



**Pairwise/sandwich-like assembly consisting of TaO<sub>3</sub> nanomesh and reduced graphene oxide for a pelletized self-supported cathode towards high-areal-capacity Li-S batteries**

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## ARTICLE

## Pairwise/sandwich-like assembly consisting of TaO<sub>3</sub> nanomesh and reduced graphene oxide for a pelletized self-supported cathode towards high-areal-capacity Li–S batteries

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Lithium-sulfur (Li-S) batteries have attracted considerable attention as a promising energy storage technology. However, the low loading and utilization of sulfur result in the poor practical energy density of these batteries, which has hindered their extensive application. Herein, we demonstrate the fabrication of molecular pairwise/sandwich-like assembly of TaO<sub>3</sub>/rGO, which can be pelletized into a self-supported cathode to improve sulfur loading and utilization. This unique pairwise/sandwich-like heterostructure of TaO<sub>3</sub>/rGO is produced through a solution process via self-assembly and identified by X-ray diffraction analysis/simulation and TEM observations. The molecular-scale heterostructure maximizes attractive features of the TaO<sub>3</sub> nanomesh: crystalline open channels, polar Ta-O bonds, Lewis acid surfaces and largely exposed active sites, by combining with electrically conductive rGO. As a benefit, the heterostructure exhibited fast Li<sup>+</sup> transfer, effective confinement of polysulfides and high catalytic activity for the conversion of lithium polysulfides and uniform deposition of Li<sub>2</sub>S, thereby contributing to high sulfur utilization. As a result, the Li-S batteries assembled with these self-supported cathodes achieved a high areal capacity of 10.5 mAh cm<sup>-2</sup> at 2 mA cm<sup>-2</sup>. This versatile strategy of fabricating electrodes with high loading of powder-like active materials can be applied to various energy storage systems, such as alkali metal batteries, promoting their practical application.

### Introduction

Li-S batteries have been regarded as one of the most promising energy storage technologies, because of their high theoretical energy density and low cost.<sup>1-5</sup> However, the low practical energy density of Li-S batteries, which is a consequence of poor utilization and mass-loading of sulfur, has hampered their wide application.<sup>6, 7</sup> Low sulfur utilization stems from several problems, such as the “shuttle effect”, sluggish reaction kinetics of lithium polysulfides conversion, high overpotential for Li<sub>2</sub>S nucleation and low conductivity of S and Li<sub>2</sub>S.<sup>8,9</sup> As a solution, the design of new host materials with high performance and the development of convenient electrode fabrication methods have been strongly demanded.<sup>10, 11</sup>

Two-dimensional (2D) materials have attracted enormous attention in recent decades because of their superior functionalities that are associated with their unique electronic, magnetic, optical and thermal properties.<sup>12-16</sup> Among them, unilamellar metal oxide nanosheets have offered promising prospects in Li-S batteries because of their acid/base surface character and abundant exposed active sites.<sup>17-20</sup> On the other hand, the extremely high aspect ratio of 2D materials often

causes a serious drawback, namely, a slow ion diffusion rate across the layers of an electrode material made of stacked 2D nanosheets. Thus, significant efforts have been devoted to drilling of 2D nanosheets, namely the artificial fabrication of in-plane pores by chemical/thermal etching and templating methods.<sup>21-24</sup> However, in general, such pores are not uniform in size, shape and arrangement, disabling the transportation of a specific ion and blocking others by so-called size-sieving effects. In contrast, an intrinsic crystalline nanomesh structure is expected to be more efficient and attractive because it provides ion-permeable channels with well-defined sizes and shapes. In addition, there is no need for the consumption of long time, energy and chemicals as exemplified by the complex template-removal process in the reported procedures<sup>25</sup>. Although a number of unilamellar metal oxides have been reported,<sup>12-16</sup> nanosheets with such a nanomesh structure is very rare. The exfoliated TaO<sub>3</sub> nanosheet is such a unique example having in-plane pores.<sup>26</sup> The TaO<sub>3</sub> nanomesh can be derived from its precursory layered oxide, RbTaO<sub>3</sub>, via soft-chemical exfoliation into colloidal single layers.<sup>27, 28</sup> The obtained TaO<sub>3</sub> nanomesh possesses the in-plane pores with an open gap of 0.1-0.2 nm, which allow the penetration of small ions such as Li<sup>+</sup>, as we experimentally confirmed.<sup>29</sup> Moreover, its Lewis acid surface and polar Ta-O bonds will provide a high catalytic activity and suitable binding to polysulfides. Accordingly, we expect that TaO<sub>3</sub> nanomesh may be effectively employed in Li-S batteries as a multifunctional host material, namely, an anchor of polysulfides and catalyst, to enhance the sulfur utilization (Scheme 1b). Despite these promising

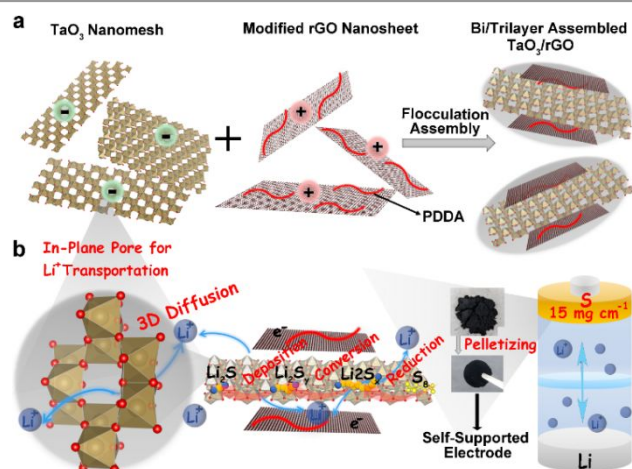
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potentials, no such study on TaO<sub>3</sub> nanomesh has been reported. One aspect to be improved for oxide nanosheets, including TaO<sub>3</sub>, is their insulating nature. We have reported that the layer-by-layer hybridization of various oxide nanosheets with reduced graphene oxide (rGO) into a superlattice composite can overcome this problem.<sup>30-43</sup>

