

Surface and defect engineered polar titanium dioxide nanotubes as an effective polysulfide host for high-performance Li-S batteries

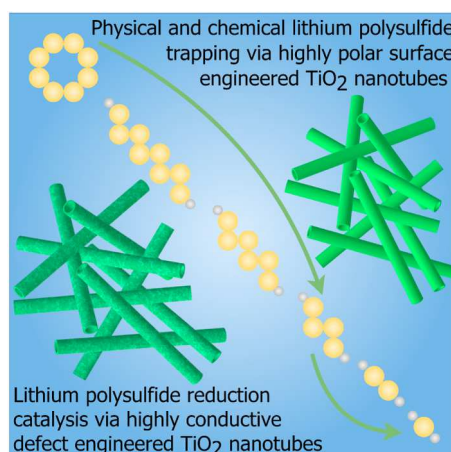
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HIGHLIGHTS

- Surface and defect engineered TiO_2 nanotubes provide a high surface area polar host material for mitigating lithium polysulfide shuttling.
- Combination of physical confinement and chemical binding adsorption.
- Robust 3D hierarchical structure for mitigating the shuttle effect of lithium polysulfide.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the surface structure of as received and ball milled (BM) titanium dioxide (TiO_2) was modified via a simple hydrothermal method to create nanotubes (TiO_2 NTs and TiO_2 BM NTs) and subsequently chemically reduced to introduce widespread oxygen vacancy defects (TiO_{2-x} NTs and TiO_{2-x} BM NTs). The high surface area, innate polar nature, and high conductivity of TiO_2 NTs allow the host material to effectively trap the lithium polysulfides both physically and chemically and improve the redox kinetics of lithium polysulfides. Chemical reduction acts to further improve the performance of the NTs by increasing the amount of polysulfides that can be adsorbed and by further increasing the conductivity of the material. Galvanostatic charge-discharge cycling testing revealed good performance for all four of the tested cathode hosts, with the best performance being achieved by TiO_2 BM NTs and TiO_{2-x} NTs, with the former delivering an initial discharge capacity of $1204.72 \text{ mAh g}^{-1}$ at 0.1 C and $767.69 \text{ mAh g}^{-1}$ at 3 C and the latter delivering an initial discharge capacity of $1005.24 \text{ mAh g}^{-1}$ at 0.1 C , 353.7 mAh g^{-1} at 3 C , and a decay rate of -0.68% per cycle over the first 300 cycles at 3 C .

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1. Introduction

In order to address the ever-growing demand for clean and sustainable energy facing our world, novel energy storage devices and/or systems that have a low environmental impact at all stages of production and use, low cost, high cycle life, and that boast higher energy densities than existing solutions are necessary. Such energy storage devices and/or systems would allow the development of longer-range electric vehicles and higher capacity batteries for mobile devices by virtue of their higher energy density and would lower the cost of high-volume energy storage for stabilizing output from renewable sources (i.e., solar or wind energy, etc.) by virtue of its lower cost and higher cycle life [1]. A prime candidate for this unfilled need is the lithium-sulfur (Li-S) battery, as it addresses all of these identified needs well. Li-S batteries boast a theoretical specific capacity of $1,675 \text{ mAh g}^{-1}$ and a theoretical energy density of $2,600 \text{ Wh kg}^{-1}$ [2–4], as compared to the theoretical specific capacity of 272 mAh g^{-1} of current lithium-ion batteries [5], about six times greater. Additionally, the sulfur cathode has several promising attributes. The average price per metric ton of sulfur in 2022 stood at 150 USD, as compared to the 68,000 USD and 25,000 USD per metric ton of cobalt and nickel respectively [6]. Sulfur is also naturally abundant and boasts superior environmental compatibility [7,8].

The commercialization and further development of Li-S batteries are currently limited by several major issues, those being 1) the large change in volume of sulfur during its reduction, 2) the insulating nature and poor ionic conductivity of sulfur and lithium polysulfides ($10^{-13} \text{ S cm}^{-1}$ for Li_2S), and 3) particularly the lithium polysulfide diffusion known as polysulfide shuttling effect (PSE), leading to low sulfur utilization and rapid capacity decay [9–11]. To overcome the technical obstructions mentioned above and promote the commercialization of Li-S batteries, various sulfur host or additive materials have been developed aiming to effectively encapsulate sulfur species and alleviate the severe shuttling issue of polysulfides. Carbon materials serving as efficient sulfur host materials have been extensively investigated due to their intrinsic high conductivity, cost-effectiveness, and outstanding structural tunability (1D, 2D, and 3D structures) [12]. However, only limited obstruction of polysulfide migration can be fulfilled by carbon host materials due to weak chemical affinity capability towards polysulfides, resulting in poor sulfur utilization, undesirable rate capability, and rapid capacity attenuation in long cycling battery tests [13].

Compared with the weak physical interaction of carbon-based sulfur host materials, metal-based polar compound materials can demonstrate strong chemical adsorption and immobilize polysulfides [14]. Metal sulfides, metal carbides, metal nitrides, and metal oxides have all been identified as viable polar host materials for Li-S batteries. Metal sulfides offer a polar interaction with lithium polysulfides, have demonstrated high catalytic abilities for lithium polysulfide reduction, and boast a high electrical conductivity compared to other metal-based compound hosts. Metal carbides demonstrate electrocatalytic abilities due to their high conductivity and transition metal carbides have been shown to demonstrate polar interactions with lithium polysulfides. Metal nitrides offer polar host interactions, high conductivity, and boast a stable structure. Metal oxides offer a strong polar interaction with lithium polysulfides due to the presence of oxygen anions in addition to metal cations, resulting in a large amount of active polar sites for adsorption [15].

Titanium dioxide (TiO_2) has been used as polar host material due to its strong polysulfide adsorption capability, desirable polar surface along the (0 1 1) plane of rutile phase TiO_2 , and chemical/electrochemical stability [16]. TiO_2 exhibits this high capacity to adsorb lithium polysulfides due to a strong chemical interaction between Ti^{4+} and lithium polysulfides and also has shown the ability to catalyze the lithium polysulfide reduction reaction [17]. Recently, numerous reports on various high surface area nanostructures of TiO_2 , such as nanoparticles [16], nanowires [18], nanosheets [19], and nanofibers [20], have demonstrated that the soluble intermediate polysulfides can be

trapped successfully to alleviate the huge loss of active material sulfur induced by PSE. The properties which make TiO_2 a suitable cathode host material for Li-S batteries can be further improved through its reduction via thermal or chemical processes to TiO_{2-x} . Reduced TiO_2 (TiO_{2-x}) boasts a higher electrical conductivity and a higher polysulfide adsorption capacity than pristine TiO_2 owing to the higher concentration of surface oxygen vacancies which act as adsorption sites. The presence of a large number of oxygen vacancies in the TiO_{2-x} material also causes it to demonstrate catalytic properties due to the presence of titanium ions with lower oxidation states such as Ti^{3+} which further increase electron mobility and serve to lower the activation energy needed to initiate the lithium polysulfide reduction reaction [21,22].

Many different nanostructures and forms of TiO_2 have already been investigated and have shown promising results. For example, Huang et al. [23] reported that hierarchically porous titanium dioxide showed excellent performance as both a polar host and as a physical immobilizer for lithium polysulfides. Nanoscopic pores in the host material demonstrated a superior ability to physically confine lithium polysulfides, and the very high surface area of $235.6 \text{ m}^2 \text{ g}^{-1}$ greatly increased the area on which polar interactions can occur. This strategy produced excellent results, able to provide a specific capacity of 786 mAh g^{-1} after 500 cycles at a charging rate of 2 C, and a maximum initial specific capacity of 1186 mAh g^{-1} at 0.1 C. Cai et al. [24] reported that TiO_2 nanowire clots have also been employed as a sulfur host material due to their very high surface area to volume ratio of $270.1 \text{ m}^2 \text{ g}^{-1}$. The high surface area of the polar host material provides more possible locations or adsorption sites for the lithium polysulfides to form polar bonds with TiO_2 , boasting retention. This method was able to provide a specific capacity of 404.5 mAh g^{-1} after 200 cycles at 2 C and boasted a maximum initial specific capacity of 1163 mAh g^{-1} at 0.1 C. Park et al. [25] reported that hollow sulfur-carbon nanospheres with a layer of polar TiO_2 were used to physically and chemically confine lithium polysulfides via polar bonds and complicated geometry. This method provided a specific capacity of 630 mAh g^{-1} after 500 cycles at 1 C and a maximum initial specific capacity of 1239 mAh g^{-1} at 0.1 C. Liu et al. [26] reported that hierarchically porous TiO_{2-x} /carbon hybrid nanofibers enabled the creation of Li-S cells with high sulfur loading and utilization that demonstrated excellent rate performance and high cycling stability. The combination of the high surface area of the polar host material and the catalytic properties of the Ti^{3+} ions present from the oxygen deficiency enabled impressive cell performance, with cells using the material demonstrating an initial specific capacity of 1360 mAh g^{-1} at a rate of 0.5 C, with a specific capacity 780 mAh g^{-1} maintained after 500 cycles.

According to the previously published work, TiO_2 nanotubes (NTs) have a specific surface area of $233.8 \text{ m}^2 \text{ g}^{-1}$ [27] and an electronic conductivity of $1 \times 10^{-7} \text{ S cm}^{-1}$ [28]. They are generally prepared via complicated procedures with multiple variables such as the anodization and electrodeposition method [29], the dealloying method [30], or the template method [31,32]. These procedures greatly increase the cost of production and hinder the large-scale commercialization of the final material. It is well acknowledged that the simple and cost-effective hydrothermal method is of great promise for the preparation of TiO_2 NTs.

The hydrothermal technique is one of the most frequently used methods for the synthesis of various well-dispersed and “homogeneous” nanomaterials. All the reactants are dissolved in an autoclave with a suitable solvent under high pressure and low-temperature ($<250^\circ \text{C}$) conditions depending on the desired composition, crystal structure, size, and shape of the nanomaterials. The main advantage of hydrothermal technique is that the hydrothermal method can produce nanomaterials with high vapor pressures and controllable exposed crystal facets (i.e., different morphologies). In addition, via liquid phase or multiphase chemical reactions, the compositions of nanomaterials to be synthesized can be precisely regulated in the hydrothermal system.

