Binder-free S@Ti₃C₂T_x sandwich structure film as a high-capacity cathode for a stable aluminum-sulfur battery

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ABSTRACT The rechargeable aluminum-sulfur (Al-S) battery is a promising alternative-energy storage device with high energy density and made of cheap raw materials. However, Al-S batteries face several obstacles, especially the shuttle effect. Herein, a binder-free S@Ti₃C₂T_x sandwich structure film with uniform sulfur dispersion was designed. The two-dimensional (2D) layered material Ti₃C₂T_x not only has the function of binder and conductive agent but also is a promising host for sulfur anchoring. As a result, S@Ti₃C₂T_x film showed an initial capacity of 489 mA h g⁻¹ at 300 mA g⁻¹ and retained the value at 415 mA h g⁻¹ after 280 stable cycles, with an average Coulombic efficiency of ~95%. The film displayed higher capacity and stability than the S + Ti₃C₂T_x cathode prepared by the slurry-coating method (the initial capacity was 317 mA h g⁻¹ and then decayed to 222 mA h g⁻¹ after 160 cycles). The main capacity of S@Ti₃C₂T_x film in the Al-S battery came from the reversible redox reaction of S²⁻ and S. This new 2D material combined with a controllable electrode structure design paves the way for the development of Al-S batteries.

Keywords: binder-free, S@Ti₃C₂T_x, MXenes, shuttle effect, aluminum-sulfur batteries

INTRODUCTION

Lithium-ion battery (LIB) technology is one of the most mature energy storage technologies in the market. However, the high cost and natural scarcity of key materials hinder the long-term and large-scale application of LIBs [1]. Several new alternative battery chemistries, such as sodium [2,3], magnesium [4], and aluminum batteries, have attracted extensive attention. Aluminum-ion batteries (AIBs) are the most promising because of their abundant reserves (Al is the most abundant metallic element in the Earth's crust), low cost, and high energy density (the theoretical capacities of Al are 2978 mA h g⁻¹ and 8034 mA h cm⁻³) [5]. The research on rechargeable AIBs has become an important trend in the field of energy storage after the publication of Dai and co-workers in 2015 [6]. To date, various types of cathode materials, including graphite [7,8], metal oxides [9], metal sulfides [10], phosphides [11], and selenides [12,13], have been investigated to fabricate effective aluminum storage systems based on ionic liquid (IL) electrolytes. However, these cathode materials either have a low specific capacity or a rapid capacity decay, which greatly affects the potential application of AIBs. By contrast, sulfur not only has

the advantages of abundant raw materials and low price, but also can provide a considerable theoretical capacity of 1675 mA h g⁻¹. Thus, this element can be used as an ideal cathode material. When sulfur cathode and aluminum anode are assembled into an aluminum-sulfur (Al-S) battery system, the theoretical energy density is as high as 1340 W h kg⁻¹ [14]. Such high energy density and cheap raw materials make Al-S battery a promising alternative-energy storage device.

Given that sulfur is a conversion-type cathode material, it will generate a series of polysulfides and sulfide during the charge-discharge process [15]. Polysulfides can easily lose electrical contact with the host and diffuse to the electrolyte or Al anode, leading to the shuttle effect, which is the main reason of low capacity, low efficiency, and rapid capacity decay. Therefore, the design of a high-performance Al-S battery system is challenging. Although the research of Al-S battery is still in the inchoate stage, it has attracted considerable attention. The rechargeable Al-S battery was confirmed by Wang's group in 2016; with the help of an activated carbon cloth host, the sulfur cathode completed a short cycle life of 20 cycles [14]. Since then, various sulfur host materials, such as multi-walled carbon nanotube/S cathode [16], carbonized metal-organic frameworks (MOF) [17], boron nitride [18], and reduced graphene oxide + CoS₂ + S composite [19], have been designed. Studies have promoted the development of Al-S batteries, but the cycle stability and reversibility of Al-S batteries still need to be improved. For example, carbonized-MOF (sulfur content is 34%), at extremely low sulfur content and sulfur loading (the total loading after adding the conductive agent and binder is 0.8 mg), exhibits a notably serious capacity attenuation. The development of Al-S batteries faces numerous obstacles, such as the low conductivity of sulfur, the shuttle effect caused by the dissolution of polysulfide intermediates, side reactions between the binder and electrolyte, and the uneven dispersion of sulfur. These problems will lead to a battery Coulombic efficiency (CE) either extremely low or abnormally greater than 100%. Notably, the CE of most reported Al-S batteries is not satisfactory [15,20–22]. Novel electrode materials and structural design strategies are needed to overcome these obstacles.

MXenes are two-dimensional (2D) transition metal carbides and nitrides with the formula of M_{n+1}X_nT_x (where M is a transition metal, X is carbon or nitrogen, *n* = 1–4, and T_x represents surface functional groups), and they are derived from MAX phases (or M_{n+1}AX_n phases are a family of inherently nanolaminated ternary compounds with hexagonal crystal structure)

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by the selective extraction of the “A” atoms (group 13 or 14 elements) [23]. The etched MXene has a unique layered structure with various surface functional groups, such as $-O$, $-F$, $-Cl$, and $-OH$. The first MXene ($Ti_3C_2T_x$) was discovered in 2011 [24], and it exhibits a metallic conductive nature, tunable surface chemistry, and the capability to intercalate other metal ions, which makes it widely used in various fields, such as catalysis [25,26] and energy storage [27–29]. MXenes can be used as an excellent host for sulfur. The functional groups on its surface have a good affinity for polysulfides, and its highly conductive network can accelerate charge transfer. Therefore, numerous studies have used MXene as the sulfur host or separator for the modification layer of lithium-sulfur batteries, resulting in greatly improved battery performance [30]. However, a limited number of studies reported the application of this excellent material to emerging AIBs, especially Al-S batteries. In 2017, MXene V_2CT_x was demonstrated as an intercalation-type cathode material for rechargeable AIBs; it exhibited an exceptional specific capacity of more than 300 mA h g^{-1} at 100 mA g^{-1} [31]. However, the capacity decayed rapidly as the cycle continued. Afterward, a composite 2D layered structure ($Ti_3C_2@CTAB-Se$) was synthesized and used as the cathode of the aluminum battery [32]. With the addition of Se, the material showed a reversible discharge specific capacity of 583.7 mA h g^{-1} at 100 mA g^{-1} , but the capacity decay became serious with the cycles. Another 2D layered material, $D-Ti_3C_2T_x@S@TiO_2$, has been used as the cathode of AIB [33]. The discharge capacity was 151.3 mA h g^{-1} at 100 mA g^{-1} , which was higher than that of $Ti_3C_2T_x$. The literature pointed out that several Ti-S bonds formed due to the reaction of sulfur with Ti ions, and the mechanisms of charge-discharge reaction were intercalation and deintercalation of $[AlCl_4]^-$ in the layers of the cathode material. Therefore, the report did not confirm whether the elemental sulfur participated in the electrode reaction, and it was still regarded as an AIB rather than an Al-S battery. New research directions should focus on the study of the electrochemical reaction mechanism and performance of sulfur in IL electrolyte consisting of aluminum chloride ($AlCl_3$) and 1-ethyl-3-methylimidazolium chloride ($[EMIm]Cl$) with $Ti_3C_2T_x$ as the host.