Electrode fabrication methods bring about a significant difference in shape, porosity, stability, wettability, electrolyte uptake and mass loading, all of which affect total battery performance, such as the energy and power densities.<sup>44</sup> However, relevant studies are scarce in comparison with electrode material design. In most of studies, thin-film electrodes with a low sulfur loading (1-2 mg cm<sup>-2</sup>) are fabricated by blade coating to guarantee the sufficient mass transfer, electrical conductivity and structural stability of these compact electrodes.<sup>45, 46</sup> Although it is an efficient method for screening studies on materials, the low sulfur loading inevitably leads to a poor energy density when practically used, which will leave a large gap between the fundamental study and practical application.<sup>47</sup> As an alternative, self-supported electrodes are promising to efficiently increase sulfur loading by reducing the proportion of inactive materials such as current collectors and binders.<sup>48-50</sup> Monolith-type<sup>51</sup> and membrane-type<sup>52</sup> electrodes are two typical self-supported electrodes, and they are usually prepared by hydrothermal/solvothermal reactions and suction filtration, respectively. In contrast to facile blade coating, these two methods require more time and energy; moreover, these methods are only applicable to a limited number of materials. These limitations have hampered their wide application. On the other hand, the pelletizing method is promising as a facile, efficient and widely applicable technique to fabricate self-supported electrodes with various materials, including powder-like materials.<sup>53</sup> Moreover, the electrode properties, such as the mass loading, porosity and contact resistance, can be controlled by adjusting the pelletizing conditions, such as the pressure and time. Accordingly, the pelletizing method is anticipated to show great promise to fabricate electrodes for Li-S batteries as well as other batteries. However, related studies are still scarce.

Herein, we designed a unique material consisting of pairwise/sandwich-like assembly of TaO<sub>3</sub>/rGO and constructed a self-supported cathode for Li-S batteries by the pelletizing method (Scheme 1). The unique nanomesh structure of TaO<sub>3</sub> was characterized by in-plane and powder X-ray diffraction (XRD) analysis and high angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) clearly revealed the unique nanomesh structure of TaO<sub>3</sub>. Li<sup>+</sup> penetration through the channels was demonstrated by density-functional theoretical (DFT) calculations as well as electrochemical experiments. The TaO<sub>3</sub> nanomesh with crystalline in-plane open pores (0.1-0.2 nm), polar Ta-O bonds, Lewis acid surfaces and abundant exposed active sites could accelerate Li<sup>+</sup> transfer, suppress the "shuttle effect", and promote the conversion of lithium polysulfides and nucleation of Li<sub>2</sub>S. Furthermore, TaO<sub>3</sub> nanomesh was intimately combined with rGO, maximizing these advantages through improving

electrical conductivity. Benefiting from the 2D morphology, the hetero-assembled material of TaO<sub>3</sub>/rGO could be facilely pelletized into a self-supported cathode with a high sulfur-loading of 15 mg cm<sup>-2</sup>, and achieved a high areal capacity of 10.5 mAh cm<sup>-2</sup> at 2 mA cm<sup>-2</sup>.

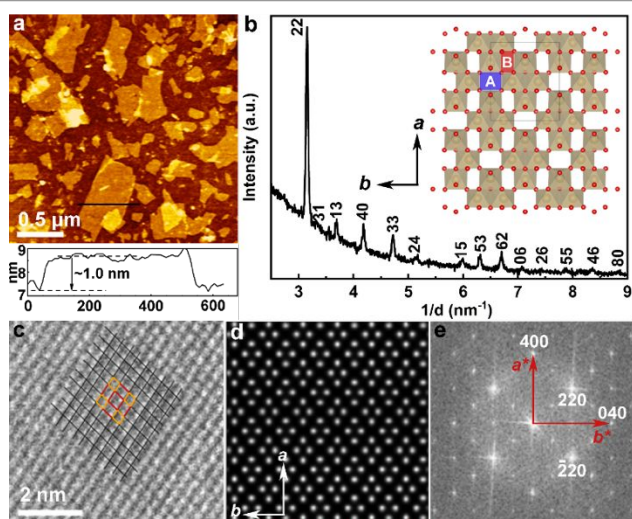


**Scheme 1.** Schematic illustration of the a) pairwise/sandwich-like assembly of TaO<sub>3</sub> nanomesh and rGO and b) fabrication of the self-supported cathode based on pairwise/sandwich-like assembly TaO<sub>3</sub>/rGO and its application in a lithium-sulfur battery.

## Results and discussion

Colloidal TaO<sub>3</sub> nanomeshes were derived from the parental layered material of RbTaO<sub>3</sub> via its soft-chemical delamination into single layers. XRD patterns of RbTaO<sub>3</sub> and its acid-exchanged form, HTaO<sub>3</sub>·1.3H<sub>2</sub>O, can be indexed in terms of monoclinic structures, agreeing with the reported results<sup>27</sup> (Fig. S1). As shown in Fig. S2-3, these materials were composed of plate-like microcrystals. Shaking HTaO<sub>3</sub>·1.3H<sub>2</sub>O in a TBAOH solution for 10 days produced a colloidal suspension with an opalescent appearance (Fig. S4), indicating successful delamination. Atomic force microscopy (AFM) analysis was performed after drying a diluted suspension on a Si substrate. We observed 2D sheets with a lateral size of submicrometers and a thickness of ~1 nm (Fig. 1a), confirming their unilamellar structure. The in-plane XRD data of their monolayer film deposited on an Si wafer exhibited sharp diffraction peaks, indicating a highly crystalline nature (Fig. 1b). The peaks can be indexed to a face-centered rectangular lattice with refined unit cell dimensions of  $a = 0.9607$  nm and  $b = 0.8479$  nm. These values are very close to the in-plane lattice parameters of the parent material (RbTaO<sub>3</sub>), indicating that the host layer architecture is preserved after exfoliation into nanosheets. The structure of the TaO<sub>3</sub> nanomesh was further examined by HAADF-STEM. As shown in a ball-and-stick model of the TaO<sub>3</sub> host layer, each Ta atom is coordinated with six O atoms and the resulting octahedra are joined into a 2D sheet having two kinds of in-plane-holes to form a regular mesh structure (Fig. S5a). These in-plane-holes are more clearly recognized in the Ta atom pattern (Fig. S5c). One is marked by the rhombus (A), and the other is by the rhomboid with a pair of parallel red lines connected with a pair of parallel yellow lines (B). These

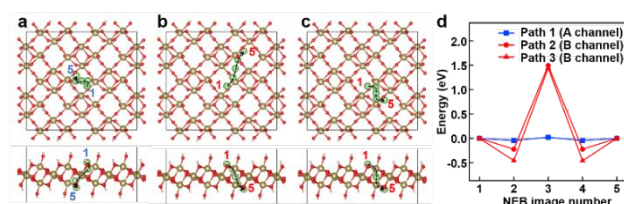
holes correspond to the designation in the inset of Fig. 1b. A HAADF-STEM image of an exfoliated TaO<sub>3</sub> nanosheet is shown in Fig. 1c. Because of the Z-contrast of the HAADF images, only the positions of the heavy Ta atoms can be identified to highlight the nanomesh structure, which is consistent with the atomic model (Fig. S5c) and the simulated HAADF image (Fig. 1d). The fast Fourier transform (FFT) pattern of this image is also compatible with the crystalline mesh structure (Fig. 1e). Accordingly, the obtained 2D sheet should have open channels as indicated by A and B (the inset of Fig. 1b and Fig. S5). The distances of orthogonally facing two oxygen atoms in the illustration are estimated as 0.39 nm and 0.46 nm (Fig. S5b), respectively, based on crystallographic data for the parent RbTaO<sub>3</sub>. Note that there are displacements of the atoms along the sheet normal, making such interatomic distances appear shorter in the top view representation. Because the oxygen ionic radius is ~0.14 nm, the channels A and B have net open gaps of 0.11 nm and 0.18 nm, respectively, which appear to be large enough to allow penetration of Li<sup>+</sup> or some other metal ion for batteries.