In this report, surface and defect engineered TiO_2 NTs are synthesized via a hydrothermal template method from two different precursor materials and subsequently chemically etched to introduce oxygen

vacancies. These four cathode host materials, TiO₂ NTs, TiO₂ ball mill (BM) NTs, TiO_{2-x} NTs, and TiO_{2-x} BM NTs respectively, were analyzed to determine the impact of initial particle size on the growth and mechanical robustness of NTs, and to determine the effects of surface and morphology engineering on the performance of TiO₂ NTs based materials as cathode hosts for Li-S batteries. Each sample is also chemically etched to determine the impact of widespread oxygen vacancies (defect engineering) on the conductivity of the material and cell performance.

2. Experimental section

2.1. Preparation of TiO₂ nanotubes

TiO₂ NTs were created through a modified one-step hydrothermal template synthesis method using rutile TiO₂ powder [33]. A titanium dioxide/sodium hydroxide solution was created by adding 2 g rutile TiO₂ powder (predominantly rutile titanium (IV) oxide, 99.999%, Acros Organics) to 80 mL 10 M NaOH (prepared from ACS sodium hydroxide pellets). This solution was then stirred vigorously for 24 h to ensure total dissolution of the TiO₂. This solution was then added to a 200 mL Teflon autoclave and sealed. Hydrothermal synthesis was performed in a programmable box furnace at 150 °C with a hold time of 72 h. After the furnace was allowed to cool to ambient temperature, the autoclave was removed and unsealed. The contents of the autoclave were poured into a vacuum filtration system, with the deposited TiO₂ NT being scraped out of the autoclave and put in the filter. The nanotubes were then washed with 40 mL 0.1 M HCl to neutralize and eliminate the remaining sodium ions and 500 mL deionized water to dissolve ions left on the TiO₂ NTs. Once filtration was complete, the filter paper was removed from the vacuum filtration system and put in a vacuum oven where it was dried for 24 h at 80 °C. This process was performed twice, once using the rutile TiO₂ powder as it was received to create TiO₂ NTs, and once using rutile TiO₂ powder that had been ball milled (TiO₂ BM) to reduce the particle size to create TiO₂ BM NTs. The latter sample was prepared to assess the impact of initial particle size on the morphology of NTs synthesized via the template method.

2.2. Preparation of TiO_{2-x} nanotubes

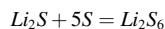
TiO_{2-x} NTs were prepared via a simple chemical etching procedure [3,34]. TiO₂ NT powder was dispersed in DI water via magnetic stirring in a 250 mL beaker to create a suspension. 10 wt percent (10 wt%) NaBH₄ (relative to the weight of TiO₂ NTs) was then added to the suspension. This mixture was then vigorously stirred for 12 h via a magnetic stirrer. The sample was then filtered and dried in a vacuum furnace for 12 h to obtain TiO_{2-x} NTs. This exact procedure was performed using TiO₂ BM NT to create TiO_{2-x} BM NT for analysis and comparison.

2.3. Preparation of electrolyte solution and Li₂S₆ catholyte solution

The electrolyte solution was prepared by combining dioxolane and dimethoxyethane (DOL: DME) (Alfa Aesar, 99%) in a 1:1 volume ratio, and adding lithium bis(trifluoromethane) sulfonimide (LiTFSI) (Adipogen Life Sciences, 99%) and LiNO₃ (Alfa Aesar, 99.999%) to create a solution containing 1 M LiTFSI and 0.5 M LiNO₃. In this solution the DOL:DME acts as a solvent for lithium ions and lithium polysulfides and the LiTFSI and LiNO₃ act as initial sources of lithium ions. Specifically, 2 mL DOL and 2 mL DME were combined with 1.15 g LiTFSI and 0.15 g LiNO₃. The solution was then stirred vigorously for 24 h in a sealed container. The resulting solution was clear and had no apparent sedimentation.

The Li₂S₆ catholyte solution was prepared by combining the prepared electrolyte solution with Li₂S (Alfa Aesar, 99.9%) and sublimed elemental sulfur powder (Alfa Aesar, 99.5%) to create a 1.0 M Li₂S₆ solution. Liquid Li₂S₆ is used as the cathodic material in the cell in place of solid sulfur because its liquid phase allows it to be adsorbed and fully

permeate the host material instead of staying on its surface. This helps to stabilize the cell by preventing quick diffusion from the cathode surface to the anode surface. Specifically, 2 mL of the prepared electrolyte solution was combined with 92 mg Li₂S (0.002 mol) and 320 mg sulfur powder (0.01 mol). The solution was then stirred vigorously at 60 °C for 24 h in a sealed container to facilitate the formation of Li₂S₆ via the reaction:



The resulting solution was a deep reddish brown and had no apparent sedimentation.

2.4. Polysulfide adsorption test

A polysulfide adsorption test was performed on the TiO₂-derived cathode host materials to validate their potential to adsorb liquid lithium polysulfides from the solution. A 0.0033 M Li₂S₆ (0.02 M S) solution was created by combining 4 mL of the prepared electrolyte solution with 13.36 µL of the prepared catholyte solution. The polysulfide test solution was a dark yellow color, with no apparent sedimentation. For the control, 10 mg of very finely cut carbon cloth (Fuel cell earth, thickness = 0.381 mm, density = 1.75 g/cm³) was added to one vial and pushed to the bottom of the vial to ensure the entire sample was submerged and sealed. 10 mg of each host powder was then added to the other vials. 320 µL of the 0.0033 M Li₂S₆ solution was quickly added to each vial and each vial was sealed. An additional vial that had been left free of host powder was also filled with the test solution to act as a color reference. Images were recorded every 10 min until the test solutions were clear.

2.5. The TiO₂ on carbon cloth electrode preparation

The TiO₂ on carbon cloth electrodes were prepared by applying a slurry of each TiO₂ derived host material to 15 mm discs which had been cut from carbon cloth (Fuel cell earth, thickness = 0.381 mm, density = 1.75 g/cm³) using a precision disc cutter. The host slurries were created by combining the host powder, super P carbon black (Alfa Aesar, 99%), and polyvinylidene fluoride (PVDF) at a 6.67:1:1 mass ratio in N-methyl-2-pyrrolidone (NMP) solvent. In this slurry, the TiO₂ derived powder acts as the polar host material and catalyst, the super P carbon black acts to boost electrical conductivity, the PVDF acts as thermosetting polymer binder to anchor the other materials to the carbon cloth, and the NMP is a solvent able to effectively dissolve the powders to form a slurry. Specifically, 50 mg of the cathode host material, 7.5 mg super P carbon black, and 7.5 mg PVDF were combined with 600 µL NMP and stirred for 24 h in a sealed container. Once the slurry had been prepared, it was applied to the carbon cloth disc via a micropipette. Testing found that a deposited mass of between 2.0 and 3.0 mg of TiO₂ NT host material showed ideal results. This was achieved by adding 30 µL of the slurry to the carbon cloth discs. Once the slurry had been applied, the cathode hosts were dried in a vacuum furnace at 60 °C or 24 h. The electrodes were obtained after vacuum drying. This process was repeated with each host material to create TiO₂ NTs@CC, TiO₂ BM NTs@CC, TiO_{2-x} NTs@CC, and TiO_{2-x} BM NTs@CC respectively.

2.6. Cell assembly

CR2032 coin-type cells were prepared in an argon-filled glove box by combining the previously synthesized materials with commercially available stainless steel battery casings, spacers, springs, and separator material. Cells were assembled by placing an electrode into a positive case and centering it. 10 µL of the catholyte solution (corresponding sulfur loading = 1.085 mg/cm²) was then applied to the center of the loaded carbon cloth cathode, followed by 30 µL of the electrolyte solution. A 19 mm disc of separator material, specifically Celgard 2500, was then placed on top of the loaded carbon cloth cathode to electronically

separate the cathode and anode side of the battery. 30 μL of the electrolyte solution was added on top of the separator. A lithium metal anode disc was then placed on top of the separator, flat side down. A stainless-steel spacer and spring were then placed on top of the lithium metal anode, followed by the negative case. The cells were then crimped closed using 100 kg/cm^2 of force via a manual hydraulic press.

2.7. Electrochemical testing

Galvanostatic charge/discharge cycling, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were then performed on completed cells at ambient temperature (at 25 °C). Galvanostatic charge/discharge cycling was performed on an MTI battery tester using a voltage window of 1.7–2.8 V and current densities ranging from 0.1 to 3 C ($1\text{C} = 1675\text{ mAh g}^{-1}$). CV measurements were taken with a Gamry Interface 1000 E Potentiostat/Galvanostat/ZRA instrument using a voltage potential window of 1.7–2.8 V and a scan rate of 0.1 mV/s. EIS measurements were taken using the same instrument, with a frequency window of 0.01–10⁵ Hz.

2.8. Materials characterization

Powder X-ray diffraction (XRD) was performed using a Philips X'Pert MRP equipped with Cu K α source (wavelength $\lambda = 0.154\text{ nm}$) at 45 kV and 40 mA on a finely ground powder sample of the nanotube material to characterize the overall crystal structure of the material and to match and compare it to database values. A scan speed of 0.06°/min was used to collect the XRD results (2θ range = 10–90°). Scanning electron microscopy (SEM) was performed using an Apreo FE-SEM to assess the surface morphology of the nanotubes, and to gain insight on qualities such as porosity and distribution of nanostructures across the particles. Transmission electron microscopy (TEM) was performed using an FEI Tecnai F-20 TEM in order to analyze the interior structure of the nanostructures and validate the TiO₂ NT was hollow. TEM samples were prepared by ultrasonically finely ground TiO₂ NT samples in a small amount of ethanol. After about 15 min of ultrasonication, a white suspension of TiO₂ NT in ethanol was created. A single drop of this suspension was applied to a 400-mesh copper grid with an ultrathin carbon film (Ted Pella Inc.), and the sample was placed in a fume hood to dry until ready for TEM analysis. EDAX was performed using integrated equipment in the Apreo FE-SEM in order to assess material chemistry and the distribution of chemical elements within the structure.