Herein, a novel binder-free sandwich structure film was designed as the cathode of the Al-S battery. The upper and lower surfaces of the film were covered with a very thin pure $Ti_3C_2T_x$ film, and the main part in the middle was composed of an $S@Ti_3C_2T_x$ composite. The composite was formed by the *in-situ* controllable chemical deposition of nano sulfur in the $Ti_3C_2T_x$ solution, which ensured the dispersion of sulfur. Different from the previously reported strategy of using graphene coating on the separator to mitigate the shuttle effect [19], a protective layer was directly added on the surface of the $S@Ti_3C_2T_x$ composite to block the polysulfides. Different from the traditional preparation method of electrode materials, the binder-free film only needed to be filtered and dried, and no additional binders, conductive agents, and toxic organic solvents were needed in the preparation process. The polymer binder, which is an inactive component that will increase the electrode mass and reduce the energy density of the battery, easily underwent side reactions with ILs. Therefore, in this designed binder-free film, $Ti_3C_2T_x$ had the function of not only a binder but also a conductive agent. In addition, density functional theory (DFT) calculation results predicted that compared with graphene, $Ti_3C_2T_x$ showed stronger binding energy toward Al polysulfides, which means

that it is a more promising host material for sulfur anchoring. As a result, the binder-free $S@Ti_3C_2T_x$ film showed a reversible capacity of 489 mA h g^{-1} at 300 mA g^{-1} after the initial short-term activation, and the capacity remained at 415 mA h g^{-1} after 280 stable cycles, with an average CE of $\sim 95\%$. Based on a series of electrochemical, spectroscopic, and microscopic tests, the reaction mechanism of the new cathode in the Al-S battery was deeply studied.

EXPERIMENTAL SECTION

Materials

$[EMIm]Cl$ (98%) was purchased from Aladdin, and it was first dried on a hot plate at 130°C for 12–24 h before use. $AlCl_3$ (99%) was bought from Macklin. Al foil ($\geq 99\%$, thickness of $100\text{ }\mu\text{m}$) was acquired from Sinopharm Chemical Reagent Co., Ltd. $Na_2S\cdot 9H_2O$ ($\geq 98\%$) was supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. Formic acid ($HCOOH$ 98%) was obtained from Macklin. The sulfur powder was supplied by Adamas. Lithium fluoride (99%) was purchased from Aladdin. Hydrochloric acid (AR: 36%–38%) was received from Sinopharm Chemical Reagent Co., Ltd. Ti_3AlC_2 MAX was bought from Jilin 11Technology Co., Ltd.

Preparation of the delaminated $Ti_3C_2T_x$ flakes and film

As a typical sample, 1 g of LiF was dissolved in 30 mL HCl (6 mol L^{-1}) to form a clear solution by stirring. Then, 1 g of Ti_3AlC_2 was added into the above solution slowly (for $\sim 10\text{ min}$), followed by vigorous stirring at 40°C for 24 h. The suspension was washed with deionized water several times and centrifuged at 3500 r min^{-1} for 5 min until a dark green supernatant was obtained or when the pH of the supernatant became higher than 5. When the dark supernatant was decanted, a swelled clay-like sediment was observed and denoted as the multi-layered $Ti_3C_2T_x$ ($M-Ti_3C_2T_x$). $M-Ti_3C_2T_x$ was then dispersed in 200 mL of deionized (DI) water and sonicated for 1 h under Ar atmosphere. An ice bath was used to avoid excessive heat generation and oxidation of MXenes during the ultrasonic treatment process. The suspension was centrifuged for 1 h at 3500 r min^{-1} . The dark green supernatant was collected as the delaminated $Ti_3C_2T_x$ solution ($D-Ti_3C_2T_x$). The concentration of the $D-Ti_3C_2T_x$ flakes was calculated by complete freeze drying of a known volume of solution and measurement of the weight of the obtained $D-Ti_3C_2T_x$ flakes. For the preparation of the $Ti_3C_2T_x$ film, a certain volume of $D-Ti_3C_2T_x$ solution, if necessary, was diluted to a fixed concentration, a cellulose membrane ($0.22\text{ }\mu\text{m}$ pore size) was used for vacuum filtration, and the film was freeze dried. The thickness and weight of the film can be adjusted flexibly based on the needs of the experiment. In this paper, the typical loading of $Ti_3C_2T_x$ film was about 2.08 mg cm^{-2} .

Preparation of the $S@Ti_3C_2T_x$ composite and binder-free film

First, a sodium polysulfide (Na_2S_4) solution (0.02 mol L^{-1}) was prepared. In a typical preparation, 0.3843 g (1.6 mmol) of $Na_2S\cdot 9H_2O$ was added to 80 mL of DI water under magnetic stirring at room temperature until dissolution. Then, 0.1536 g (4.8 mmol) of sulfur was added to the above solution under stirring. Ultrasonic assistance can be used to obtain a clear solution.

The second step was the synthesis of the $S@Ti_3C_2T_x$ composite. Typically, 200 mL of $Ti_3C_2T_x$ aqueous solution

(0.6 mg mL⁻¹) was mixed with 62.5 mL of Na₂S₄ solution (0.02 mol L⁻¹) and then stirred for 30 min. Then, 12.5 mL of formic acid (0.2 mol L⁻¹ HCOOH) solution was divided into 13 batches and slowly added to the above suspension. After addition, the pH of the solution was ~6. The mixed suspension was stirred for another 30 min and then allowed to stand for 30 min. During this process, the following disproportionation reaction occurred: Na₂S₄ + 2HCOOH → 2HCOONa + 3S↓ + H₂S↑. Sulfur nanoparticles were homogeneously nucleated and decorated *in-situ* on the Ti₃C₂T_x flakes. After centrifugation of the suspension at 9000 r min⁻¹ for 5 min, the precipitate was collected and freeze dried to obtain the S@Ti₃C₂T_x composite. Sulfur loading can be regulated by adjusting the mass ratios of Na₂S₄ and HCOOH to the D-Ti₃C₂T_x solution. In this paper, the mass fraction of sulfur in the S@Ti₃C₂T_x composite was ~36.6 wt%, according to the result of thermogravimetric analysis (TGA).

A binder-free sandwich structure S@Ti₃C₂T_x film was prepared using an alternating filtration method. Specifically, 5 mL of Ti₃C₂T_x solution was filtered through a cellulose membrane to yield a thin Ti₃C₂T_x layer. Then, 10 mL of S@Ti₃C₂T_x suspension was filtered on the top of the Ti₃C₂T_x layer. Afterward, another 5 mL of Ti₃C₂T_x solution was filtered on the top of the S@Ti₃C₂T_x layer to form a sandwich-like structure. The free-standing S@Ti₃C₂T_x film was obtained after complete freeze drying. Given that the concentrations of Ti₃C₂T_x solution and S@Ti₃C₂T_x suspension were both adjustable, the loading and proportion of each component of the sandwich structure film can also be adjusted. In this research, the mass ratio of the S@Ti₃C₂T_x composite to the Ti₃C₂T_x coating on the upper and lower surfaces was about 8:1:1. The typical loading of S@Ti₃C₂T_x film was about 1.84–2.21 mg cm⁻². Therefore, the corresponding sulfur loading was about 0.54–0.65 mg cm⁻².