**Fig. 1.** a) AFM image and height profile of the TaO<sub>3</sub> nanomeshes. b) In-plane XRD pattern of a monolayer film of TaO<sub>3</sub> nanomeshes (inset: top-view of the TaO<sub>3</sub> layer<sup>S5d</sup>). c) HAADF-STEM image of the TaO<sub>3</sub> nanomesh. d) Simulated HAADF image of Ta atom positions in the TaO<sub>3</sub> layer. e) FFT pattern of the HAADF-STEM image of the TaO<sub>3</sub> nanomesh in (c).

To examine the penetration possibility of metal ions such as Li<sup>+</sup>, energy barriers of each channel were estimated by the nudged elastic band (NEB) method<sup>55</sup> based on the DFT calculations using the Vienna ab initio simulation package (VASP)<sup>56</sup> combined with the VTST code<sup>57</sup>. Fig. 2a-c show the minimum energy paths (MEPs) by the NEB calculations for Li<sup>+</sup> ion penetration through A or B channels, and the energy barriers of each MEP are plotted in Fig. 2d. It should be noted that a TaO<sub>3</sub> slab-supercell model with surface proton was employed for establishing a charge neutral state of the nanomesh (Fig. S6) and two penetration paths for the B channel (as shown in Fig. 2b and 2c) were yielded due to the surface-proton configuration. As shown in Fig. 2d, the energy barrier for the A channel penetration is estimated to be nearly zero, while that for the B channel is rather large, ~1.5 eV. These evaluations suggest that the Li<sup>+</sup> ion is most likely to pass

through the TaO<sub>3</sub> nanomesh via A channel at room temperature, and this is consistent with our previous result<sup>29</sup>. The energy barriers for penetration of Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> were also examined (Fig. S7), giving a lower barrier for the A channel in all the cases. The calculations indicate the easier penetration of A channel than B channel and the order of the ion penetration possibilities is, roughly, Li<sup>+</sup> (most penetrative) > Mg<sup>2+</sup> > Na<sup>+</sup> >> K<sup>+</sup> (less penetrative), being compatible with an intuitive picture of “a smaller ion penetrates easier”<sup>58</sup>. It is noteworthy that barrier heights of ~1 eV suggests the penetration wait time in order of 10 h at room temperature from a simple rate constant analysis based on the harmonic transition state theory.<sup>59</sup> Thus we could conclude that Na<sup>+</sup> (>2 eV) and K<sup>+</sup> (>8 eV) are hard to penetrate both A and B channels. In contrast, Li<sup>+</sup> and Mg<sup>2+</sup> can pass through the TaO<sub>3</sub> nanomesh along the A channel because almost zero barrier energies are expected. TaO<sub>3</sub> nanomeshes can provide channels for Li<sup>+</sup> and Mg<sup>2+</sup> to promote the diffusion especially in the vertical direction of the nanosheets, expecting the potential application opportunities of TaO<sub>3</sub> nanomesh in the Li<sup>+</sup> and Mg<sup>2+</sup> related metal ion batteries.



**Fig. 2.** Theoretical simulation results of Li<sup>+</sup> penetration through TaO<sub>3</sub> nanomesh. MEP images for a) penetration path 1 (A channel), b) path 2 (B channel) and c) path 3 (B channel). d) NEB relative energies for each MEP. In the initial (1<sup>st</sup>) and final (5<sup>th</sup>) images, Li<sup>+</sup> ions are located at metastable positions at the front and back side of the TaO<sub>3</sub> nanomesh. Each third image refers to a Li<sup>+</sup> ion *just-in-the hole* (bottleneck) structure yielding a penetration barrier energy.

Apart from the TaO<sub>3</sub> nanomesh, we prepared rGO according to the standard procedure. The modified Hummers' method was applied to synthesize graphite oxide (Fig. S8), which was delaminated by ultrasonication, modified with polycation, PDDA, and finally reduced with hydrazine.<sup>60, 61</sup> This PDDA-modified rGO sample had a lateral size of several micrometers and a thickness of ~1.5 nm (Fig. S9). The zeta potential verifies that its surface charge changed from negative to positive through the modification with PDDA and the reduction, whereas the surface charge of the TaO<sub>3</sub> nanomesh was negative (Fig. S10).

To combine these 2D materials, namely, the TaO<sub>3</sub> nanomesh and PDDA-modified rGO, their suspensions were dropwise added to water at a specific ratio and the obtained composite is named as S-TaO<sub>3</sub>/rGO (Scheme 1a) where “S” denotes the self-assembled.<sup>62-64</sup> As a control, a composite named R-TaO<sub>3</sub>/rGO (“R” denotes random) was prepared by adding suspensions of the negatively charged TaO<sub>3</sub> nanomesh and unmodified rGO into a PDDA solution. In addition, as a reference, self-restacked samples of TaO<sub>3</sub> nanomesh and rGO were prepared by flocculation with PDDA solution followed by freeze-drying. Fig. 3 shows powder XRD data of these samples. The freeze-dried sample of the TaO<sub>3</sub> nanomesh showed strong peaks at 4.7° and 9.9°, which are attributable to the basal diffraction series from the restacked structure of the TaO<sub>3</sub> nanomesh, accommodating TBA<sup>+</sup> in the intersheet gallery (*d* =

1.90 nm). On the other hand, the peaks at  $14.3^\circ$ ,  $28.4^\circ$ ,  $33.3^\circ$ ,  $37.7^\circ$  and  $43.0^\circ$  can be indexed to the in-plane diffraction of the 110, 220, 130, 400 and 040 crystal planes of the face-centered rectangular unit cell ( $a = 0.96$  nm,  $b = 0.85$  nm). The freeze-dried sample of rGO was rather featureless, due to the small scattering factor of carbon. The material (S-TaO<sub>3</sub>/rGO) obtained via electrostatic assembly of TaO<sub>3</sub> nanomesh and PDDA-modified rGO showed a series of in-plane reflections from TaO<sub>3</sub>. No peak from rGO was detected, which should be due to the same reason above. The material showed an enhanced background toward small angles, which is superimposed by a characteristic wavy profile with humps at approximately  $7^\circ$  and  $12^\circ$  as indicated by arrows. The feature in this small angular range should be associated with the stacking structure of the 2D sheets, namely, how the TaO<sub>3</sub> and rGO are organized.