3. Results and discussion

3.1. Characterization before cycling

Fig. 1 shows XRD data recorded for precursors and host materials to assess chemical and structural similarities. Fig. 1 (a and d) show data recorded for as received rutile TiO₂ and ball milled rutile TiO₂. The typical dominant peaks of rutile TiO₂ are located at 27.51°, 36.16°, 41.34°, 54.46°, 56.78° and 69.20°, representing the (1 1 0), (1 0 1), (1 1 1), (2 1 1), (2 2 0), and (3 0 1) planes respectively. This indicates that the ball milling procedure has only impacted the morphology of the precursor material and has not impacted structural or chemical characteristics. Fig. 1 (b) and e show data recorded for nanotubes synthesized via the hydrothermal template method with as received and ball-milled precursors respectively. XRD analysis indicated a mixed phase, comprised of rutile and anatase TiO₂ phases. The most dominant peaks recorded for both samples were located at 27.51°, 36.16°, 54.46°, and 69.20°, representing the (1 1 0), (1 0 1), (2 1 1), and (3 0 1) planes of the rutile phase and at 25.50°, 38.16°, 48.40°, and 63.25°, representing the (1 0 1), (0 0 4), (2 0 0), and (2 0 4) planes of the anatase phase. This mixed phase composition is supported by previous work which synthesized TiO₂ NTs via a hydrothermal method [35,36]. The mixed phase XRD reading stems from the fact that TiO₂ NTs are anatase phases,

grown on the surface of a rutile phase precursor [37]. Fig. 1 (c and f) show data recorded for chemically reduced TiO₂ NTs and TiO₂ BM NTs. The dominant peaks recorded for these samples were the same as those recorded for TiO₂ NTs and TiO₂ BM NTs, however there were several disparities in peak intensity between the two samples. For example, the peak of the (2 1 1) rutile plane is much less intense in Fig. 1 (f) than in Fig. 1 (c). This could be due to the smaller particle size of the BM-derived NT samples producing a more fragile structure. This can be assessed using SEM imaging of each of the samples. The crystalline size estimation by XRD is provided in the supporting information (Table S1).

The difference in morphology between the TiO₂ NTs and TiO₂ BM NTs can quickly be assessed by comparing Fig. 2 (a and c) respectively. The larger initial particle size of the TiO₂ NT sample causes the NTs to form as a sort of “mat” on the surface of the particle, where nanotubes are dispersed in a regular density at irregular orientations. The topography of the TiO₂ NTs is dense and uniform with NTs layered on top of one another, causing a widespread porosity due to the gaps between the layered NTs. The smaller initial particle size of the TiO₂ BM NTs results in a significantly different topography. Rather than growing on the surface of the particles, the NTs grew between the smaller particles, forming a sort of “web” between particles of TiO₂ which links them together and forms larger particles. The pores of the TiO₂ BM NT sample are much larger, as they are gaps between the NT linked BM particles rather than gaps between layered NTs. This results in much deeper porosity, though at a larger scale. Fig. 2 (b and d) correspond with TiO_{2-x} NTs and TiO_{2-x} BM NTs respectively. These images were captured at 35,000x rather than 50,000x due to severe charging issues with the materials making them difficult to image at high magnifications. TiO_{2-x} NTs have a similar appearance to TiO₂ NTs, with a widescale mat of NTs still visible. The NTs in the TiO_{2-x} NTs sample are significantly damaged from the chemical etching process; however, they are widely visible across the surface of the particles. The more fragile NTs of the TiO_{2-x} BM NTs sample cannot be identified in the SEM imaging, and likely have been destroyed by the chemical etching. The NT “web” of the TiO_{2-x} BM NTs has much less support than the NT “mat” of the TiO_{2-x} NTs, resulting in it being a much less robust material. The resulting material is still extremely high surface area due to the deep pores between the small, linked particles.

In order to confirm the presence of hollow nanotubes in the TiO₂ NT sample and to characterize the crystal structure of the material, TEM imaging and analysis were performed (Fig. 3 (a-c)). A regular TEM image (Fig. 3 (a)) was first obtained to demonstrate the interior structure of the nanostructures. As TEM shows the “shadow” of matter, the darker portions can be interpreted to be thicker (mass-thickness contrast mechanism), and thus interpreted as the walls of a hollow structure.

After this had been validated, high-resolution TEM images (Fig. 3 (b-c)) were taken to examine the crystalline planar spacing and an average tube diameter of the TiO₂ NT after grinding and ultrasonication to isolate individual structures. The analysis yields a result of a plane spacing of roughly 0.74 nm along the (2 0 0) plane, consistent with the results from other work which synthesized TiO₂ NTs via similar hydrothermal methods [38]. The TEM images were then analyzed to determine the diameter of the TiO₂ NTs. Analysis from different points on the structure yielded an average of about 11.2 nm, with values being clustered between 12 nm and 10 nm. A length could not be determined for the TiO₂ NTs, as the structures had to be pulverized and ultrasonicated in order to disperse them thinly enough to analyze single structures via TEM.

3.2. Li₂S₆ adsorption test

A polysulfide adsorption test was conducted to assess the chemical affinity capability of the synthesized TiO₂ NT as a host. Two tests were conducted, one analyzing the carbon cloth host material and the other analyzing the TiO₂ NT powder. The carbon cloth test acted as a control, to assess whether the adsorption of the lithium polysulfides was due to

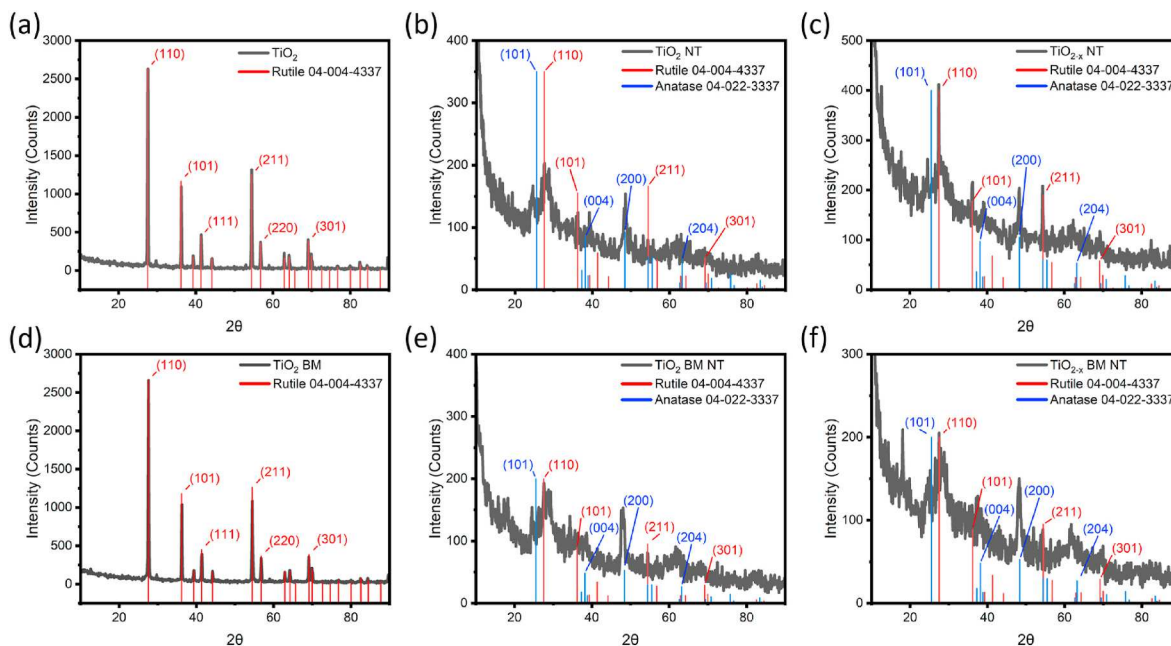


Fig. 1. XRD data obtained from each powder sample. Fig. 1 (a–c) show data for NTs synthesized using as-received TiO_2 powder whereas Fig. 1 (d–f) show data for NTs synthesized using BM TiO_2 . Fig. 1 a and d show XRD peaks for TiO_2 and TiO_2 BM, demonstrating that the low energy ball milling procedure has not changed the structure of the material in any way, only reduced the size of the particles. Fig. 1 b and e show the XRD peaks for TiO_2 NTs and TiO_2 BM NTs. Fig. 1 c and f show the XRD peaks for TiO_{2-x} NTs and TiO_{2-x} BM NTs.

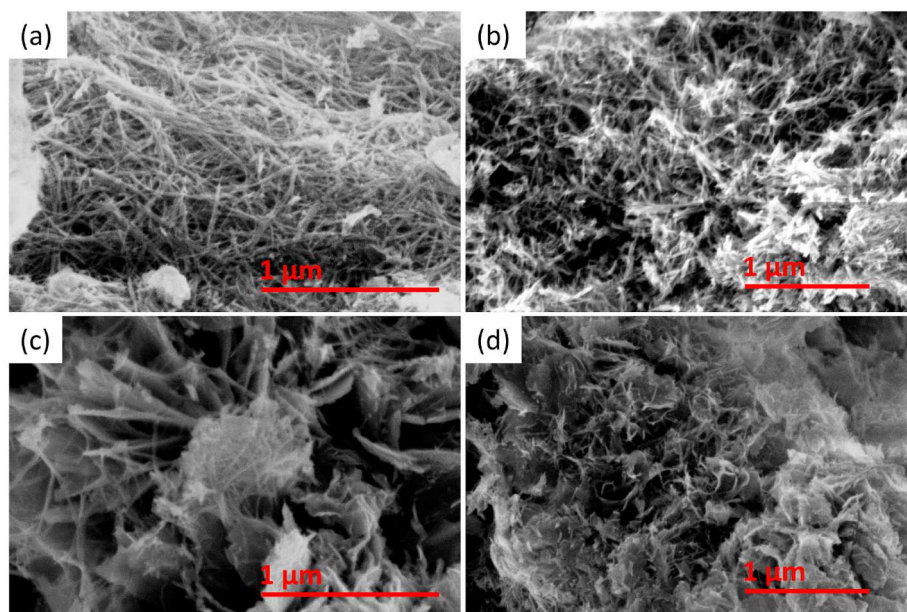


Fig. 2. SEM images of: (a): TiO_2 NTs, (b): TiO_{2-x} NTs, (c): TiO_2 BM NTs and (d): TiO_{2-x} BM NTs. Fig. 2 a and c were captured at 50,000x magnification while Fig. 2 b and d were captured at 35,000x magnification.

the TiO_2 NT or due to the carbon cloth.

The adsorption test (Fig. 4 (a and b)) showed favorable results for the adsorption of liquid Li_2S_6 lithium polysulfide. Li_2S_6 was chosen for the adsorption test as it is the liquid phase lithium polysulfide present in the catholyte solution and one of the species vulnerable to PSE. The 0.0033 M Li_2S_6 solution achieved a high level of adsorption in some samples, indicated by the change in intensity of the yellow coloration experienced over time. Adsorption is measured visually by referencing columns a) and b) of Fig. 4 (a), as these columns show the test solution with no host material and the carbon cloth used as an electrode and support structure

for the polar materials respectively. As evidenced by column b) of Fig. 4 (a), the carbon cloth electrode has no adsorptive capability, owing to the fact that carbon is a non-polar material. As shown in columns c) and d) of Fig. 4 (a), the raw materials, TiO_2 and TiO_2 BM respectively, demonstrate very little capability to adsorb the liquid polysulfides, indicating that any adsorptive capability of the material is due to the presence of nanotubes.