Preparation of the S + Ti₃C₂T_x composite

As a reference, S + Ti₃C₂T_x composite was also prepared by a conventional slurry-coating method. The D-Ti₃C₂T_x flakes obtained after freeze drying and sulfur were mixed and ground evenly. The mass fraction of sulfur was ~36.6 wt%. The obtained S + Ti₃C₂T_x composite (active material) was mixed with acetylene black (conducting agent) and polyvinylidene difluoride (PVDF) binder at a mass ratio of 8:1:1 in *N*-methyl-2-pyrrolidone solvent. Then, the mixture was stirred to form a homogeneous slurry, which was uniformly coated onto a tantalum (Ta) foil current collector. Finally, the electrode disks were dried in a vacuum oven at 60°C for 12 h. The loading of the coated slurry on the Ta foil was within the same scope as the S@Ti₃C₂T_x film.

Theoretical calculations

The DFT-based first-principles calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [34]. For the optimization of the geometric structure, the projected augmented wave method [35,36] was applied to describe ion-electron interactions along with the Perdew-Burke-Ernzerhof exchange-correlation function within the generalized gradient approximation [37]. In all calculations, the DFT-D3 method was employed for the van der Waals correction [38]. The cutoff energy for the plane-wave basis was set at 520 eV, which is 30% larger than the VASP default values. The structure optimization continued until an energy convergence threshold of 10⁻⁵ eV and an atomic force threshold of 0.01 eV Å⁻¹ were reached. We

adopted a 4 × 4 × 1 supercell that contains 32 atoms for the single-atomic graphene layer (with lattice parameters of *a* = *b* = 9.84 Å) and a 3 × 3 × 1 supercell containing 63 atoms for the seven-atomic Ti₃C₂O₂ layer (with lattice parameters of *a* = *b* = 9.21 Å). To avoid a periodic image interaction between the two nearest neighbor unit cells, we set the vacuum space to 15 Å in the *c*-direction and employed the dipole correction. The Brillouin zone integration was performed using a 3 × 3 × 1 *k*-point mesh for all structure optimizations. The VASP kit was used for data processing and analysis [39].

Electrochemical measurement

The batteries were assembled with a Swagelok-type configuration in a glove box. The binder-free S@Ti₃C₂T_x and Ti₃C₂T_x films were cut into free-standing electrode disks with the diameter of 12 mm. The Swagelok-type battery was constructed with the cathodes (S@Ti₃C₂T_x film, S + Ti₃C₂T_x, and Ti₃C₂T_x film), Ta current collector, Al anode, a piece of glass fiber separator, and 100 μL mg_(total)⁻¹ IL electrolyte. The synthesis of IL electrolyte was performed in a glove box (O₂, H₂O < 1 ppm) by the slow addition of AlCl₃ powder to [EMIm]Cl under vigorous stirring. The mole ratio of AlCl₃/[EMIm]Cl was fixed at 1.3. After AlCl₃ was added, the resulting IL was continuously stirred for at least 12 h inside the glove box.

Galvanostatic charge/discharge measurements were tested on a LAND battery testing system (Wuhan, China) in the potential range of 0.01–1.8 V at room temperature. Current densities and specific capacities were calculated based on the mass of sulfur in the cathodes. For Ti₃C₂T_x film, the current density was calculated based on the assumed sulfur mass. Cyclic voltammetry (CV) experiments were tested in the range of 0.01–1.8 V *versus* Al/AlCl₄⁻ by a CHI 760E (Shanghai, China) electrochemical workstation after the batteries were cycled for 10 cycles at 250 mA g⁻¹. For each CV scan at scanning rates of 0.1–1 mV s⁻¹, the battery was scanned first from the open-circuit voltage to 0.01 V and increased to 1.8 V. Then, two full scans were performed, and the last full scan was selected to investigate the charge storage kinetics.

Characterization and analysis

The S@Ti₃C₂T_x film cathodes in different states were characterized by X-ray photoelectron spectroscopy (XPS). The discharged 0.01 V state and the charged 1.8 V state were obtained after 14 discharge-charge cycles at 250 mA g⁻¹. Then, the batteries were placed in the glove box for sample preparation. Fully charged or discharged cathodes were immersed in anhydrous methanol to dissolve the residual IL electrolyte. Then, the cathodes were dried in the glove box to remove methanol. Finally, the films were smashed and sealed in a glass bottle to avoid reactions with oxygen and moisture before characterization.

Scanning electron microscopy (SEM, Carl Zeiss Ultra55) and transmission electron microscopy (TEM, TALOS F200X) with energy-dispersive X-ray spectroscopy (EDS) were utilized to investigate the morphologies and microstructure. The X-ray diffraction (XRD) patterns were measured by a poly-functional X-ray diffractometer (D8 Advance, Bruker Corporation) using Cu Kα radiation at a scanning rate of 5° min⁻¹ in the 2θ range of 5°–70°. The electrical conductivity was measured by a 4-point-probe resistivity tester (RTS-8, Guangzhou Four-Probe Technology Co., Ltd). The X-ray photoelectron spectroscopy (XPS)

analyses of the cathodes were performed with an X-ray photoelectron spectrometer (Kratos Axis UltraDLD). TGA results were recorded on a thermogravimetric analyzer (STA 449F3, NETZSCH) under a N_2 atmosphere from room temperature to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Fig. 1 schematically shows the preparation of the binder-free $S@Ti_3C_2T_x$ film, pure $Ti_3C_2T_x$ film, and traditional $S + Ti_3C_2T_x$ cathodes for Al-S batteries. First, a multi-layered $Ti_3C_2T_x$ ($M-Ti_3C_2T_x$) was prepared by etching the Ti_3AlC_2 MAX (Fig. S1a) to form a porous lamellar structure (Fig. S1b) [40]. The delaminated $Ti_3C_2T_x$ ($D-Ti_3C_2T_x$) colloidal suspension was obtained by bath sonication, and it was enriched with predominantly single-layered flakes (Fig. S1c). After mixing the Na_2S_4 solution and $D-Ti_3C_2T_x$ suspension evenly, $HCOOH$ solution was added slowly, and the mixture was stirred to make the reaction uniform and sufficient. Given the reaction between Na_2S_4 and $HCOOH$, nano sulfur was formed *in-situ* on the $D-Ti_3C_2T_x$ flakes. After the reaction, the suspension was centrifuged, and the precipitate obtained was the $S@Ti_3C_2T_x$ composite.