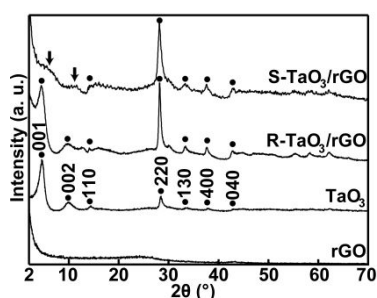


Fig. 3. Powder XRD patterns of the restacked PDDA-modified rGO, restacked TaO<sub>3</sub> nanomesh, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO.

To gain insight into the stacking structure of the samples, we simulated the XRD profile, the calculation details of which are given in the Experimental section. Fig. 4a depicts the calculated patterns of individual TaO<sub>3</sub> nanomesh and rGO. The intensity steeply and monotonously increases with decreasing the  $2\theta$  angle. When these two sheets are paired with a separation of 1.5 nm, as illustrated in the model (Fig. S11a), the wavy profile with the gradually enhancing background (red line in Fig. 4b) reasonably reproduces the experimental pattern (Fig. 3, S-TaO<sub>3</sub>/rGO). On the other hand, repeating this paired assembly (Fig. S11b) brings about the evolution of diffraction peaks together with small ripples associated with the Laue interference function (blue line in Fig. 4b). These calculation results strongly suggest that the structure of the product obtained with the TaO<sub>3</sub> nanomesh and PDDA-modified rGO is close to their paired assembly. From a viewpoint of chemical structure, it may be more reasonable to assume a sandwich-like architecture of rGO/TaO<sub>3</sub>/rGO where rGO on one side is half of TaO<sub>3</sub> in the paired assembly (Fig. S11c). In practice, this rGO/TaO<sub>3</sub>/rGO unit shows a very similar profile to that of the TaO<sub>3</sub>/rGO pair as well as the experimentally observed data for S-TaO<sub>3</sub>/rGO (Fig. 4c). TEM analysis provides a straightforward support for this unique sandwich-like structure, showing three parallel fringes with a distance of 1.5 nm (Fig. 4d, inset). Another composite of R-TaO<sub>3</sub>/rGO prepared by mixing suspensions of TaO<sub>3</sub> nanomesh and rGO in a PDDA solution showed a profile similar to that of S-TaO<sub>3</sub>/rGO obtained by self-assembly, except for rather strong basal peaks at  $4.5^\circ$  and  $9.8^\circ$  (Fig. 3). These peaks may be identified as a self-restacked structure of PDDA/TaO<sub>3</sub>. These results indicate that R-TaO<sub>3</sub>/rGO is rather heterogeneous and is composed of the pairwise or sandwich-like assembly of S-TaO<sub>3</sub>/rGO and self-

restacked TaO<sub>3</sub> (and probably rGO). The segregative restacking may be reasonable, considering the mixing mode where two suspensions of negatively charged TaO<sub>3</sub> nanomesh and rGO were simultaneously added into the polycation solution.

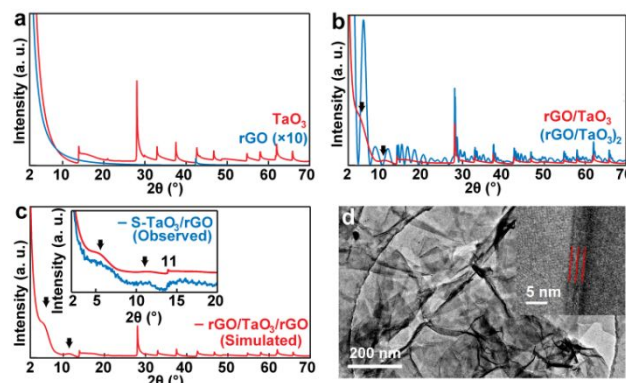


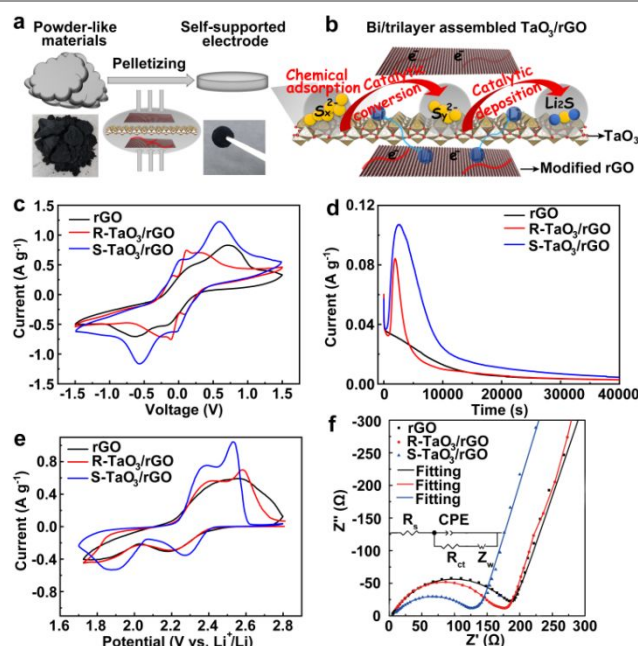
Fig. 4. Simulated XRD patterns of a) single-layer TaO<sub>3</sub> and single-layer rGO, b) single-unit of rGO/TaO<sub>3</sub> and double-unit rGO/TaO<sub>3</sub>/rGO/TaO<sub>3</sub> and c) sandwich-like architecture of rGO/TaO<sub>3</sub>/rGO (inset: comparison with the observed XRD pattern of S-TaO<sub>3</sub>/rGO in a low angular region. The simulated one is plotted with some offset for clarity). d) TEM image of S-TaO<sub>3</sub>/rGO (inset: a high-resolution TEM image of the cross-section of the S-TaO<sub>3</sub>/rGO sandwiched structure).