Columns e) and f) of Fig. 4 (a) show adsorption tests for TiO_2 NTs and TiO_2 BM NTs respectively and indicate that TiO_2 NTs demonstrate a superior adsorptive capability than their ball-milled counterparts. This

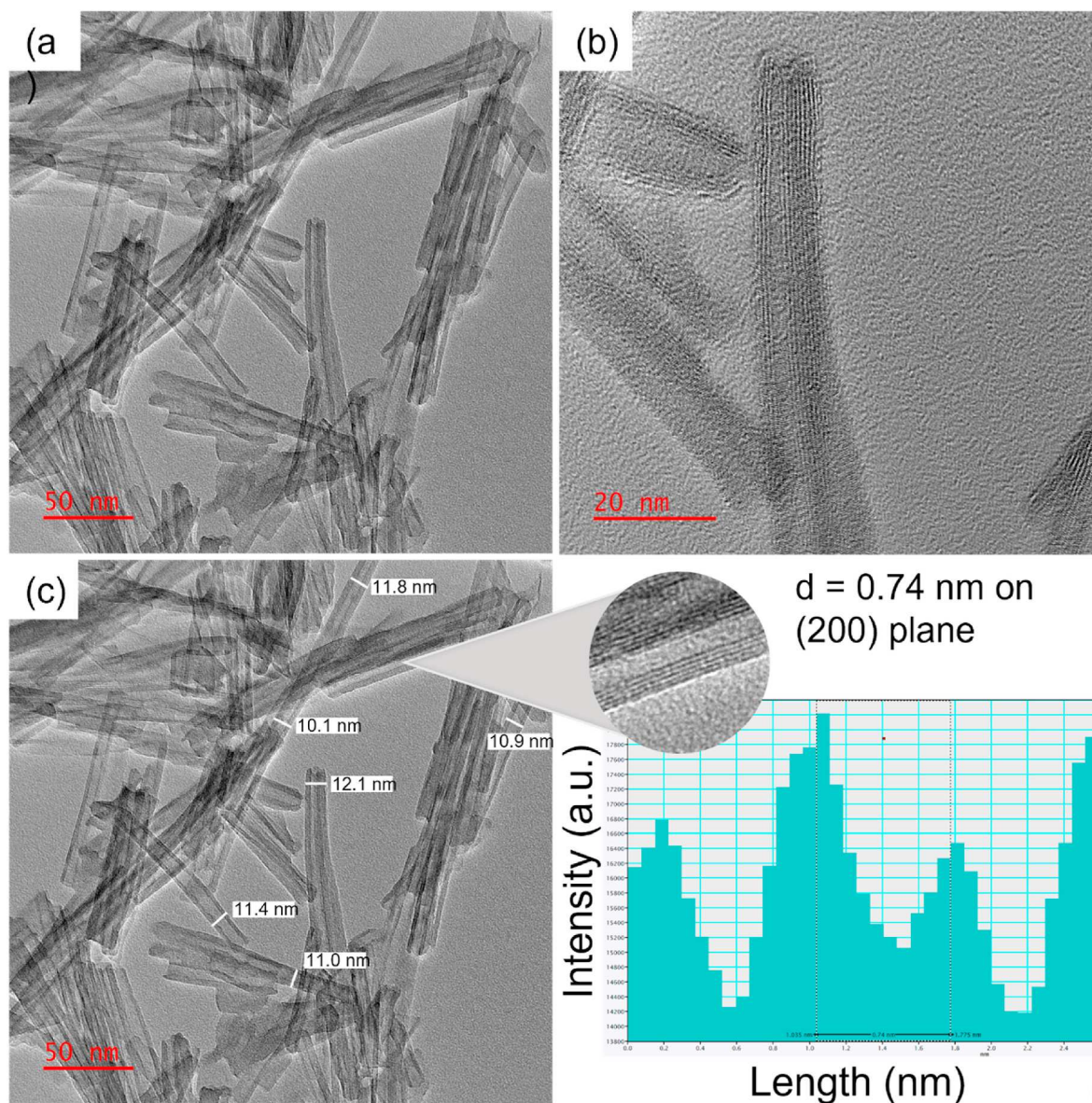


Fig. 3. (a) TEM image of TiO_2 NTs. (b–c) High-resolution TEM images and the analysis of the diameter and the plane spacing of TiO_2 NTs.

is indicated by the fact that the test conducted using TiO_2 NTs was able to fully adsorb the Li_2S_6 after about 190 min, whereas the test conducted using TiO_2 BM NTs was not visibly clear until the next morning. Columns g) and h) of Fig. 4 (a) show adsorption tests for TiO_{2-x} NTs and TiO_{2-x} BM NTs respectively. The test conducted using the TiO_{2-x} NTs noticeably changed color immediately after the introduction of the test solution, achieving full clarity after less than 1 h. The test conducted using TiO_{2-x} BM NTs did not demonstrate the same performance, however it did demonstrate a slightly superior performance than the test using TiO_2 BM NTs. Columns e), f), g) and h) are displayed at various intervals to show the shifts in the color of the solution more clearly in Fig. 4 (b). Two clear trends are observed in these images, firstly, that TiO_2 NTs based host materials outperform the TiO_2 BM NTs samples significantly in terms of the speed of liquid polysulfide adsorption in both reduced and unreduced cases and secondly, that the reduced host materials outperform the unreduced host materials in both cases. The TiO_{2-x} NTs sample demonstrated the best overall performance owing to several factors. Firstly, the highly robust high surface area material is able to accommodate a high level of adsorption. This is due to the higher presence of nanotubes than the TiO_2 BM NTs based samples increasing the overall

available surface area for lithium polysulfides to be adsorbed on. Secondly, the TiO_2 NTs are able to withstand chemical reduction to TiO_{2-x} NTs, unlike the TiO_2 BM NTs, allowing their adsorptive properties to be further boosted over the unreduced material. All four samples showed near total adsorption after being left overnight. These results suggest that the TiO_2 NT based materials should all be suitable cathode host materials, as they are able to rapidly adsorb large amounts of soluble lithium polysulfides, helping to prevent the diffusion of polysulfides and the subsequent shuttling effect by “trapping” the sulfur species as soon as they dissolve into the electrolyte during the reduction reaction [39]. This is due to the aforementioned chemical affinity between Ti^{4+} and lithium polysulfides, giving TiO_2 a superior adsorption capability than other metal oxide hosts which rely on the affinity between oxygen and lithium polysulfides for adsorption [17]. This test also demonstrates that the TiO_2 NTs outperform the TiO_2 BM NTs in both unreduced and reduced states, indicating that their more robust geometry from the larger initial particle size allows them to better adsorb liquid polysulfides. The excellent performance of the TiO_{2-x} NTs sample is likely due to a combination of the robust geometry of the material and the high presence of adsorptive Ti^{3+} ion sites from chemical reduction.

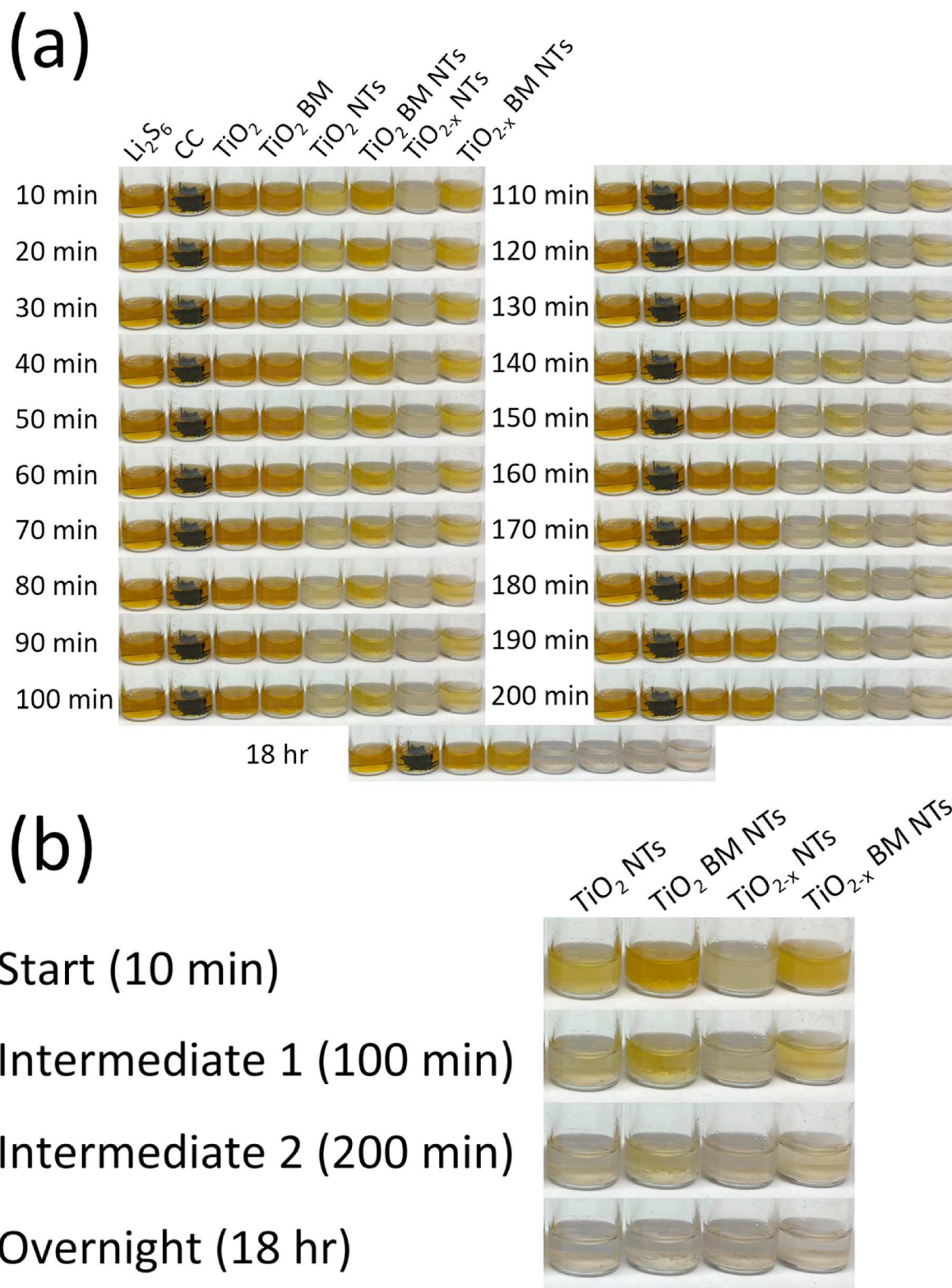


Fig. 4. (a) Images taken at 10-min intervals displaying a polysulfide adsorption test for TiO₂ derived host materials. Column a) shows the test solution for reference, b) shows carbon cloth, c) shows TiO₂, d) shows TiO₂ BM, e) shows TiO₂ NT, f) shows TiO₂ BM NT, g) shows TiO_{2-x} NT, and h) shows TiO_{2-x} BM NT respectively for comparison. (b) images taken at various intervals for TiO₂ NT, TiO₂ BM NT, TiO_{2-x} NT, and TiO_{2-x} BM NT respectively for comparison.