The SEM image shows that after *in-situ* sulfur loading, the $S@Ti_3C_2T_x$ composite (Fig. 2b) was denser and cross-linked with each other than $D-Ti_3C_2T_x$ ultrathin flakes (Fig. 2a) with loose folds. The homogeneous distribution of S on the $D-Ti_3C_2T_x$ flakes was confirmed by EDS element mapping (Fig. S2). For comparison, the SEM and EDS images of $S + Ti_3C_2T_x$ composite (Fig. 2c and Fig. S3) obtained by mechanical grinding show uneven and caking morphology, and the undispersed sulfur particles were attached to the surface of $D-Ti_3C_2T_x$. Given that its surface contained electronegative functional groups (such as $-O$ and $-OH$), $D-Ti_3C_2T_x$ easily dispersed in water and provided abundant sites for sulfur nucleation. In addition, given the electrostatic interaction, the growth of sulfur on $D-Ti_3C_2T_x$ flakes was limited to the nanometer scale [41]. Therefore, the *in-situ* chemical sulfur loading method is conducive to the uniform distribution and fixation of sulfur. This finding was also confirmed by the TEM images (Fig. 2d–f). As shown in Fig. 2d, the $Ti_3C_2T_x$ flakes presented an ultrathin transparent laminated structure, to which the sulfur nanoparticles were homogeneously anchored, suggesting the good interaction between $Ti_3C_2T_x$

flakes and S. The High-resolution TEM (HRTEM) image (Fig. 2e) indicated two distinctly different lattices with spacings of ~ 0.344 and ~ 0.23 nm, which can be assigned to the S (026) and $Ti_3C_2T_x$ (103) planes, respectively [42], demonstrating that S and $Ti_3C_2T_x$ were present and closely connected. The EDS element mapping images of the $S@Ti_3C_2T_x$ composite in Fig. 2f suggest the homogenous distribution of C, S, Ti, O, and F in the hybrids.

XRD was employed to characterize the crystalline structures of Ti_3AlC_2 , $M-Ti_3C_2T_x$, $D-Ti_3C_2T_x$, and $S@Ti_3C_2T_x$ composite. As shown in Fig. 2g, h, the disappearance of the (104) peak of Ti_3AlC_2 at $\sim 39^\circ$ and the shifting of the (002) peak from $\sim 9.70^\circ$ to $\sim 8.23^\circ$ indicated that the MAX phase was completely etched onto $M-Ti_3C_2T_x$. With etching, delaminating, and sulfur loading, the (002) peak gradually moved to a lower angle, widened, and finally flattened, indicating that the interlayer spacing expanded and the crystallinity decreased. Using the Bragg formula, the interlayer spacing was calculated as $10.73 \text{ \AA}$ for $M-Ti_3C_2T_x$, whereas the values increased to $12.28 \text{ \AA}$ for $D-Ti_3C_2T_x$, with a significant increase of $1.55 \text{ \AA}$. The increase in the interlayer spacing of $D-Ti_3C_2T_x$ was beneficial to the dispersion of nano sulfur, and it was further promoted when a large amount of nano sulfur was adsorbed onto the surface of $Ti_3C_2T_x$. The evident sulfur peaks appeared in the XRD pattern of $S@Ti_3C_2T_x$ due to the high sulfur content. No peaks of anatase nor rutile type TiO_2 were observed, indicating that no remarkable oxidation of ultrathin $Ti_3C_2T_x$ occurred. TGA was conducted to determine the S content in the $S@Ti_3C_2T_x$ composite (Fig. 2i). A small weight loss ($\sim 6.1\%$) occurred at the onset temperature for the $D-Ti_3C_2T_x$ host material, presumably due to the release of entrapped structural water [43]. By contrast, a large weight loss ($\sim 42.7\%$) was observed for the $S@Ti_3C_2T_x$ composite. This finding suggests that the composite consisted of $\sim 36.6 \text{ wt\% S}$.

After vacuum filtration of $D-Ti_3C_2T_x$ colloidal suspension and freeze drying, the binder-free $Ti_3C_2T_x$ film was obtained (Fig. 3d). The cross-sectional SEM image (Fig. 3a) indicated that the thickness of the $Ti_3C_2T_x$ film was $\sim 7.4 \mu\text{m}$. The $Ti_3C_2T_x$ film exhibited a compactly stacked parallel lamellar structure, which provided the material with certain flexibility (Fig. S4). The EDS mapping images of the cross-section of $Ti_3C_2T_x$ film revealed that C, Ti, and O were distributed on the section (Fig. S5). In

Figure 1 Schematic of the fabrication of binder-free $S@Ti_3C_2T_x$ film, pure $Ti_3C_2T_x$ film, and traditional $S + Ti_3C_2T_x$ cathodes for Al-S batteries.

Figure 2 SEM images of (a) D-Ti₃C₂T_x flakes, (b) S@Ti₃C₂T_x composite, and (c) S + Ti₃C₂T_x composite. (d) TEM image of S@Ti₃C₂T_x composite. (e) HRTEM image of S@Ti₃C₂T_x composite. (f) Scanning TEM and EDS elemental mapping of S@Ti₃C₂T_x composite showing C, S, Ti, O, and F. (g and h) XRD patterns of Ti₃AlC₂ MAX, M-Ti₃C₂T_x, D-Ti₃C₂T_x, and S@Ti₃C₂T_x composite. (i) Thermogravimetric curves of S@Ti₃C₂T_x composite and D-Ti₃C₂T_x.

addition, the surface of the Ti₃C₂T_x film (Fig. S6) showed a compact and flat film structure, and the corresponding distribution of C, Ti, and O confirmed the existence of MXene flakes. An alternating filtration method was used to prepare the S@Ti₃C₂T_x film (Fig. 3d). First, the D-Ti₃C₂T_x suspension was filtered into a thin layer of Ti₃C₂T_x film. Then, the S@Ti₃C₂T_x suspension was filtered into a film on the top of the Ti₃C₂T_x layer. Finally, a thin layer of Ti₃C₂T_x film was covered on the upper layer to form a sandwich-like structure. The cross-sectional SEM image of the S@Ti₃C₂T_x film (Fig. 3b) shows that the total thickness was ~13 μm, and the thickness of the Ti₃C₂T_x coating on the upper or lower surfaces was ~1.3 μm. The Ti₃C₂T_x coating exhibited a layered stacking structure similar to that of the Ti₃C₂T_x film, whereas the S@Ti₃C₂T_x film in the middle part presented a folded cross-linked porous structure. In addition, the cross-sectional element mapping images of S@Ti₃C₂T_x film (Fig. 3c) show that S nanoparticles were uniformly distributed on the Ti₃C₂T_x flakes in the middle part. From the top-view SEM images and elemental mapping of the S@Ti₃C₂T_x film (Fig. S7), the surface was covered with a thin layer of Ti₃C₂T_x film. Given its very thin thickness, the uniform distribution of sulfur in the

S@Ti₃C₂T_x composite was also detected.