TEM image of the self-assembled product of S-TaO<sub>3</sub>/rGO displays a lath-like morphology with high transparency, indicating its ultrathin structure (Fig. 4d). The scanning electron microscope (SEM) images reveal a loosely interconnected microstructure with a lateral size of several micrometers (Fig. S12), which will provide an electron conductive framework and electrolyte permeation path that contribute to the low ohmic and diffusion resistances. The uniform distribution of C, O and Ta was verified by energy-dispersive X-ray spectroscopy (EDS), indicating high homogeneity (Fig. S13). The sample underwent dehydration up to 200 °C, as revealed by thermogravimetric and differential thermal analysis (TG-DTA) (Fig. S14). The weight loss from 200 °C to 450 °C can be ascribed to the phase transition of TaO<sub>3</sub> to Ta<sub>2</sub>O<sub>5</sub> and combustion of rGO. On the basis of the TG data, the mass ratio of TaO<sub>3</sub> to rGO is estimated to be  $\sim 4.3$ , which is close to the mass ratio (4.8) for preparation. Neglecting PDDA in TG calculation may be responsible for the small difference between TG calculation and preparation. All these results support the formation of the pairwise/sandwich-like assembly of TaO<sub>3</sub> nanomesh with rGO through the present process involving flocculation via electrostatic self-assembly, suppressing their self-restacking.

The nanostructure/morphology of powder materials influences the structural adhesion effect of the pelletizing approach for fabricating self-supported electrodes. Thus, powder materials in various morphology, such as 1D carbon nanotubes (CNTs), 2D rGO and 3D activated carbon (Fig. S15), were chosen as model samples to explore structural adhesion behaviour. As illustrated in Fig. S16a and S16b, 1D CNTs failed to form a self-supported electrode at a pressure of 2 MPa and could be shaped into a brittle entity by the pressure of 14 MPa. A higher pressure of 28 MPa led to strong adhesion between the CNTs and mold substrate, and the electrode was cracked when being separated (Fig. S16c). The 3D activated carbon hardly formed a self-supported agglomerate at all the pressures (Fig. S16g-i). Small pieces were obtained at high pressure, leaving

residual fragments, which indicates that a higher pressure may be needed to obtain self-supported electrodes with activated carbon. In contrast, an intact rGO self-supported electrode was easily obtained at the pressures of 2, 14 and 28 MPa (Fig. S16d-f). This large pressure range for pelletizing demonstrates the high structural adhesion behaviour of rGO. The thickness of pelletized electrodes could be controlled by the pressure (Fig. S17), suggesting that the electrode performance can be optimized by the pelletizing parameter for various application occasions. The self-supported electrodes maintained the original intact disk structure with large variability in their thickness, indicating that these electrodes may tolerate a large volume change during charge/discharge processes, and thus, they may contribute to an excellent stability during long-term cycle. These findings suggest a strong structural adhesion characteristic of 2D materials, due to their high aspect ratio and ability to be readily stacked into a stable self-supported film, yielding remarkable benefits for facile electrode fabrication by pelletizing. The optimized pressure of 2 MPa was applied to reserve porosity for electrolyte permeability and guarantee the structural strength of electrode for battery assembly, simultaneously. As a result, the S-TaO<sub>3</sub>/rGO constructed with 2D blocks of monolayer rGO and TaO<sub>3</sub> nanomesh was easily pelletized into the self-supported electrodes (Fig. 5a). Self-supported electrodes based on rGO, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO were fabricated by pelletizing to examine the catalytic activity to the lithium polysulfide conversion reaction and Li<sub>2</sub>S nucleation process in Li<sub>2</sub>S<sub>6</sub> symmetric batteries and Li<sub>2</sub>S<sub>8</sub> batteries. The catalytic activity of rGO, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO in regard to the conversion of lithium polysulfides was studied by cyclic voltammetry (CV) with Li<sub>2</sub>S<sub>6</sub> symmetric batteries. The CV curve of rGO showed two pairs of redox peaks with oxidation peaks at 0.14 V and 0.71 V and reduction peaks at -0.18 V and -0.64 V, respectively, suggesting a two-step reaction on rGO (Fig. 5c). R-TaO<sub>3</sub>/rGO showed a much smaller peak separation of its two redox peaks than rGO, indicating that R-TaO<sub>3</sub>/rGO has higher reversibility. This may be ascribed to the Lewis acidic surface of TaO<sub>3</sub> nanomesh, which contributes to the high catalytic activity for the conversion of lithium polysulfides as a Lewis base.<sup>65</sup> On the other hand, the insulating nature of TaO<sub>3</sub> and its segregative restacking with rGO lead to a lower current response than that of rGO. The highest current response observed for S-TaO<sub>3</sub>/rGO indicates that it has the highest catalytic activity among the tested electrodes, verifying the advantages of the self-assembled pairwise or sandwich structure to maximize the number of exposed reaction sites. This feature is further supported by their electrochemical impedance, which was estimated by electrochemical impedance spectroscopy (EIS). As shown in Fig. S18, the impedance data were fitted with two compressed semicircles and one linear segment. These two semicircles correspond to the two-step reaction in the conversion process of long-chain lithium polysulfides to short-chain ones. The response from rGO, having the largest charge transfer resistance ( $R_{ct1} = 61.0 \Omega$ ,  $R_{ct2} = 15.4 \Omega$ ), suggests the slowest reaction kinetics for lithium polysulfide conversion. R-TaO<sub>3</sub>/rGO showed a smaller charge transfer resistance ( $R_{ct1} = 34.0 \Omega$ ,  $R_{ct2} = 26.5 \Omega$ ) but a higher ohmic resistance ( $R_s = 12.5 \Omega$ ) than rGO ( $R_s = 5.7 \Omega$ ). The smallest charge transfer resistance ( $R_{ct1} = 3.8 \Omega$ ,  $R_{ct2} = 8.1 \Omega$ ) and ohmic resistance ( $R_s = 2.0 \Omega$ ) of S-TaO<sub>3</sub>/rGO validate the highest electrical conductivity and fastest reaction kinetics,

which may be ascribed to the molecular-level face-to-face contact between the TaO<sub>3</sub> nanomesh and rGO as well as the abundant exposed active sites.