3.3. Electrochemical characterization

In order to quantify the electrochemical performance and assess the redox kinetics of each of the TiO₂ NT based cathode host materials, CR-2032 coin cells with an aerial sulfur loading of 1.085 mg/cm² were

created. EIS with a frequency window of 0.01–10⁵ Hz was conducted to explore the kinetics of the Li-S electrochemical reaction and determine the internal impedance of the cell. Warmup cycling is performed to fully activate the cathodic material and allow the cell to reach its electrochemical equilibrium before analysis begins, allowing for a more

accurate reading to be obtained. The results of EIS testing are subsequently analyzed via the creation of a Nyquist plot to determine the internal resistances of the cells. The Nyquist plot is obtained by graphing Z_{real} (Z') against the negative of $Z_{\text{imaginary}}$ (Z'') and can be divided into three distinct regions, each indicating a different property of the cell. The first semicircle is in the high frequency region and indicates the interfacial (SEI: solid electrolyte interphase) resistance. The second semicircle is in the intermediate frequency region and indicates the charge transfer resistance. The third is the positive sloping line which falls in the low frequency region and indicates the Warburg impedance (W_0), resistance which can be attributed to the diffusion of lithium ions in the electrolyte. Resistance values are obtained from the three inflection points on the Nyquist plot, with the electrolyte resistance (R_s) being found from the initial value, SEI resistance (R_f) being found from the inflection point after the first semicircle, and charge transfer resistance (R_{ct}) being found from the inflection point after the second semicircle [40]. The results of this testing are shown in Fig. 5 (a and b), and the equivalent circuit is shown in Fig. 5 (c).

As demonstrated by Fig. 5 (b), all cells demonstrated impressively low internal resistances. R_s values for each cell type were similar, owing to the fact that all cells used identical electrolyte solutions and were constructed in a nearly identical fashion. R_f values differed some, with the cell employing a TiO_2 NTs@CC cathode demonstrating a significantly lower resistance due to SEI. This can be attributed to the higher surface area of the TiO_2 NTs material than the other three TiO_2 based hosts, as this cathode is able to “spread out” the SEI and reduce the impact at any one point. R_{ct} values varied significantly, with the TiO_2

NTs@CC cathode demonstrating the worst performance. The TiO_{2-x} NTs@CC and TiO_{2-x} BM NTs@CC cathode demonstrated impressively low resistance to charge transfer, owing to their increased conductivity from the introduction of oxygen vacancies via chemical reduction. The TiO_2 BM NTs@CC cathode demonstrated the best charge transfer performance of the samples, potentially owing to its high surface area or an unidentified factor related to the ball milling process.

Similarly, CV measurement with a potential window of 1.7–2.8 V and a scan rate of 0.1 mV/s was conducted to analyze the impact of the various cathode host materials on cell performance. Fig. 5 (d) shows the results from CV testing on cells that have been “warmed up” by cycling them at 0.2 C for 5 cycles, the same “warm up” used for galvanostatic charge-discharge testing.

During the cathodic scan of CV, measurements of the cells exhibit two related reduction peaks at around 2.3 and 2.0 V, which are assigned to the electrochemical reduction of sulfur into soluble polysulfides ($\text{S}_8 \rightarrow \text{Li}_2\text{S}_x$, $x \geq 4$, referred to as C I) and the subsequent reduction of long-chain polysulfides into insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ ($\text{Li}_2\text{S}_x \rightarrow \text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, $x \geq 4$, referred to as C II), respectively. In the following anodic scan, the characteristic oxidation peaks correspond to the reverse conversion from insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ to the long-chain polysulfides ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S} \rightarrow \text{Li}_2\text{S}_x$, $x \geq 4$) and final oxidation into element sulfur ($\text{Li}_2\text{S}_x \rightarrow \text{S}_8$, $x \geq 4$, referred to as A).

Analyzing the peaks of the CV graphs shown in Fig. 5 (d) allows for analysis of the polarization potential of each of the cells. By finding the change in voltage between the cathodic peak near 2.0 V and the anodic peak near 2.5 V, the polarization potential can be obtained. A

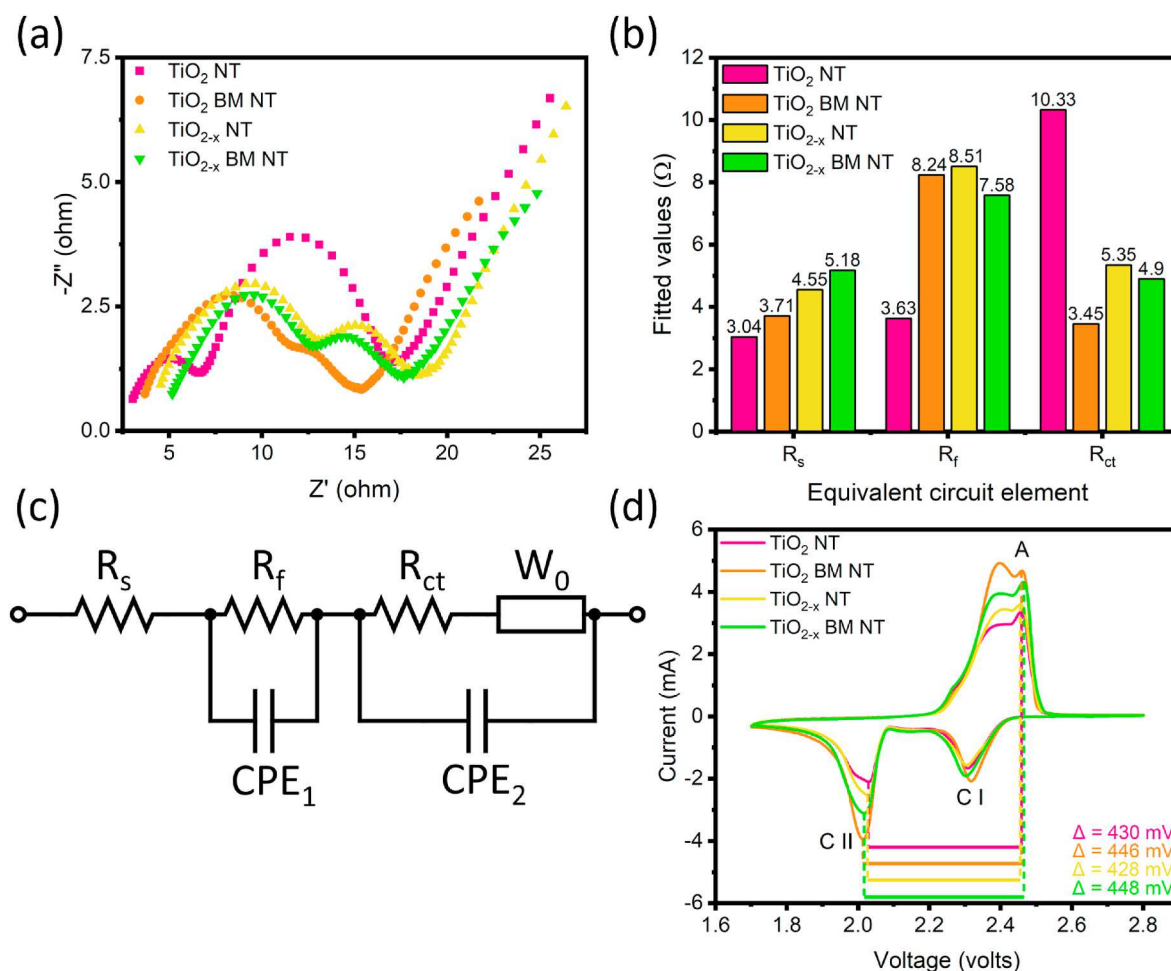


Fig. 5. (a) Experimental EIS data displayed as Nyquist plots for each sample, (b) Processed EIS data showing electrolyte, SEI and charge transfer resistance respectively for each cell, (c) Equivalent circuit diagram for the EIS testing, and (d) Experimental CV data for each sample.

polarization potential with a lower value indicates that the reaction has been catalyzed and is experiencing improved redox kinetics. Fig. 5 (d) shows a polarization potential of 430 mV for TiO₂ NTs@CC, 446 mV for TiO₂ BM NTs@CC, 428 mV for TiO_{2-x} NTs@CC, and 448 mV for TiO_{2-x} BM NTs@CC cells. The polarization potentials of all four cells were fairly similar, though there was a slight disparity between TiO₂ NTs based and TiO₂ BM NTs materials, with the slightly lower polarization potential of TiO₂ NTs based cathodes indicating that the material has a slight catalytic effect when compared to TiO₂ BM NTs. The lower polarization potential of the cells containing TiO₂ NT based materials in both pristine and reduced cases can be attributed to the polar metal oxide microstructures catalyzing the reduction of lithium polysulfides by acting as an electron bank and consequently increasing the speed of the reaction. The effect is more pronounced in cells containing TiO₂ NTs based materials due to the higher prevalence of NTs in these samples.

Fig. 5 (d) demonstrates maximum oxidation and reduction currents of 3.36 mA for peak A, 1.66 mA for peak CI, and 2.10 mA for peak CII for TiO₂ NTs@CC cells, 4.68 mA for peak A, 2.08 mA for peak CI, and 3.95 mA for peak CII for TiO₂ BM NTs@CC cells, 3.60 mA for peak A, 1.56 mA for peak CI, and 2.52 mA for peak CII for TiO_{2-x} NTs@CC cells, and 4.31 mA for peak A, 1.91 mA for peak CI, and 3.11 mA for peak CII for TiO_{2-x} BM NTs@CC cells. Increased maximum current implies a higher rate of charge transfer by the cathode, corresponding to a higher conductivity of the cathode host material. In the case of the TiO₂ NTs based cells, the cells employing TiO_{2-x} NTs outperformed the cells employing TiO₂ NTs, owing to the increased conductivity from the chemically induced oxygen vacancies. This trend is not followed by the TiO₂ BM NTs based cells, as the cells employing TiO_{2-x} BM NTs are significantly outperformed by the TiO₂ BM NTs based cells. This result echoes the phenomenon observed in Fig. 2, indicating that chemical reduction is not compatible with the fragile structure of the TiO₂ BM NTs material. The best overall performance is demonstrated by cells employing TiO₂ BM NTs, indicating that increased and larger scale porosity has a large effect on the ability of the material to trap and reduce liquid lithium polysulfides.