The prepared binder-free films (Fig. 3d and Fig. S4) show certain flexibility, and they can be cut into electrode pieces and directly used as the cathodes of AIBs. The measured electrical conductivity of the Ti₃C₂T_x film was 2954 S cm⁻¹, indicating that it can provide a good conductive network as a host material of sulfur. XPS was conducted to further analyze the chemical composition of the prepared Ti₃C₂T_x film. The full spectrum of the Ti₃C₂T_x film (Fig. S8) shows the peaks of C 1s, Ti 2p, O 1s, F 1s, and Cl 2p. However, the peak of Al 2p was not detected, indicating that the etching of Ti₃AlC₂ was relatively complete. The C 1s spectrum (Fig. 3e) can be fitted into four peaks at 282.2, 284.3, 286.4, and 288.8 eV corresponding to C-Ti, C-C, C-O, and O-C=O (or C-F) bonds, respectively, which indicate the presence of various functional groups on the surface of Ti₃C₂T_x [44,45]. These functional groups play an anchoring effect on sulfur and polysulfides. The high-resolution Ti 2p spectrum (Fig. 3f) reveals four pairs of asymmetric peaks corresponding to Ti-C, C-Ti-OH, C-Ti-O, and TiO₂ in the Ti₃C₂T_x film [46]. The binding energies at 455.24 and 460.1 eV were assigned to the Ti-C bond, and those at 455.81 and

Figure 3 Cross-sectional SEM images of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ film cathode and (b) $\text{S@Ti}_3\text{C}_2\text{T}_x$ film cathode. (c) Cross-sectional SEM of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film and the corresponding EDS elemental mapping images of C, S, and Ti. (d) Photographs of binder-free $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{S@Ti}_3\text{C}_2\text{T}_x$ films. High-resolution XPS spectra of (e) C 1s and (f) Ti 2p in the $\text{Ti}_3\text{C}_2\text{T}_x$ film.

461.5 eV belonged to $\text{Ti}^{2+} 2p_{3/2}$ and $\text{Ti}^{2+} 2p_{1/2}$, respectively. The binding energies at 456.94 and 462.6 eV were assigned to $\text{Ti}^{3+} 2p_{3/2}$ and $\text{Ti}^{3+} 2p_{1/2}$, respectively. The binding energies at 459.5 and 465.2 eV corresponded to $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$, respectively. The existence of multiple terminal groups may effectively suppress Li_2S_x dissolution and shuttling and exhibit effective electrocatalytic capability for Li_2S decomposition [47]. Based on the unique properties of $\text{Ti}_3\text{C}_2\text{T}_x$, a binder-free sandwich cathode was designed, and this electrode structure can greatly improve the performance of Al-S batteries.

Rate-capability tests were conducted at different current densities from 200 to 500 mA g^{-1} (Fig. 4a). Given the unique lamellar porous structure, the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film showed the highest discharge capacities of ~871, 456, 380, 288, and 246 mA h g^{-1} at 200, 250, 300, 400, and 500 mA g^{-1} , respectively. Notably, the capacity of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film was 246 mA h g^{-1} at 500 mA g^{-1} , which was more than twice that of $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ (119 mA h g^{-1}), indicating that the utilization rate of sulfur was significantly improved at high current densities. $\text{Ti}_3\text{C}_2\text{T}_x$ flakes cross-linked to form a porous network, which was conducive to the transport of ions in the electrolyte and the improvement of the rate performance of the Al-S battery. When the discharge rate was brought back to 300 mA g^{-1} , the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film showed a discharge capacity of 408 mA h g^{-1} after 34 cycles (273 mA h g^{-1} for $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$). This finding demonstrates that the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film had good reversibility and stability under different current densities. The capacity of $\text{Ti}_3\text{C}_2\text{T}_x$ film was consistently less than 85 mA h g^{-1} throughout the cycle. This result indicates that $\text{Ti}_3\text{C}_2\text{T}_x$ contributed an extremely low capacity to the battery.

The galvanostatic charge-discharge curves of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film, $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$, and $\text{Ti}_3\text{C}_2\text{T}_x$ film cathodes under different current densities were investigated to compare their performance differences (Fig. 4c–e). Given the low specific capacity of $\text{Ti}_3\text{C}_2\text{T}_x$

film, the changes in charge-discharge capacities at different current densities were negligible, and no evident charge-discharge platform was observed. By contrast, the charge-discharge capacities of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film and $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ decreased significantly with the increase of the current density. However, the rate capacities of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film were always higher than those of $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ and substantially higher than those of the $\text{Ti}_3\text{C}_2\text{T}_x$ film. In addition, both materials showed evident charge and discharge platforms due to the participation of sulfur in the electrode reaction. Fig. S9 shows that the potential gap (ΔV) between the charge and discharge plateaus of the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film was significantly lower than that of the $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ cathode at various current densities. The results indicate that the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film cathode can improve the utilization rate of sulfur, reduce the polarization significantly, and improve the electrode reaction kinetics. For the $\text{S@Ti}_3\text{C}_2\text{T}_x$ film, the curve recovery to 300 mA g^{-1} (the 31st cycle) showed higher discharge voltage and lower potential gap between charge and discharge plateaus than the previous curves at 300 mA g^{-1} (the 14th cycle). The reason may be the full activation of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film cathode after more than 25 cycles under different rates. In addition, the electrolyte fully penetrated and contacted with the active material, thus significantly reducing the polarization.

Fig. 4b displays the cycling performances of $\text{S@Ti}_3\text{C}_2\text{T}_x$ film, $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$, and $\text{Ti}_3\text{C}_2\text{T}_x$ film cathodes at 300 mA g^{-1} . The $\text{S@Ti}_3\text{C}_2\text{T}_x$ film exhibited a reversible capacity of 489 mA h g^{-1} after the initial short-term activation, and the capacity remained at 415 mA h g^{-1} after 280 stable cycles. By contrast, the initial maximum capacity of the $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ cathode reached 317 mA h g^{-1} and then gradually decayed to 222 mA h g^{-1} after 160 cycles. The capacity of the previously reported binder-free film electrode [7,10] and VS_4 nanowires [48] also increased in the first dozens of cycles, which may be due to the need for the penetration of electrolyte to the cathode, especially sulfur, at

Figure 4 (a) Rate performances of S@Ti₃C₂T_x film, S + Ti₃C₂T_x, and Ti₃C₂T_x film cathodes from 200 to 500 mA g⁻¹. (b) Cycling performances of S@Ti₃C₂T_x film, S + Ti₃C₂T_x, and Ti₃C₂T_x film cathodes at 300 mA g⁻¹. Galvanostatic discharge-charge curves of (c) S@Ti₃C₂T_x film, (d) S + Ti₃C₂T_x, and (e) Ti₃C₂T_x film cathodes at various current densities. CV curves of (f) S@Ti₃C₂T_x film, (g) S + Ti₃C₂T_x, and (h) Ti₃C₂T_x film cathodes for the first three cycles at 0.1 mV s⁻¹.