**Fig. 5.** a) Schematic illustration showing the fabrication of self-supported electrodes based on powder-like materials. b) Schematic explanation for the effects of the pairwise or sandwich structure of TaO<sub>3</sub>/rGO on improved sulfur utilization when used in Li-S batteries. c) CV curves at a scan rate of 1 mV s<sup>-1</sup> of the Li<sub>2</sub>S<sub>6</sub> symmetric battery. d) Current vs. time curves of a potentiostatic process at 2.05 V (vs. Li<sup>+</sup>/Li) of the Li<sub>2</sub>S<sub>8</sub> battery assembled with self-supported electrodes of rGO, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO. e) CV curves at 0.1 mV s<sup>-1</sup> and f) EIS curves of Li-S batteries assembled with self-supported sulfur-loaded cathodes of rGO, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO (sulfur loading: 5 mg cm<sup>-2</sup>).

The catalytic activity of rGO, R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO to the Li<sub>2</sub>S nucleation process was studied by the potentiostatic amperometry on Li<sub>2</sub>S<sub>8</sub> batteries (Fig. 5d). There are three regions in the curves of R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO and two regions for rGO. The first region, where the reduction current quickly decreased over time, corresponds to a liquid-liquid conversion process of soluble long-chain lithium polysulfides to short-chain ones. The second region where a peak appeared, specifically for R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO, is due to a liquid-solid nucleation process to generate solid Li<sub>2</sub>S<sub>2</sub> or Li<sub>2</sub>S.<sup>66</sup> The rise of the current for S-TaO<sub>3</sub>/rGO started earlier than that for R-TaO<sub>3</sub>/rGO, suggesting faster Li<sub>2</sub>S deposition. Because the peak area is related to the amount of deposited Li<sub>2</sub>S, the deposition capacity of S-TaO<sub>3</sub>/rGO is much larger than that of R-TaO<sub>3</sub>/rGO. The third region where the current decreased and leveled off corresponds to the conversion of soluble lithium polysulfides for diffusion control. These current vs. time curves were fitted based on the mechanism and kinetics of Li<sub>2</sub>S deposition on these samples (Fig. S19-S21). Based on the fitting results, the electrodeposition capacities of Li<sub>2</sub>S of the R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO were 64 mAh g<sup>-1</sup> and 184 mAh g<sup>-1</sup>, respectively. The final products were characterized by Raman spectroscopy. The band at 373 cm<sup>-1</sup> observed for R-TaO<sub>3</sub>/rGO and S-TaO<sub>3</sub>/rGO is diagnostic of Li<sub>2</sub>S, verifying its nucleation on these materials (Fig. S22). The absence of such a Raman band for rGO, as well as a peak in the time dependence of the current, indicates that a higher

overpotential is needed to drive the nucleation of  $\text{Li}_2\text{S}$ . These results indicate that  $\text{TaO}_3$  nanomesh can efficiently promote the electrochemical deposition of  $\text{Li}_2\text{S}$ , reducing the overpotential for its nucleation. The electrochemical resistance of the samples after the potentiostatic process was monitored by EIS (Fig. S23), and an increase in the electrode resistance is expected due to the poor electrical conductivity of  $\text{Li}_2\text{S}$ . The large difference in the EIS curves between rGO (two compressed semicircles) and R- $\text{TaO}_3/\text{rGO}$  and S- $\text{TaO}_3/\text{rGO}$  (one compressed semicircle) may be mainly caused by the different overpotential for  $\text{Li}_2\text{S}$  nucleation.  $\text{Li}_2\text{S}$  nucleation reaction is the main process on R- $\text{TaO}_3/\text{rGO}$  and S- $\text{TaO}_3/\text{rGO}$  in the  $\text{Li}_2\text{S}_8$  electrolyte with tetraglyme. Because of the high overpotential for  $\text{Li}_2\text{S}$  nucleation, only lithium polysulfides conversion reaction still occurs on rGO, which is verified by the similar EIS curves of rGO in  $\text{Li}_2\text{S}_6$  electrolyte with DOL/DME and  $\text{Li}_2\text{S}_8$  electrolyte with tetraglyme. S- $\text{TaO}_3/\text{rGO}$  maintained the smallest ohmic resistance ( $R_s = 5.7 \Omega$  vs.  $7.9 \Omega$  for R- $\text{TaO}_3/\text{rGO}$ ,  $9.5 \Omega$  for rGO) even after the deposition of the largest amount of  $\text{Li}_2\text{S}$ . This superior performance may be due to the uniform distribution of  $\text{Li}_2\text{S}$  and intimate contact between  $\text{Li}_2\text{S}$  and S- $\text{TaO}_3/\text{rGO}$ .

The effect of the pairwise or sandwich-like structure on the affinity to lithium polysulfides was studied by using  $\text{Li}_2\text{S}_6$  as a representative example. Although a light-yellow colour of the  $\text{Li}_2\text{S}_6$  solution was remained when in contact with R- $\text{TaO}_3/\text{rGO}$ , the solution became colourless with S- $\text{TaO}_3/\text{rGO}$ , demonstrating the excellent affinity and adsorption by S- $\text{TaO}_3/\text{rGO}$  (Fig. S24). The high adsorption capacity benefits from the pairwise or sandwich structure to maximize the exposed adsorption sites of the polar Ta-O bonds, which have excellent affinity for lithium polysulfides. Accordingly, it is expected that S- $\text{TaO}_3/\text{rGO}$  blocks lithium polysulfides within the electrodes to reduce the crossover of lithium polysulfides and effectively overcome the "shuttle effect". All these results indicate that S- $\text{TaO}_3/\text{rGO}$  demonstrates desirable confinement of lithium polysulfides, high catalytic activity for lithium polysulfides and effective nucleation of  $\text{Li}_2\text{S}$ , all of which will yield high electrochemical performance and largely enhanced sulfur utilization (Fig. 5b).

Self-supported sulfur-loaded cathodes based on rGO, R- $\text{TaO}_3/\text{rGO}$  and S- $\text{TaO}_3/\text{rGO}$  were fabricated by impregnation method, wherein the pelletized self-supported electrode was immersed into the solution of sulfur in  $\text{CS}_2$ , to explore their application in Li-S batteries. Different from conventional film cathodes, these self-supported sulfur-loaded cathodes do not contain binders or current collectors, thereby increasing active materials content and sulfur loading (Fig. S25). This will eventually lead to Li-S batteries with a high areal capacity and energy density. The weight content of sulfur in these cathodes was controlled at around 50%. Their electrochemical performance was first examined by CV. The rGO cathode showed two reduction peaks at 2.17 V and 1.81 V and one broad oxidation peak at  $\sim 2.6$  V (Fig. 5e). The R- $\text{TaO}_3/\text{rGO}$  cathode showed two reduction peaks similar to those of rGO and two oxidation peaks at 2.39 V and 2.56 V. These two obvious oxidation peaks had a higher current than rGO, suggesting that R- $\text{TaO}_3/\text{rGO}$  has higher electrochemical activity than rGO, which may result from the higher catalytic activity of  $\text{TaO}_3$ . The S- $\text{TaO}_3/\text{rGO}$  cathode displayed two pairs of redox peaks, wherein the reduction peaks at 2.26 V and 1.87 V are ascribed to the conversion of sulfur to lithium polysulfides with

long chains, then to those with short chains, and eventually to  $\text{Li}_2\text{S}$ . The reverse reaction took place during the reversed potential scan. The S- $\text{TaO}_3/\text{rGO}$  cathode exhibited a much higher peak current and smaller separation of the peak potentials than R- $\text{TaO}_3/\text{rGO}$ , demonstrating its superior activity and reversibility.