Galvanostatic charge discharge cycling with a voltage window of 1.7–2.8 V was conducted to assess the capacity retention and overall stability of cells employing the TiO₂ NT host material over many cycles. Cyclic loading of cells at different charge rates (C), with 1 C being 1675 mAh g⁻¹, was conducted via several different methods.

The maximum initial capacity and overall stability were assessed via a “step” test in which the C rate was changed every five cycles in the following order: 0.1, 0.2, 0.5, 1, 2, 3, 2, 1, 0.5, 0.2, 0.1 C. This test is shown in Fig. 6 (a–e) and summarized numerically in Table 1. This test is performed to determine how much the C rate influences the specific capacity of the cell and if high-rate cycling has a negative impact on specific capacity by allowing a comparison of cycling at low C rates before and after cycling at high C rates. Fig. 6 (a–c) show the best performance for each rate for each sample, while Fig. 6 (e) shows the full results of this test for TiO₂ NTs, TiO₂ BM NTs, TiO_{2-x} NTs, TiO_{2-x} BM NTs, and TiO₂ BM. A TiO₂ BM sample was used in this test to act as a baseline to measure the performance impact of each cathode host material. The TiO₂ BM host material was only used as a reference for the steps test

because it is unable to maintain stability over long-term cycling. Each cathode host material demonstrated stable performance, with the best performance in terms of specific capacity being demonstrated by TiO₂ BM NTs. As Fig. 6 (e) shows, specific capacities at each of the low C rates are unchanged after cycling. This loss of capacity at high C rates can be attributed to the kinetic nature of the lithium polysulfide electrochemical reaction, as the extent of the reaction in either direction is dependent on the amount of time provided for the lithium polysulfides to diffuse and react. TiO₂ BM NTs outperformed TiO_{2-x} BM NTs at both high and low C rates and maintained consistent performance after high-rate cycling. TiO₂ NTs significantly outperformed their chemically reduced counterparts at high C rates, however similar performance was observed at lower C rates. Each of the NTs based cathode materials significantly outperformed the TiO₂ BM sample at low C rates, and all but the TiO_{2-x} NTs sample outperformed the TiO₂ BM sample at high C rates.

Long-term stability tests were conducted at 3.0 C (Fig. 6 (f and g)). These tests showed very favorable results, shown in Table 2. Data collection beyond when the specific capacity of each sample falls below 95 mAh g⁻¹ is not displayed, as allows for an even comparison between cells and a focus on the number of cycles for which the cells can deliver a useful capacity. TiO₂ NTs demonstrated the best overall performance, boasting a capacity decay rate of only 0.004% per cycle for the first 300 cycles. TiO₂ BM NTs boasted a high initial capacity of 625 mAh g⁻¹, however these cells also demonstrated a very low stability, with a capacity decay rate of 0.26% per cycle and only maintaining a useful capacity above 95 mAh g⁻¹ for 322 cycles. This difference in performance based on the synthesis method indicates a correlation between the mechanical robustness of the NT host material and the long-term stability. While the more porous TiO₂ BM NTs are able to achieve a higher initial capacity (as seen in Fig. 6 (e–g)), their fragile structure causes their capacitive performance to quickly fall off after extended cycling. While the more robust TiO₂ NTs do not achieve the same capacity performance due to their less porous structure, they are able to achieve a much higher useable cycle life than TiO₂ BM NTs, 676 as opposed to the 322 cycles it took for cells using TiO₂ BM NTs to demonstrate a reversible capacity below 95 mAh g⁻¹.

Long-term stability tests conducted on chemically reduced samples, TiO_{2-x} NTs and TiO_{2-x} BM NTs respectively, demonstrated different results but indicated a similar trend. TiO_{2-x} NTs demonstrated superior stability (decay rate of -0.68% per cycle over 300 cycles vs 0.022%) and higher initial capacity performance (383 mAh g⁻¹ vs 358 mAh g⁻¹) to TiO_{2-x} BM NTs over 300 cycles, however, cells utilizing the TiO_{2-x} NTs host failed at roughly 300 cycles. This trend indicates that, based on cycling data, the TiO_{2-x} BM NTs were significantly damaged by chemical reduction, leading to a dramatic decrease in performance when compared to TiO₂ BM NTs. TiO_{2-x} NTs, on the other hand, were able to hold up to the chemical reduction process as they demonstrated superior to TiO₂ NTs over 300 cycles.

The positive per cycle capacity “decay” experienced by the cell using the TiO_{2-x} NTs cathode host shown in Table 2 is a result of the lithium polysulfide reaction reaching equilibrium after extended cycling. A maximum capacity is reached at roughly 100–150 cycles as more sulfur becomes activated and the cell stabilizes once its electrochemical equilibrium is reached. In tests run at low charge rates, this capacity gain can offset the capacity loss from the cyclic electrochemical wear on the cell, especially if the initial capacity is much lower than the maximum capacity reached at equilibrium. This combination of factors leads to a positive “decay”, as the full capacity of the cell is not reached until enough sulfur is activated to reach the electrochemical equilibrium conditions of the cell [41–43].

As shown in Fig. S1, the battery with the TiO_{2-x} NT electrode displayed an initial discharge capacity of 1134 mAh g⁻¹. After 100 cycles, the capacity of the TiO_{2-x} NT electrode remained at 1065 mAh g⁻¹. However, the Li-S batteries with the TiO₂ NT electrode, the TiO_{2-x} BM NT electrode, and the TiO₂ BM NT electrode demonstrated a slightly

Table 1

Initial discharge capacity of tested cells employing TiO₂ NTs, TiO₂ BM NTs, TiO_{2-x} NTs, and TiO_{2-x} BM NTs respectively from Fig. 6(a–d).

Charge Rate	TiO ₂ NTs	TiO ₂ BM NTs	TiO _{2-x} NTs	TiO _{2-x} BM NTs	TiO ₂ BM
C	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹	mAh g ⁻¹
0.1	1014	1205	1005	1054	848
0.2	898	1125	876	944	750
0.5	754	1024	806	848	677
1	689	927	738	770	616
2	614	843	571	679	552
3	551	768	354	616	495

Table 2

Values for initial, maximum, and final capacity for each sample for the cycling performed at 3.0 C in Fig. 6 (f and g).

Sample	Initial Capacity (mAh g ⁻¹)	Capacity at 300 Cycles (mAh g ⁻¹)	Final Capacity (mAh g ⁻¹)	Cycle Count	Per Cycle Capacity Decay (%) (300 cycles)	Per Cycle Capacity Decay (%)
TiO ₂ NTs	429	424	95	676	0.004%	0.12%
TiO ₂ BM NTs	625	133	94	322	0.26%	0.26%
TiO _{2-x} NTs	383	459	~	294	-0.68%	~
TiO _{2-x} BM NTs	358	334	95	500	0.022%	0.15%

poor initial discharge capacity of 1084 mAh g⁻¹, 1030 mAh g⁻¹, and 961 mAh g⁻¹ respectively. After 100 cycles, the capacity of the TiO₂ NT electrode, the TiO_{2-x} BM NT electrode, and the TiO₂ BM NT electrode decayed to 997 mAh g⁻¹, 939 mAh g⁻¹, and 829 mAh g⁻¹ respectively. It can be seen that the initial discharge capacity and the final discharge capacity of the TiO_{2-x} NT electrode was higher than the other three electrodes, confirming the superiority of polysulfides adsorption capability of TiO_{2-x} NT. Defected TiO_{2-x} NT with implanted oxygen vacancies can strengthen the polysulfides adsorption capability and improve the electronic conductivity. Additionally, it was reported that the normal TiO₂ structure can deform due to impact forces released by the collision of milling media [44], so the destruction of the tubular structures of the TiO₂ nanotubes can be caused by high-energy ball milling and affect their performance.

Since the TiO_{2-x} NT electrode demonstrated the most favorable electrochemical performance under low sulfur loading among all the samples, furthermore, taking the practical commercialization into account, the electrochemical measurement for the TiO_{2-x} NT electrode with high areal sulfur loading (5 mg cm⁻²) was carried out (Fig. S2). The TiO_{2-x} NT cell displayed an initial capacity of 766 mAh g⁻¹ and retained at 718 mAh g⁻¹ after 50 cycles. The cycling performance under high sulfur loading is one of the most powerful pieces of evidence for the TiO_{2-x} NT as a promising sulfur host. It is clear that TiO_{2-x} NT can effectively trap soluble polysulfides via polar-polar chemical interactions [45–47]. The outstanding cycling stability under high sulfur loading demonstrate the TiO_{2-x} NT cell is full of promise, becoming an outstanding candidate for practical applications.

3.4. Characterization after cycling

To qualitatively and quantitatively determine the impact of the TiO₂ NTs based cathode host materials on PSE, cells cycled using a cathode with the TiO₂ NTs host material, the host material which demonstrated the most stable long-term performance, were compared to cells cycled using unmodified TiO₂ as a cathode host material. This comparison was done twice, once with cells using cathodes of both types cycled under identical conditions to analyze the extent of PSE on the separator material qualitatively, and once using cells of both types cycled at as high of a rate and as for long of a duration as each cell was capable of to determine the impact of PSE on the surface of the lithium metal anode both qualitatively and quantitatively.

