}N_{28}0_{37}$, the molar ratio of TiO_2/TiN is calculated to be 12:15. This new description is added and highlighted in XPS section (main text) as:
"Additionally, the molar ratio of TiO_2/TiN was calculated to be 12:15, indicating a high portion of surface TiN has been converted to TiO_2 owing to the natural oxidization."

2. What is the mechanism of "N" release from g-C_3N_4? Is it N_2? Is C_3N_4 prepared in the authors' lab or purchased? What about the cost of using this material as an N-source?

Response: We appreciate the reviewer's good question on the N source.

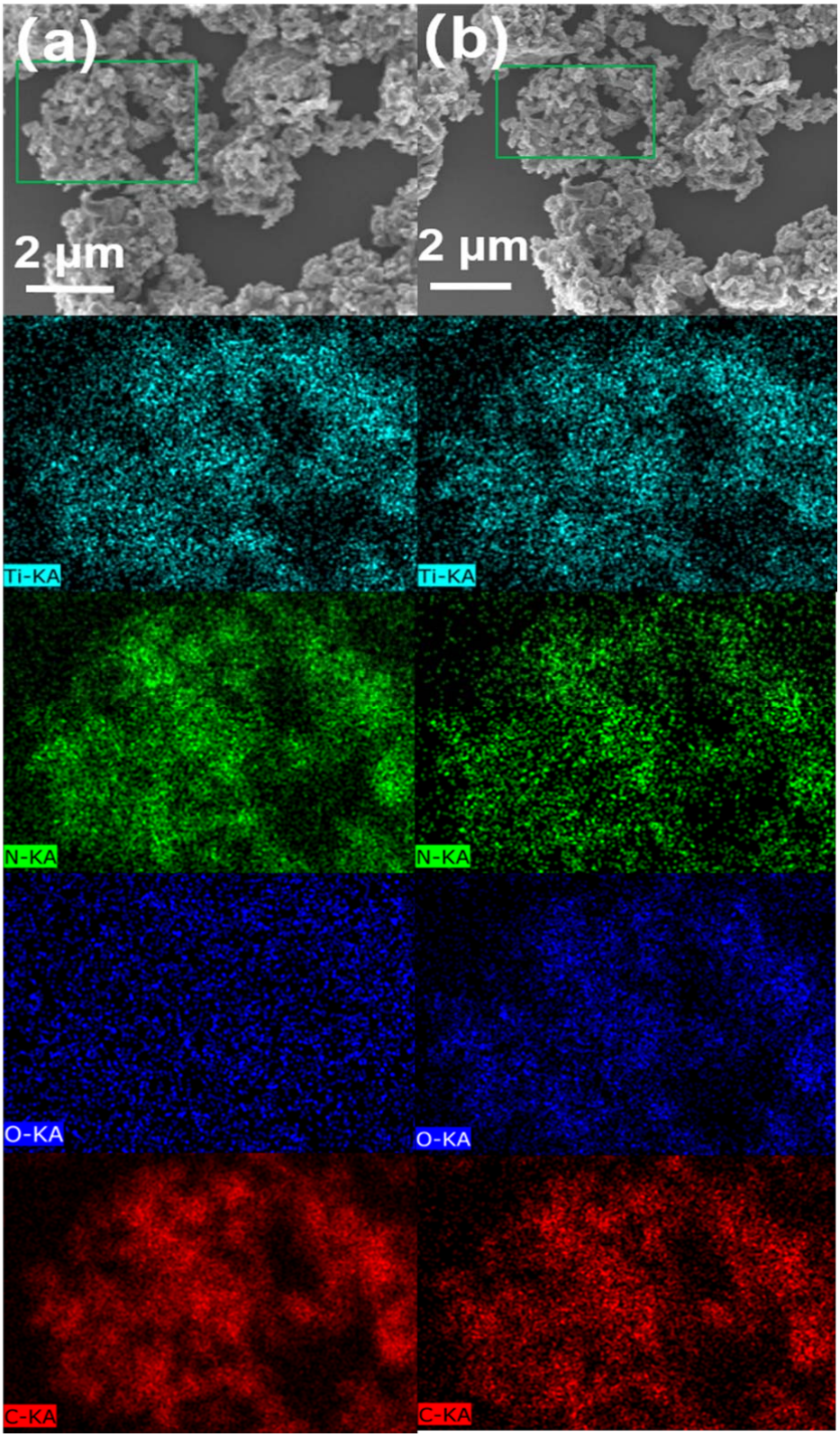
1) For the mechanism of "N" release: NH_3 is largely released when g-C_3N_4 is heated above 500 °C and thus g-C_3N_4 can act as N source to obtain TiN.[2]
2) For the preparation of g-C_3N_4: g-C_3N_4 was prepared in our lab after heating melamine at 550°C for 4 h in muffle furnace. [3]
3) For the cost of using g-C_3N_4: The yield is around 50-60 wt%. Checking the price in Sigma-Aldrich, melamine is only 0.0748 AU$/g. Therefore, employing g-C_3N_4 as the N source is a very economic and safe approach in comparison with the toxic NH_3 gas.