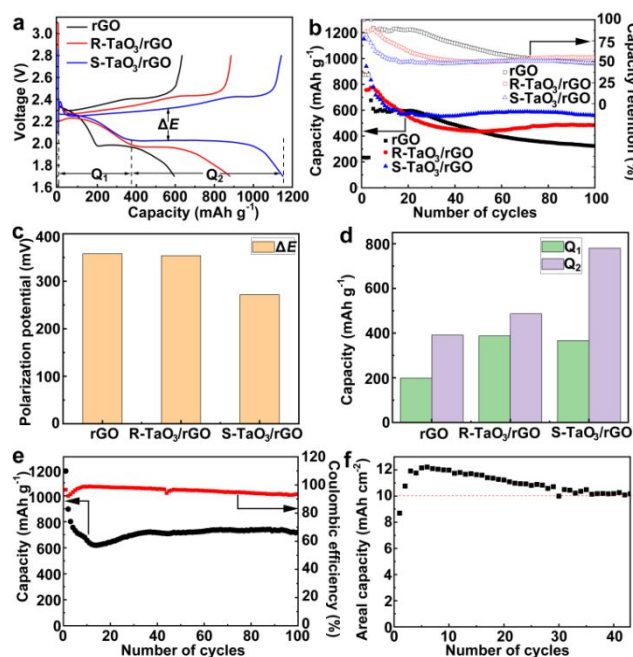
A fast mass transfer of  $\text{Li}^+$  will enhance the rate performance of Li-S batteries to achieve fast charge/discharge process, which is especially crucial for cathodes with high sulfur loading. Thus, the  $\text{Li}^+$  transfer capacity in these cathodes was evaluated by CV at different scan rates (Fig. S26, S28 and S30). All samples showed an approximately linear relationship between the peak current ( $I_p$ ) and the square root of the scan rate ( $v^{1/2}$ ), indicating a diffusion-controlled process (Fig. S27, S29 and S31). Namely, the diffusion coefficient of  $\text{Li}^+$  is proportional to the slope of the  $I_p$  vs.  $v^{1/2}$  curve, indicating the mass transfer capacity. The S- $\text{TaO}_3/\text{rGO}$  cathode showed the largest slope among the examined samples, indicating the highest mass transfer rate. Together with DFT calculation on  $\text{Li}^+$  penetration, these results validate the efficiency of the intrinsic crystalline in-plane pores in the  $\text{TaO}_3$  nanomesh as the channels for generating a 3D transfer mode and decreasing the  $\text{Li}^+$  diffusion distance, leading to a superior rate performance.

A polysulfide permeability test was also performed to evaluate the size-sieving capability of the  $\text{TaO}_3$  nanomesh overcoming the "shuttle effect". The original colourless solvent in the right tube turned light yellow after 0.5 h (Fig. S32b), indicating the crossover of polysulfides through the Celgard separator. The colour became darker and darker over time, as a result of an increasingly more serious crossover of polysulfides (Fig. S32a-d). In contrast, polysulfide crossover was substantially suppressed by modifying the Celgard separator with  $\text{TaO}_3$  nanomesh, indicating that the  $\text{TaO}_3$  nanomesh can efficiently confine polysulfides (Fig. S32e-h). This result agrees well with the geometrical considerations based on the crystallographic data that the polysulfides are too large to pass through the channels of  $\text{TaO}_3$  nanomesh. These results reveal that S- $\text{TaO}_3/\text{rGO}$  exerts superior performance, allowing the penetration of  $\text{Li}^+$  while blocking polysulfides. Recently, similar behaviour has been reported in  $\text{Ti}_{0.87}\text{O}_2$  nanosheets.<sup>67</sup> The larger number of the open channels in the  $\text{TaO}_3$  nanomesh can provide a more efficient penetration path for  $\text{Li}^+$  compared with  $\text{Ti}_{0.87}\text{O}_2$ , where Ti site vacancies work as a migration route.

The electrochemical resistance of these cathodes was estimated by EIS. All samples showed a similar response profile: a semicircle in the high-frequency region corresponding to the charge transfer resistance and a linear segment in the low-frequency region (Fig. 5f). The S- $\text{TaO}_3/\text{rGO}$  cathode showed the smallest charge transfer resistance ( $R_{ct} = 119.5 \Omega$  vs.  $159.7 \Omega$  for R- $\text{TaO}_3/\text{rGO}$  and  $188.3 \Omega$  for rGO), indicating the highest catalytic activity. These results demonstrate the excellent electrochemical performance of S- $\text{TaO}_3/\text{rGO}$ , verifying the advantages of the pairwise/sandwich structure and promoting its application in Li-S batteries.

Charge/discharge tests were performed with Li-S batteries assembled with the self-supported cathodes with a high sulfur loading to demonstrate their practical application. Compared with sulfur-loaded host cathodes (Fig. 6a and 6b), unloaded host electrodes contributed a negligible capacity to Li-S batteries (Fig. S33), identifying that sulfur is the active material. Upon charging/discharging at  $2 \text{ mA cm}^{-2}$  with a sulfur

loading of 5 mg cm<sup>-2</sup>, the S-TaO<sub>3</sub>/rGO cathode delivered a discharge capacity of 1139 mAh g<sup>-1</sup>, while the rGO cathode and R-TaO<sub>3</sub>/rGO cathode displayed capacities of 584 mAh g<sup>-1</sup> and 871 mAh g<sup>-1</sup>, respectively (Fig. 6a). All cathodes showed two couples of charge/discharge plateaus; the charge/discharge plateaus at the higher potential may correspond to the conversion between sulfur and long-chain lithium polysulfides, while those at the lower potential correspond to the conversion between long-chain lithium polysulfides and short-chain ones all the way to Li<sub>2</sub>S. The corresponding capacities of these two processes in the discharging process are marked as Q<sub>1</sub> and Q<sub>2</sub> (Fig. 6a). The potential difference ( $\Delta E$ ) between the charge and discharge plateaus indicates the battery polarization. A large battery polarization will reduce the sulfur utilization. The S-TaO<sub>3</sub>/rGO cathode showed a reduced polarization potential (Fig. 6c), contributing to a high battery capacity. The shorter plateau at higher potential compared with that at lower potential in the discharging process indicates Q<sub>1</sub> < Q<sub>2</sub>, suggesting a smaller capacity contribution of the conversion process from sulfur to long-chain lithium polysulfides (Fig. 6d). The S-TaO<sub>3</sub>/rGO cathode showed a much larger Q<sub>2</sub> and a slightly larger or even similar Q<sub>1</sub> than that of rGO and R-TaO<sub>3</sub>/rGO, indicating the efficient conversion from long-chain lithium polysulfides to short-chain ones and eventually to nucleated Li<sub>2</sub>S.