After cycling, the extent of polysulfide trapping, and conversely the extent of alleviation of PSE, can be determined qualitatively by disassembling used cells and examining the separator material. When unused, the separator is white, picking up color from molecules retained in the electrolyte. Sulfur appears yellow under visible light, and thus the amount of sulfur that was not retained by the host material can be assessed by assessing color. This is shown in Fig. 7. Note that black particles and very dark areas are due to carbon cloth pulverization during the cell's sealing process and has no effect on performance. Fig. 7 (a) displays the separator material from a cell cycled 300 times at 1.0 C with the TiO₂ NTs@CC cathode. Fig. 7 (b) displays the separator material from a cell cycled 100 times at 1.0 C with a TiO₂@CC cathode. This material was chosen as a reference for poor performance due to the fact that raw TiO₂ does not improve cell performance but allows cathodes to be made in an identical fashion. Despite undergoing 3 times as much cycling as the other sample, samples containing TiO₂ NT display

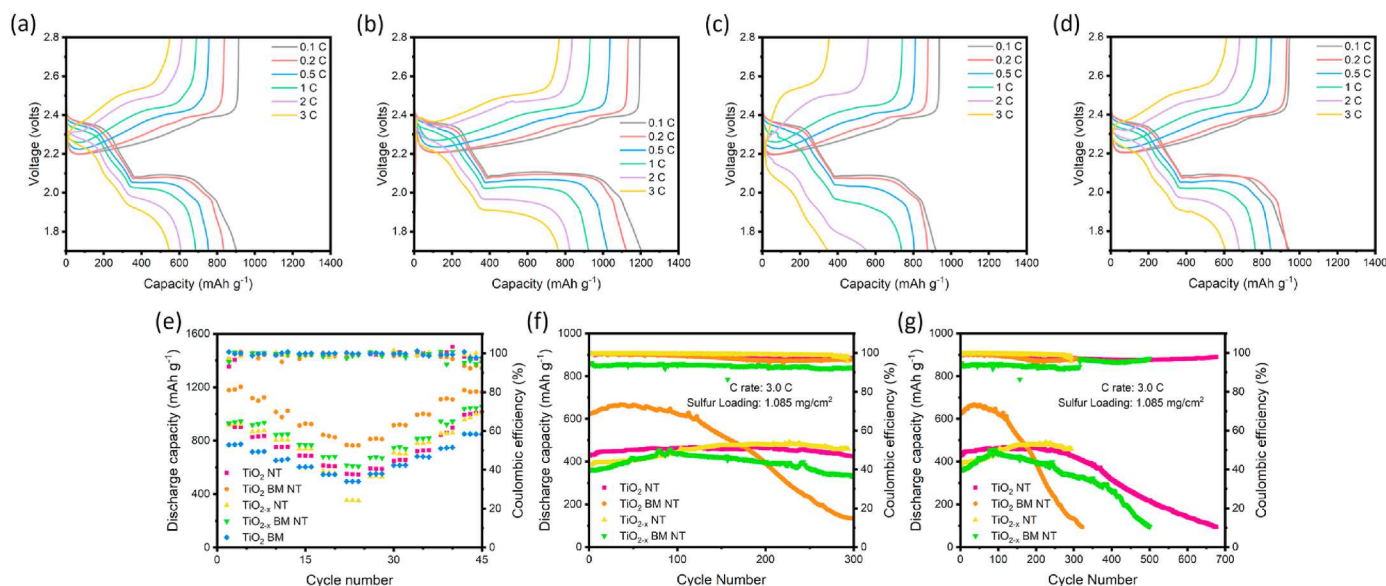


Fig. 6. (a–d) Charge-discharge cycling profiles of Li-S batteries at various charge rates using TiO₂ NTs, TiO₂ BM NTs, TiO_{2-x} NTs, and TiO_{2-x} BM NTs based host materials on carbon cloth as cathodes respectively. (e) displays “steps” tests conducted on Li-S batteries between charge rates of 0.1 and 3.0 C for TiO₂ NTs, TiO₂ BM NTs, TiO_{2-x} NTs, TiO_{2-x} BM NTs, and TiO₂ BM based host materials. (f and g) display of long cycling tests conducted at 3.0 C, showing the first 300 cycles and the performance of each cell until failure or a capacity of less than 95 mAh g⁻¹ respectively.

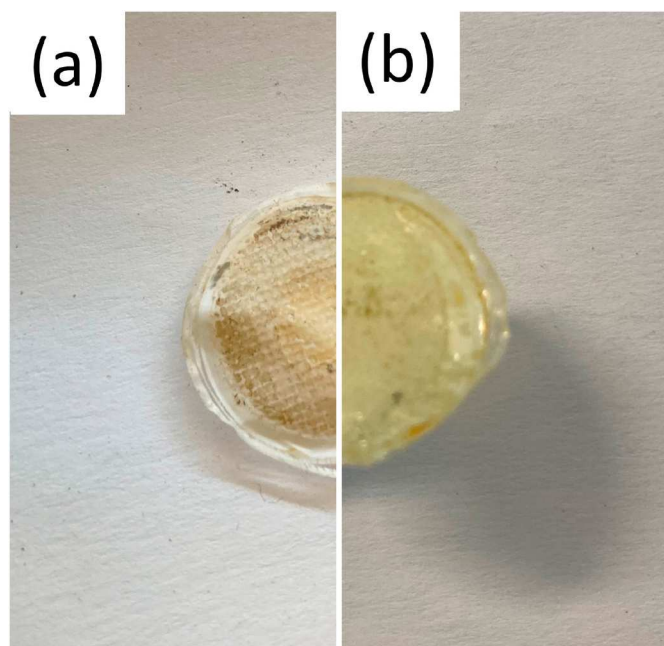


Fig. 7. (a) Image of the separator of a cell employing TiO_2 NT after 300 cycles at 1.0 C and (b) image of the separator of a cell employing TiO_2 after 100 cycles at 1.0 C.

superior polysulfide retention due to their lighter coloration. Both images were taken immediately after the disassembly of the cells and show the coloration of the electrolyte they are saturated with.

The extent of elimination of PSE can also be measured by analyzing the contact surface of the lithium anode. PSE causes the surface to dissolve and deposit unevenly, as it causes the passivation of parts of the anode, creating “dead” zones that can no longer interact with the electrolyte. Fig. 8 (a and c) show the SEM images of the contact surface of a lithium anode after 300 cycles at 1 C with a TiO_2/CC cathode with large-scale defects labeled. Fig. 8 (b and d) show the SEM images of the contact surface of a lithium anode after 1000 cycles at 3 C with TiO_2 NTs/CC as a cathode. This disparity in cycling conditions is due to the fact that the TiO_2/CC cathode was not stable enough to support cycling at very high rates or over long durations. Despite being run at a charge rate three times higher and for more than three times as long, the contact surface from the cell employing TiO_2 NTs demonstrates a smooth surface, indicating that no regions are “dead”, implying PSE has been minimized. Fig. 8 (a and c) demonstrate the impact of PSE, showing the dendrites and porosity formed from uneven dissolution and deposition of the lithium ions back onto the surface. This is supported by energy dispersive X-ray analysis (EDAX) of both anodes, shown in Fig. 8 (e and f). EDAX allows for analysis of the surface composition of a material by indicating what elements are present on the surface and their relative concentrations from surface area fraction. In this case, it is used to identify zones of the anode where sulfur is present, as it indicates the dead zones on the surface where passivation films have been formed. A higher surface area fraction of sulfur indicates that more of the surface of the lithium anode’s contact surface has been passivated via a film of solid lithium sulfide, implying a more severe impact from PSE. EDAX analysis revealed the presence of 9.6 wt % sulfur on the surface of the anode of the cell using the unrefined TiO_2 host cathode and the presence of 6.6 wt % sulfur on the surface of the anode of the cell using the TiO_2 NTs cathode. These results show that the anode from the cell employing TiO_2 NTs has a lower presence of sulfur on its surface despite being cycled for more than three times as many cycles at an intensity 3 times greater. This indicates that the presence of TiO_2 NTs in the cathode has a dramatic impact on PSE, able to prevent a significant amount of polysulfide diffusion via adsorption.

3.5. Discussion

The effectiveness of TiO_2 NTs based host materials as lithium polysulfide hosts in Li-S batteries can be attributed to their complex geometry and polar nature. The synergy of these two properties creates a host material that is able to both physically and chemically confine liquid lithium polysulfides, effectively immobilizing them during the intermediate liquid phases of electrochemical reduction and severely limiting the impact of PSE. Fig. 9 shows SEM images demonstrating the complex structure of the TiO_2 NTs, with both interior and exterior portions able to make contact with the electrolyte solution and interact with ions in the solution. The conductivity and polar nature of the TiO_2 NTs based host materials were found to be further improved by chemical reduction, however the initial TiO_2 NTs material had to be mechanically robust enough to withstand chemical treatment without losing the NT structures from its surface. Of the four TiO_2 NTs derived materials, the best overall performance in terms of capacity and performance was attributed to the TiO_2 BM NTs based cathode host materials, while the TiO_{2-x} NTs based cathode host demonstrated the best overall stability. The TiO_2 BM NTs sample was too mechanically fragile for the chemical reduction process, and additionally was unable to stand up to cycling over extended periods of time due to the same factor. Cells employing the TiO_2 BM NTs cathode host achieved a maximum initial specific capacity of $1204.72 \text{ mAh g}^{-1}$ at 0.1 C and a maximum initial specific capacity of $767.69 \text{ mAh g}^{-1}$ at 3.0 C, however were only able to provide a specific capacity greater than 95 mAh g^{-1} for 322 cycles at 3.0 C, with a moderate capacity decay rate of 0.26% per cycle. Similarly, cells employing the TiO_{2-x} BM NTs cathode also demonstrated high initial specific capacities, showing a maximum initial specific capacity of $1054.35 \text{ mAh g}^{-1}$ at 0.1 C and a maximum initial specific capacity of $616.22 \text{ mAh g}^{-1}$ at 3.0 C. Despite the decreased initial specific capacities at every charge rate, the TiO_{2-x} BM NTs cathode was able to cycle 500 times before falling below a capacity of 95 mAh g^{-1} , demonstrating an impressively low capacity decay rate of 0.022% per cycle for the first 300 cycles and an overall decay rate of 0.15% per cycle. The more stable TiO_2 NTs cathode was able to maintain a specific capacity above 95 mAh g^{-1} for 676 cycles, boasting an impressively low capacity decay rate of 0.004% per cycle for the first 300 cycles, and 0.12% per cycle overall. Cells using this cathode host material achieved a maximum initial specific capacity of $1013.7 \text{ mAh g}^{-1}$ at 0.1 C and a maximum initial specific capacity of $551.41 \text{ mAh g}^{-1}$ at 3.0 C. The TiO_{2-x} NTs cathode demonstrated the best stability in the first 300 cycles with a capacity decay rate of -0.68% per cycle, however this cathode was only able to cycle for a maximum of 294 cycles before becoming unstable. Cells using this cathode material demonstrated a maximum initial specific capacity of $1054.35 \text{ mAh g}^{-1}$ at 0.1 C and a maximum initial specific capacity of $616.22 \text{ mAh g}^{-1}$ at 3.0C. TiO_2 NTs based cathodes and TiO_{2-x} NTs based cathodes both demonstrated impressive stability in the first 300 cycles, however the TiO_{2-x} NTs cathodes suffered significantly decreased performance at high charge rates. All four materials demonstrated a severe performance drop off after 300-400 cycles, with this effect being especially prominent with the more mechanically fragile cathode host materials such as TiO_2 BM NTs.