high current densities. In the activation process, the CE was higher than 100% [49], which may be due to the side reactions of the electrolyte, such as the electrolyte decomposition and the formation of solid electrolyte interface (SEI) layer. After the activation, the average CEs of the S@Ti₃C₂T_x film and S + Ti₃C₂T_x were ~95% and ~102%, respectively. At present, the reported AIBs have unreasonable CE, such as those with a CE greater than 100% [9,32,49], whereas most literature lacks information on CE [10,14,33]. In this paper, the unreasonable CE was due to the formation of the SEI layer and the side reaction caused by electrode materials (such as polysulfides) and IL. For the Ti₃C₂T_x film, the initial capacity was 93 mA h g⁻¹ and the capacity of 41 mA h g⁻¹ remained after 160 cycles, which verified that the high capacity of the S@Ti₃C₂T_x film mainly originated from sulfur. Fig. S10 shows the charge-discharge curves of the S@Ti₃C₂T_x film, S + Ti₃C₂T_x, and Ti₃C₂T_x film cathodes at 300 mA g⁻¹. Only the S@Ti₃C₂T_x film and S + Ti₃C₂T_x had evident platforms, which verified that sulfur was the main capacity source. Meanwhile, the voltage hysteresis between the charge and discharge curves of S@Ti₃C₂T_x film (Fig. S10a)

decreased with the increase in cycles, which implied a low barrier of reaction kinetics. By contrast, S + Ti₃C₂T_x (Fig. S10b) showed lower specific capacity and higher voltage hysteresis, indicating poorer S utilization and lower reversibility. At a high current density of 400 mA g⁻¹, S@Ti₃C₂T_x film still showed a good cycle performance (Fig. S11). The film achieved a maximum capacity of 566 mA h g⁻¹ at the 18th cycle and retained 248 mA h g⁻¹ at the end of the 250th cycle. By contrast, the Ti₃C₂T_x film delivered a maximum capacity of 76 mA h g⁻¹, with 38 mA h g⁻¹ remaining after 250 cycles.

The CV curves of S@Ti₃C₂T_x film, S + Ti₃C₂T_x, and Ti₃C₂T_x film cathodes (Fig. 4f–h) were measured at 0.1 mV s⁻¹ between 0.01 and 1.8 V. For the S@Ti₃C₂T_x film (Fig. 4f), a wide peak at 0.279 V (R₁) indicated the reduction of S to S²⁻ during the aluminization reaction. Meanwhile, the corresponding oxidation peaks at 1.046 (O₁) and 1.705 V (O₂) can be assigned to the oxidation of S²⁻ to S_x²⁻ and S_x²⁻ to S during the dealuminization reaction, respectively. The redox peaks in the second and third curves were relatively stable, demonstrating remarkable cycling stability and excellent reversibility of the S@Ti₃C₂T_x film. For

comparison, the CV curves for S + Ti₃C₂T_x (Fig. 4g) showed a wide reduction peak at 0.279 V (R₁) and two oxidation peaks at 1.36 (O₁) and 1.73 V (O₂). The voltage hysteresis of S + Ti₃C₂T_x (1.081 V) between the redox peaks R₁–O₁ was considerably greater than that of S@Ti₃C₂T_x film (0.767 V), demonstrating that the S@Ti₃C₂T_x film cathode exhibited a smaller polarization and enhanced reversibility. In addition, a shrinkage in the redox peaks with prolonged cycling agreed with the capacity decay behavior of S + Ti₃C₂T_x. The peak intensities and integral areas were less than those of the S@Ti₃C₂T_x film, which suggested a low specific capacity. For the Ti₃C₂T_x film (Fig. 4h), a small peak at 0.865 V (R₁) proved the reduction of [AlCl₄][−] to [AlCl₄][−] during the deintercalation of [AlCl₄][−]. Meanwhile, the corresponding oxidation peaks at 0.57 (O₁) and 1.03 V (O₂) can be ascribed to the oxidation of [AlCl₄][−] to [AlCl₄] during the staged intercalation of [AlCl₄][−]. However, the peaks almost disappeared, and the integral areas were negligible compared with those of the S@Ti₃C₂T_x film, which suggests that sulfur was a key contributor to the total capacity of the S@Ti₃C₂T_x film.

To further explore the charge storage kinetics, we determined the CV curves of S@Ti₃C₂T_x and Ti₃C₂T_x film cathodes in the sweep rate range of 0.2–1 mV s^{−1} (Fig. 5a, d). The charge storage mechanism can be distinguished through Equations (1) and (2):

$$i = av^b, \quad (1)$$

$$\log i = \log a + b \log v, \quad (2)$$

where i is the measured current density (A g^{−1}), v is the scan rate (mV s^{−1}), and a and b are fitting constants. The slope of the $\log i$ – $\log v$ plots corresponds to the b -value, which reflects the electrochemical reaction mechanism. A b -value close to 0.5 indicates that ion diffusion control is dominant, whereas a b -value close to 1 indicates the dominant role of the pseudocapacitive effect. Fig. 5b displays the b -value for each redox peak (R₁, O₁, and O₂) of the S@Ti₃C₂T_x film, namely, 0.70, 0.91, and 0.75, respectively. Equations (3) and (4) can be applied to quantitatively separate the contributions of the diffusion-controlled process and surface-limited capacitive behavior:

$$i(V) = k_1 v + k_2 v^{1/2}, \quad (3)$$

$$i / V^{1/2} = k_2 + k_1 v^{1/2}, \quad (4)$$

where $k_1 v$ and $k_2 v^{1/2}$ represent the capacitive and diffusion contributions, respectively. The fraction of current due to each of these contributions can be quantified by k_1 and k_2 , which are fitted from Equation (4) (Fig. S12a). The pink boxes in Fig. 5c show the ion-diffused behavior, whereas the orange ones denote the pseudocapacitance behavior. The capacitive behavior of the S@Ti₃C₂T_x film increased gradually as the scan rate increased. For R₁, although the contribution of capacitance increased from 30.7% to 49.7%, the diffusion-controlled process, which can impart improved energy characteristics, still played a leading role. This finding can be due to the sluggish diffusion of Al³⁺ in the Al₂S₃ and at the S/Al₂S₃ interface during sulfur reduction. For O₁ and O₂, the proportion ranges of capacitance contribution that can produce improved power characteristics were 73.0%–85.8% and 41.6%–61.4%, respectively. This result means that the kinetics of the oxidation of S^{2−} to S_x^{2−} in the former stage was faster than that of S_x^{2−} to S in the latter stage. Compared with that of the S@Ti₃C₂T_x film, the peak position of the Ti₃C₂T_x film was significantly different (Fig. 5d), and the peak intensity was greatly reduced. Fig. 5e shows the b -value for each

redox peak (R₁, O₁, and O₂) of the Ti₃C₂T_x film, that is, 0.91, 1.0, and 0.87, respectively. The fraction of the current due to capacitive and diffusion contributions can be quantified by the linear relationship in Fig. S12b. Fig. 5f shows that for R₁, the contribution of capacitance reached 74.3%–86.6%. For O₂, the contribution of capacitance was 66.5%–81.6%, and almost all the capacity of O₁ originated from the contribution of capacitance. This finding indicates that the intercalation and deintercalation of [AlCl₄][−] between Ti₃C₂T_x layers were mainly a surface-controlled pseudocapacitance behavior. The intensity of the redox peaks in the Ti₃C₂T_x film was very weak compared with that of the S@Ti₃C₂T_x film, which again verified that S was the main source of capacity in the S@Ti₃C₂T_x film. Given the instability of S + Ti₃C₂T_x cathode (such as uneven sulfur dispersion and shuttle of polysulfides), the oxidation peaks in the CV curves under different scanning rates were inevident and irregular (Fig. S12c). Meanwhile, the reduction peaks were relatively remarkable and have been used to study the charge storage kinetics. Fig. S12d displays that the b -value for the reduction peak (R) of S + Ti₃C₂T_x was 0.53, which revealed that the diffusion-controlled process was dominant, and the kinetics of the reduction of S to S^{2−} was slower than that of the S@Ti₃C₂T_x film.