3. For the TiN oxidation in air, the humidity would have a large impact. What is the humidity level? To reply on the SEM EDX mapping is not convincing to demonstrate that a significant extent of oxidation has taken place unless such EDX mapping is also done on a controlling sample.

Response: We appreciate your constructive suggestion on humidity. We did the oxidization experiment in ambient condition and the lab humidity is around 67.1%.

To make a better comparison on the effect of surface oxidation, TiN-OMC was firstly casted on Si substrate for SEM EDX mapping (**Supplementary Figure 2a**). After this test, the

sample was kept in ambient condition for 3 days to obtain TiN-O-OMC. Afterwards, a new SEM EDX mapping was performed on the same area (**Supplementary Figure 2b)**. This SEM EDX mapping clearly shows the effective oxidization of TiN when exposed in ambient condition.



Supplementary Figure 2 | Elemental mapping. SEM elemental mapping images of **(a)** TiN-OMC and **(b)** TiN-O-OMC.

4. The whole study has been conducted with flooded electrolyte conditions. What about lean electrolytes?

Response: Thanks for your good question on lean electrolyte. In this work, the ratio of electrolyte (uL)/sulphur (mg) (E/S) was controlled at 25 uL mg^{-1}. Experiment with lower ratios of 15 and 5 was also performed (**Figure 1**). Taking 0.2 C for instance, the discharge capacity is 712 and 420 mAh g^{-1} when the E/S ratios is controlled at 15 and 5. While in a high E/S ratio of 25, capacity increases to 1264 mAh g^{-1} which is similar to previous report.[4] We ascribe this to the insufficient infiltration of electrolyte. This work mainly forces on the strong polysulphides binding ability and enhanced electrochemical catalytic of surface oxidized TiN. Future work will be paid to this area especially on discovering new additives as reported elsewhere.[5]

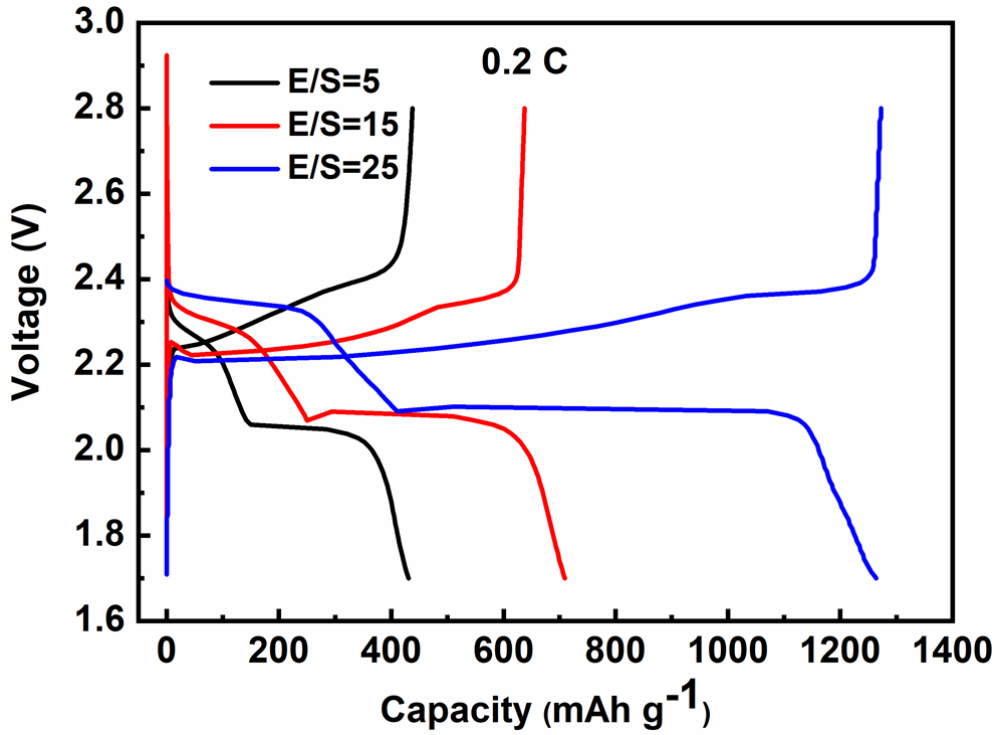
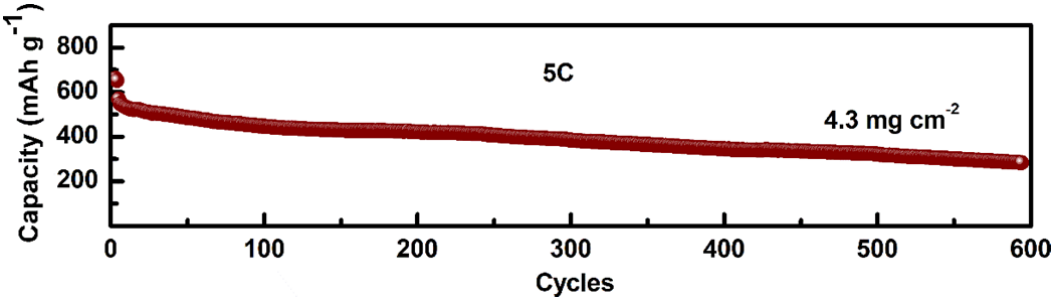


Figure 1. Galvanostatic charge/discharge voltage profiles at 0.2 C with an E/S ratio of 5, 15 and 25 for TiN-O-OMC electrode.