This examination gave clear results indicating the superior ability of TiO_2 NT based materials to alleviate PSE, as all cells containing NTs were able to demonstrate impressive capacity and stability performance over 300 cycles. A clear impact of initial particle size for nanotube synthesis on cell performance was observed, with the use of ball-milled particles resulting in a more open nanotube structure which was able to demonstrate higher capacities than its more closed counterpart, although for a shorter cyclic duration. The introduction of oxygen vacancies onto the nanotube structures via chemical reduction was also tested, revealing a positive impact on the conductivity of samples mechanically robust enough to withstand it. The advantage and disadvantage of TiO_2 NTs, compared With TiO_2 quantum dots, TiO_2 nanoparticles, TiO_2 hollow spheres, TiO_2 nanowires and TiO_2

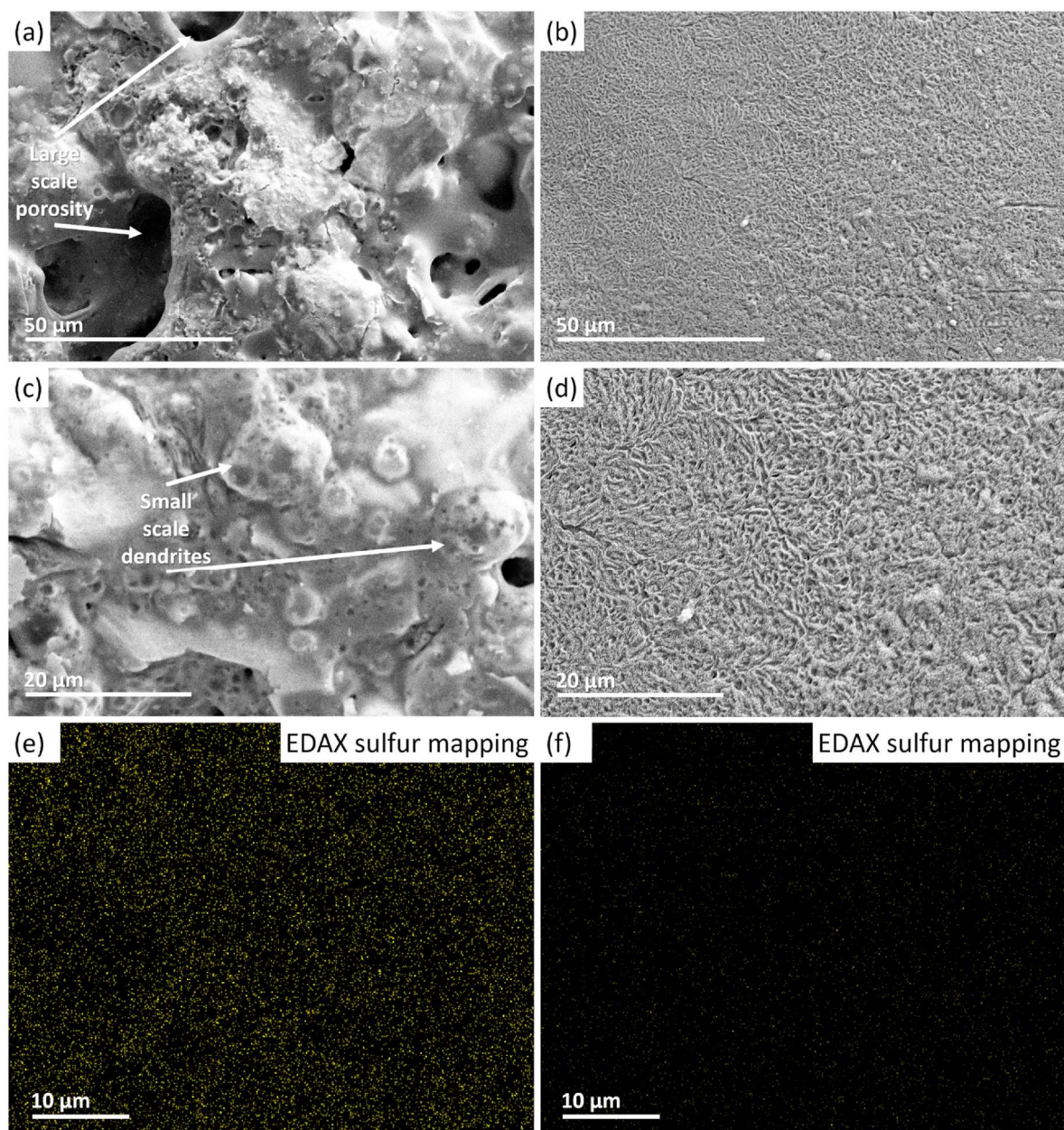


Fig. 8. SEM images of the contact surface of the lithium anode for (a) a cell that employed TiO_2 at 1000x, (b) a cell that employed TiO_2 NTs at 1000x, (c) a cell that employed TiO_2 at 2000x, (d) a cell that employed TiO_2 NT at 2000x. EDX scans at 2000x magnification showing the presence of sulfur in yellow for (e) a cell that employed TiO_2 and (f) a cell that employed TiO_2 NTs.

nanosheets for the applications in Li-S battery are shown in supporting information (Table S2).

4. Conclusion

TiO_2 NTs were prepared via a simple hydrothermal template synthesis method and employed as a polar cathode host material for Li-S batteries. Samples were prepared from unmodified and ball milled rutile TiO_2 powders, and subsequently chemically reduced to create oxygen vacancies to synthesize four distinct cathode host materials, TiO_2 NTs, TiO_2 BM NTs, TiO_{2-x} NTs, and TiO_{2-x} BM NTs respectively. SEM and TEM analysis techniques revealed the structures as hollow tubes, with exposed structures belonging primarily to the (2 0 0) crystal plane of anatase phase TiO_2 . SEM analysis indicated a large difference in the topography and geometry of the TiO_2 NTs and TiO_2 BM NTs samples, with the TiO_2 NTs demonstrating a much more mechanically robust

structure due to the larger initial particle size causing the NTs to grow as a “mat” on the surface of the particles, and the TiO_2 BM NTs demonstrating a much more porous and open structure due to the smaller initial particle size causing the NTs to grow as a “web” between the particles. The more mechanically robust TiO_2 NTs and TiO_{2-x} NTs particles showed better overall performance, as the delicate nature of the TiO_2 BM NTs based materials caused the NTs structure to be destroyed by long-term cycling and chemical reduction. While the TiO_2 BM NTs showed the best performance in terms of capacity, achieving an initial specific capacity of $1204.72 \text{ mAh g}^{-1}$ at 0.1 C and $767.69 \text{ mAh g}^{-1}$ at 3 C, they lacked considerable stability, only able to provide a specific capacity above 95 mAh g^{-1} for 322 cycles at 3 C and demonstrating a high decay rate of 0.26% per cycle. TiO_2 NTs and TiO_{2-x} NTs were able to deliver lower initial specific capacities, 1013.7 and $1005.24 \text{ mAh g}^{-1}$ at 0.1 C and 551.41 and $616.22 \text{ mAh g}^{-1}$ at 3 C respectively, and extremely low decay rates over the first 300 cycles, 0.004% and -0.68% per cycle

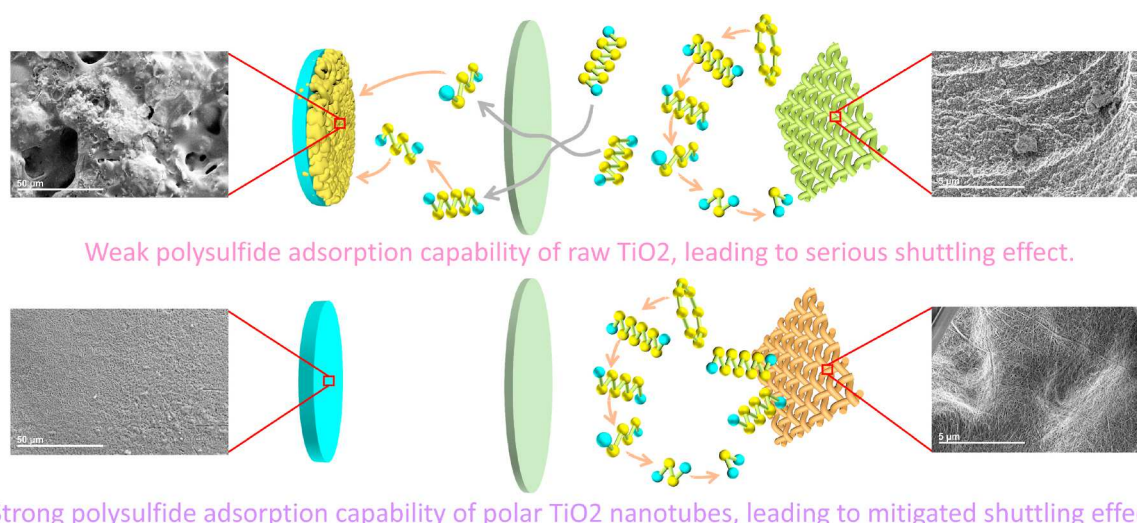


Fig. 9. Schematic demonstrating how TiO_2 NTs based cathode host materials can help to mitigate PSE.

respectively. The TiO_2 NTs were able to cycle above 95 mAh g^{-1} for 676 cycles, whereas the TiO_{2-x} NTs only achieved 294 stable cycles. The negative capacity decay rate of the TiO_{2-x} NTs indicates that the cell was still reaching equilibrium around 300 cycles, indicating very stable performance for cells using this cathode that cycle stability. Overall, this work determined that Li-S battery cathode host materials must demonstrate a high level of mechanical robustness to endure long cycling, as evidenced by the superior long-term performance of the TiO_2 NTs host material. The chemical reduction was shown to be a suitable method to introduce oxygen deficiency in TiO_2 nanostructures, as evidenced by the superior electrochemical performance and lower internal resistance of cells using the TiO_{2-x} NTs host material. This work explores the use of polar host materials which chemically and physically bind and confine liquid lithium polysulfides and alleviate the polysulfide shuttling effect, indicating the direction for further investigation, and incrementing toward the feasibility of commercial Li-S batteries.

CRediT authorship contribution statement

Zephyr Barlow: Investigation, Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **Zhen Wei:** Formal analysis, Writing – review & editing. **Ruigang Wang:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2023.128316>.

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