To further elucidate the electrochemical reaction mechanism of the S@Ti₃C₂T_x film, we conducted XPS tests on the surface of the cathodes in different states: pristine cathode discharged to 0.01 V and charged to 1.8 V. Fig. S13 shows the results of the full spectra. The pristine cathode mainly contained C, Ti, S, O, Cl, and F. Compared with the Ti₃C₂T_x film, the cathode lacked Al, and S appeared due to sulfur loading. In the fully charged or discharged cathode, Al emerged, and it originated from either the discharge product (polysulfide/sulfide) or the trapped electrolyte. Fig. 5g–j show the narrow spectrum results. The C 1s in the pristine S@Ti₃C₂T_x film was mainly composed of C–Ti (282 eV) and C–C bonds (284.5 eV) and a small amount of C–O (286.4 eV) and O–C=O (C–F) (288.8 eV) bonds. After more than ten cycles of activation, the relative strength of the C–O bond and O–C=O (C–F) bond increased in the cathodes with the charged or discharged state. This result is probably due to the intercalation and deintercalation of [AlCl₄][−] in the Ti₃C₂T_x flakes, resulting in the exposure of more functional groups on its surface. The Ti 2p spectra of S@Ti₃C₂T_x film in different states (Fig. 5h) displayed four pairs of asymmetric Ti 2p_{3/2} and Ti 2p_{1/2} orbital splitting peaks corresponding to Ti–C, Ti²⁺, Ti³⁺, and Ti⁴⁺. Table S1 shows the binding energy and percentage of Ti–C, Ti²⁺, Ti³⁺, and Ti⁴⁺ in the S@Ti₃C₂T_x film in different states. The binding energies of Ti–C (455.15/460.3 eV), Ti²⁺ (455.8/461.5 eV), Ti³⁺ (456.9/462.6 eV), and Ti⁴⁺ (459.3/465 eV) in the S@Ti₃C₂T_x film remained stable after charging and discharging. However, the proportion of each component changed slightly. For Ti⁴⁺, after charging and discharging, the proportion decreased from 10.1% to 9.2% and 9.2%, respectively. For Ti³⁺, after charging and discharging, the proportion decreased from 46.3% to 42.7% and 43.3%, respectively. The original proportion of Ti²⁺ was 29.2%, which increased to 33.1% after charging and 29.8% after discharging. The original proportion of Ti–C was 14.4%, which increased to 15.0% after charging and 17.8% after discharging. The slight changes in the valence states of Ti may be caused by the insertion and removal of [AlCl₄][−] during charging and discharging. On the other hand, this phenomenon may be caused by the interaction between Ti₃C₂T_x and polysulfides produced by electrochemical reactions. This finding implies that

Figure 5 CV curves of (a) S@Ti₃C₂T_x film and (d) Ti₃C₂T_x film cathodes at scan rates of 0.2–1 mV s⁻¹. (b and e) Logarithmic curve of peak current versus scan rate from (a and d), respectively. (c and f) Relative contribution of the capacitive and battery behaviors at various scan rates (0.2–1 mV s⁻¹). XPS spectra of the C 1s (g), Ti 2p (h), Al 2p (i), and S 2p (j) regions of the S@Ti₃C₂T_x film in different states.

the main role of Ti₃C₂T_x was assisting in the charge and ion transport between conductive matrix and polysulfides, but it contributed little to the capacity.

Fig. 5i shows the XPS spectra of Al 2p. No Al 2p signal was detected before charging/discharging, indicating that Al in Ti₃AlC₂ was likely to be completely etched. The peak of Al 2p was observed after charging and discharging due to the [AlCl₄]⁻ intercalation/deintercalation between the layers of Ti₃C₂T_x. The Al 2p signal was still observed after discharging, indicating that either the [AlCl₄]⁻ was not completely de-intercalated, or the discharge products Al₂S₃ or Al₂S_x were generated. Fig. 5j presents the S 2p spectra of the S@Ti₃C₂T_x film cathode in various states. The S 2p spectrum of the pristine cathode contained two components at 163.27 and 164.43 eV, which were attributed to the S 2p_{3/2} and S 2p_{1/2} bands for elemental sulfur (S₂₋₄), respectively. The absence of the S–Ti bond (162.3 eV) [50] indicated that no

chemical bond formed during the *in-situ* solution growth of sulfur at room temperature. After discharging, two new peaks appeared at 161.65 and 162.81 eV, which were attributed to the S 2p_{3/2} and S 2p_{1/2} bands for fully reduced sulfur (S²⁻), respectively. This result indicates that S was partially reduced to S²⁻ species after discharging to 0.01 V at a high current density. This result is consistent with the capacity of the S@Ti₃C₂T_x film at 250 mA g⁻¹, that is, 456 mA h g⁻¹, which is considerably lower than the theoretical capacity of S (1675 mA h g⁻¹) [14]. When charging to 1.8 V, the peak intensity of S²⁻ species weakened and almost disappeared, indicating that most of the sulfide species were oxidized to sulfur, which further proved the reversibility and stability of the S@Ti₃C₂T_x film cathode. As a reference, the XPS S 2p spectra of the S + Ti₃C₂T_x cathodes in charge/discharge states were detected (Fig. S14). After full discharge, S⁰ (164.16/165.32 eV), S⁻ (162.41/163.57 eV), and

S^{2-} (161.18/162.34 eV) components appeared in the S 2p spectra of S + $Ti_3C_2T_x$. This finding indicates that a part of sulfur was reduced to polysulfides and sulfides. After charging, the relative contents of sulfide and polysulfides decreased, indicating that they were partially oxidized to sulfur again. No evident S^{2-} peaks were detected in the S@ $Ti_3C_2T_x$ film cathode, but they were detected in S + $Ti_3C_2T_x$. Thus, the S@ $Ti_3C_2T_x$ film had a strong anchoring effect on polysulfides and improved the reversibility of their transformation. By contrast, S + $Ti_3C_2T_x$ contained PVDF, which is easily corroded, and the anchoring effect of conductive carbon black on polysulfides was very weak. Thus, the polysulfides were easily separated and exposed from the conductive matrix. This condition will lead to the shuttle effect and poor reversibility. Photographs of the separator and Al foil after cycling (Figs S15 and S16) also confirmed the shuttle effect. After 14 cycles, S + $Ti_3C_2T_x$ disintegrated and penetrated into the separator and reached the Al anode. This finding shows that the polysulfides produced by the traditional electrode structure are easy to separate from the conductive matrix, resulting in capacity attenuation and poor reversibility.