**Fig. 6.** a) Galvanostatic charge/discharge curves at 2 mA cm<sup>-2</sup> and b) cycle performance of Li-S batteries assembled with self-supported cathodes with sulfur-loading of 5 mg cm<sup>-2</sup>. c) Potential difference  $\Delta E$  and d) capacities Q<sub>1</sub> and Q<sub>2</sub> observed in (a). Cycle performance of Li-S batteries assembled with self-supported S-TaO<sub>3</sub>/rGO cathodes with sulfur loading of e) 10 mg cm<sup>-2</sup> and f) 15 mg cm<sup>-2</sup> upon charging/discharging at e) 1 mA cm<sup>-2</sup> and f) 2 mA cm<sup>-2</sup>.

The stability of these cathodes was examined by repeating the charge/discharge cycle. As shown in Fig. 6b, the higher initial discharge capacity of S-TaO<sub>3</sub>/rGO than R-TaO<sub>3</sub>/rGO and rGO means the higher sulfur utilization in S-TaO<sub>3</sub>/rGO. The huge quantity of underutilized sulfur in R-TaO<sub>3</sub>/rGO and rGO offset their capacity decrease, resulting in a comparable discharge capacity of R-TaO<sub>3</sub>/rGO to S-TaO<sub>3</sub>/rGO between cycles 10-20

and an even higher discharge capacity of rGO than R-TaO<sub>3</sub>/rGO between cycles 20-50. Nevertheless, the discharge capacity of the S-TaO<sub>3</sub>/rGO cell gradually decreased from 1139 mAh g<sup>-1</sup> to 559 mAh g<sup>-1</sup> in the first ~10 cycles, and then the capacity was well maintained over 100 cycles. The cells based on R-TaO<sub>3</sub>/rGO and rGO also showed the decreasing discharge capacities in 100 cycles from 879 mAh g<sup>-1</sup> to 484 mAh g<sup>-1</sup> and from 593 mAh g<sup>-1</sup> to 326 mAh g<sup>-1</sup>, respectively. All the samples obtained the similar capacity retention around 50% after 100 cycles. The observed capacity decrease in the first 10 cycles may be because the lithium polysulfides formed during the charge/discharge cycle were gradually escaped from the cathodes. However, the largest capacity was preserved owing to the effective confinement of polysulfides as well as high catalytic activity for Li<sub>2</sub>S deposition in the S-TaO<sub>3</sub>/rGO. The S-TaO<sub>3</sub>/rGO cathodes with higher sulfur loading were further explored to develop their practical application. With a sulfur-loading of 10 mg cm<sup>-2</sup>, S-TaO<sub>3</sub>/rGO cathode delivered an initial discharge capacity of 1190 mAh g<sup>-1</sup> at 1 mA cm<sup>-2</sup>, which decreased to 741 mAh g<sup>-1</sup> after 100 cycles (Fig. 6e). With a sulfur loading of 15 mg cm<sup>-2</sup>, a lower capacity was observed in the initial several cycles, which may be attributed to the poor distribution of sulfur due to high sulfur-loading as well as thick cathode. It recovered soon after improvement by an activation process (Fig. 6f). A high areal capacity of 12.2 mAh cm<sup>-2</sup> was attained at 2 mA cm<sup>-2</sup>, and 10.5 mAh cm<sup>-2</sup> and above was retained after 40 cycles, corresponding to a capacity of 674 mAh g<sup>-1</sup>. Compared with the reported results, the areal capacity and sulfur loading are significantly enhanced by S-TaO<sub>3</sub>/rGO in this study (Fig. S34). These results demonstrate that S-TaO<sub>3</sub>/rGO achieves a high capacity with a high sulfur loading, significantly improving the sulfur utilization and leading to a high practical energy density.

## Conclusions

We reported a strategy to develop high-performance Li-S batteries using a unique 2D material with open channels. TaO<sub>3</sub> nanomesh was self-assembled with rGO into the pairwise/sandwich-like assembly, which was pelletized into self-supported electrodes with high sulfur loading. The pairwise or sandwich-like composite of S-TaO<sub>3</sub>/rGO not only efficiently catalyzed the conversion to lithium polysulfides and Li<sub>2</sub>S nucleation, but also promoted Li<sup>+</sup> transfer and polysulfides confinement. These multifunctionalities were realized by maximizing the synergistic effects derived from the TaO<sub>3</sub> nanomesh with its polar Ta-O bonds, Lewis acid surfaces and intrinsic in-plane pores with size between Li<sup>+</sup> and polysulfides, and rGO with high electrical conductivity. Owing to the sticking property of the composite featuring a 2D morphology, a self-supported cathode with high sulfur loading could be easily fabricated at room temperature by the pelletizing-impregnation method to enhance the practical energy density of Li-S batteries. As a result, a Li-S battery employing the designed self-supported S-TaO<sub>3</sub>/rGO cathode achieved an areal capacity as high as 10.5 mAh cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> after 40 cycles. This work has verified a new process to develop self-supported cathodes with a high sulfur loading, accelerating the application and commercialization of Li-S batteries.



Furthermore, this approach can be applied to other energy storage systems, such as Li-ion and Mg-ion batteries.

### Author Contributions

**Chenhui Wang:** Methodology, Validation, Investigation, Writing - Original Draft, Visualization. **Nobuyuki Sakai:** Writing - Review & Editing. **Yasuo Ebina:** Investigation. **Takayuki Kikuchi:** Investigation. **Shigeru Suehara:** Validation. **Daiming Tang:** Investigation. **Renzhi Ma:** Writing - Review & Editing. **Takayoshi Sasaki:** Conceptualization, Supervision, Writing - Review & Editing.

### Conflicts of interest

There are no conflicts to declare.

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