5. Mass loading is quite low. What about the performance with a higher mass loading i.e., > 3 mg/cm^2?

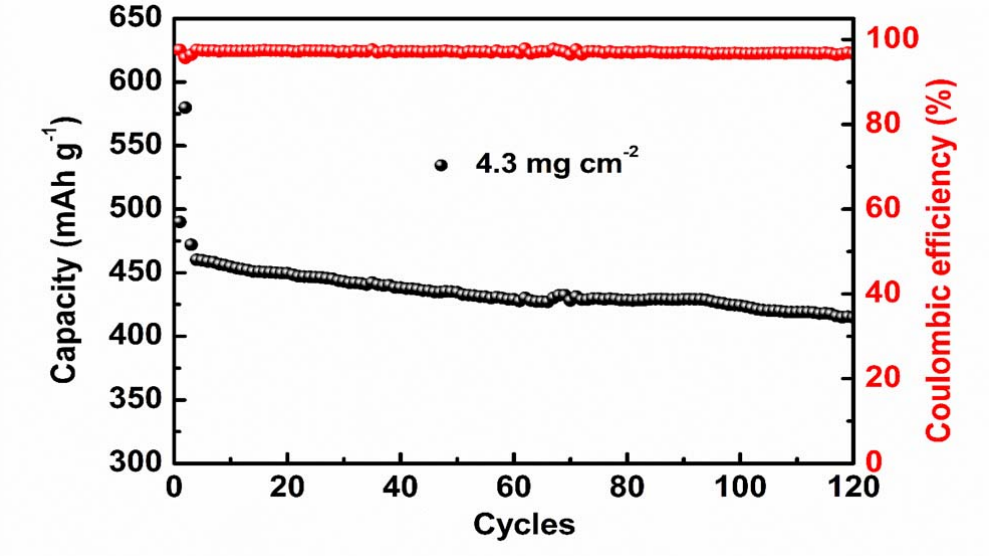
Response: Thanks for your question.

1) For coin cell, we had collected the cycling performance at 5 C with a high sulphur loading of ~4.3 mg cm^{-2} for TiN-O-OMC@S electrode. The result is shown in **Supplementary Figure 11**. And we highlighted the following description in main text (first paragraph of Electrochemical Performance section):
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 rate of 5 C (**Supplementary Figure 11**)."



Supplementary Figure 11 | Li-S performance. Cycling stability of TiN-O-OMC@S electrode at 5 C with a high sulphur mass loading of 4.3 mg cm^{-2}.

2) For pouch cell, we had assembled the pouch cell with a high sulphur loading of ~ 4.3 mg cm^{-2} and the result is shown in **Supplementary Figure 17**. Because the higher sulphur content would impede the diffusion of electrolyte and increase the charge transfer resistance. As a result, the utilization of sulphur was lower and the redox kinetics was more sluggish. Therefore, after 120 cycles, the capacity is 210 mA h g^{-1} lower than that at a lower sulphur loading of 1.4 mg cm^{-2} (Figure 6e). However, the cycling performance at such high sulphur loading is still good with a fading rate of 0.06% after the third cycle.



Supplementary Figure 17 | Cycling stability of pouch cell. Cycling performance and Coulombic efficiency at 0.2 C with a sulphur loading of 4.3 mg cm^{-2}.

6. Line 69: "superconductivity" is mentioned. Do the authors really mean it?

Response: Thanks for the reviewer's comment. It is an error. We want to emphasize the superior conductivity of TiN compared to metal oxides Thus "superconductivity" is deleted from the main text (second paragraph, Introduction section).

Reference

1. Jun Y, Hong W, Antonietti M. Mesoporous, 2D hexagonal carbon nitride and titanium nitride/carbon composites. *Adv. Mater.* **21**: 4270-4274 (2009).

2. Saha N, Tompkins H. Titanium nitride oxidation chemistry: An x-ray photoelectron spectroscopy study. *J. Appl. Phys.* **72**: 3072-3079 (1992).

3. Wang X, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater*. **8**, 76 (2009).

4. Sun K, Matarasso A K, Epler R M, et al. Effect of Electrolyte on High Sulfur Loading Li-S Batteries. *J. Electrochem. Soc.* **165**: 416-423 (2018).

5. Pan H, Han K S, Engelhard M H, et al. Addressing passivation in Lithium–Sulfur battery under lean electrolyte condition. *Adv. Funct. Mater.* **28**: 1707234 (2018).

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