The above analyses and previous literature [15,19] suggest that aluminum polysulfides (Al_2S_x , $x = 3, 6, 12, 18$) produced in the process of charging and discharging will cause the shuttle effect, resulting in the deterioration of battery performance. Here, we used DFT calculations to predict the adsorption of polysulfides on $Ti_3C_2T_x$ and used common graphene materials as a reference to highlight the advantages of $Ti_3C_2T_x$. Graphene cannot be well dispersed in water for *in-situ* sulfur loading and cannot be filtered into a self-supporting film such as $Ti_3C_2T_x$. Thus, this paper cannot compare and verify the performance of $Ti_3C_2T_x$ and graphene experimentally. The theoretical calculation results can provide a possible explanation for the excellent performance of $Ti_3C_2T_x$ in this paper and useful guidance for future research. The structures of sulfur (S_8) and Al_2S_x were optimized first to find the most stable conformations. Fig. 6a shows the optimal structures of S_8 and Al_2S_3 , where S_8 is a 3D crown-like orthorhombic structure, Al_2S_3 prefers a planar bent structure, and with more S atoms of Al_2S_x , the structures preferentially form 3D cluster shapes without dangling bonds to be geometrically stable. Fig. S17 provides more details on the structures. Fig. 6b shows the optimized structure of the $4 \times 4 \times 1$ supercell of the monolayer graphene, with lattice constants of $a = b = 9.84 \text{ \AA}$, which is highly consistent with experimental data [51,52]. Fig. 6c shows the optimized structure of $3 \times 3 \times 1$ supercell of $Ti_3C_2O_2$ with oxygen as the terminal sites and lattice constants of $a = b = 9.21 \text{ \AA}$. More lattice parameters are provided in Table S2. The optimized conformations of S_8 and Al_2S_x on the monolayer graphene and $Ti_3C_2O_2$ are provided in Fig. 6d, e (side view) and Figs S18 and S19 (top view), where the S_8 , Al_2S_x monolayer graphene, and $Ti_3C_2O_2$ showed no serious structural deformation, indicating the relatively strong physical interactions between them. Fig. 6f shows the energies of S_8 and Al_2S_x , corresponding to those in Fig. 6a, and the energies of S_8 and Al_2S_x on graphene and $Ti_3C_2O_2$ are provided in Table S3. The binding energies corresponding to the most stable sites of S_8 and Al_2S_x on the monolayer graphene (blue) and $Ti_3C_2O_2$ (red) are shown in Fig. 6g, where the binding energies of S_8 and Al_2S_x on $Ti_3C_2O_2$ were $-0.98, -5.01, -2.92, -1.22$, and -1.31 eV , which were notably lower than those of S_8 and Al_2S_x on the monolayer graphene. Thus, $Ti_3C_2O_2$ can enhance its adsorption significantly with S_8/Al_2S_x and effectively inhibit the shuttle effect of poly-

sulfides. Fig. 6h shows the calculated Gibbs free energy diagrams of the main reactions from S_8 to Al_2S_3 ($S_8 \rightarrow Al_2S_{18} \rightarrow Al_2S_{12} \rightarrow Al_2S_6 \rightarrow Al_2S_3$) on the monolayer graphene (blue) and $Ti_3C_2O_2$ (red). The reaction from S_8 to Al_2S_3 was spontaneous given the negative change in Gibbs free energy, and $Ti_3C_2O_2$ was more conducive to promoting the occurrence of this reaction (-4.17 eV for $Ti_3C_2O_2$ and -3.32 eV for graphene). For $Ti_3C_2O_2$, the conversion from Al_2S_{18} to Al_2S_x ($x = 12, 6, 3$) was nearly a thermodynamical equilibrium, and the maximum reaction energy of Al_2S_{12} to Al_2S_6 was 1.12 eV , which was considerably lower than that (2.82 eV) on graphene. Therefore, these theoretical analyses indicate that $Ti_3C_2O_2$ can significantly reduce the reaction energy barrier of polysulfide conversion and improve the reversibility of Al-S batteries.

Based on the above results, the discharge-charge reaction mechanism of the Al-S batteries can be reasonably expressed as follows (the arrows to the right and left denote the charging and discharging reaction, respectively).

For the $Ti_3C_2T_x$ cathode:

For the S@ $Ti_3C_2T_x$ film cathode:

For the $Ti_3C_2T_x$ film cathode, its low capacity mainly originated from the intercalation and deintercalation of $[AlCl_4]^-$ in the $Ti_3C_2T_x$ flakes. For the S@ $Ti_3C_2T_x$ film cathode, its high capacity mainly came from the redox reaction between S^{2-} and S. The intermediate processes were accompanied by the formation of polysulfides, and the conversion of sulfur was incomplete at high rates. The corresponding anodic reactions of the two cathodes were the same, that is, the deposition and dissolution of Al in the acidic IL electrolyte. Fig. 7 compares the working-principle diagrams of the S + $Ti_3C_2T_x$ and S@ $Ti_3C_2T_x$ film cathodes. The S + $Ti_3C_2T_x$ cathode had the following problems: The PVDF binder was easily corroded and dissolved by IL, resulting in the destruction of the electrode structure. In addition, the traditional conductive carbon black has poor adsorption performance for polysulfides, resulting in the easy loss of discharge products. Therefore, the S + $Ti_3C_2T_x$ cathode showed disadvantages, such as low capacity, fast attenuation, and short cycle life, due to the evident shuttle effect. By comparison, the unique electrode structure design of the S@ $Ti_3C_2T_x$ film cathode improved its performance: the uniform dispersion of sulfur and porous layered cross-linked conductive channels greatly improved the utilization of sulfur. Thus, it still attained a high specific capacity at high current densities. The $Ti_3C_2T_x$ coatings on the upper and lower surfaces of the film formed a sandwich structure, which can effectively prevent the shedding of active materials and alleviate the shuttling of polysulfides to maintain high capacity and long cycle life. Compared with the recently reported cathode materials for AIBs (Table S4), the S@ $Ti_3C_2T_x$ film exhibited numerous advantages, such as high specific capacity and capacity retention at a high rate, long cycle life, and reasonable CE.

CONCLUSIONS

In summary, we demonstrated a stable Al-S battery using an elaborately designed binder-free S@ $Ti_3C_2T_x$ sandwich structure film with uniform sulfur dispersion as the cathode. The

Figure 6 Theoretical computations. (a) Optimal structures of S_8 and Al_2S_x ($x = 3, 6, 12, 18$). (b) Top and side views of the optimal structure of monolayer graphene. (c) Top and side views of optimal structures of $Ti_3C_2O_2$. (d) Optimized structures of S_8 and Al_2S_x on monolayer graphene (side view). (e) Optimized structures of S_8 and Al_2S_x on $Ti_3C_2O_2$ (side view). (f) Energies of optimal structures of S_8 and Al_2S_x . (g) Binding energies of S_8 and Al_2S_x on monolayer graphene (blue) and $Ti_3C_2O_2$ (red). (h) Gibbs free energy profiles of S_8 and Al_2S_x on monolayer graphene (blue) and $Ti_3C_2O_2$ (red).

$S@Ti_3C_2T_x$ film showed an initial capacity of 489 mA h g^{-1} at 300 mA g^{-1} and retained a value of 415 mA h g^{-1} after 280 stable cycles, with an average CE of $\sim 95\%$. This film displayed a higher capacity and stability than the $S + Ti_3C_2T_x$ cathode prepared by the slurry-coating method (the initial capacity was 317 mA h g^{-1} , and it decayed to 222 mA h g^{-1} after only 160

cycles). Various characterizations confirmed that the high capacity comes from the reversible redox reaction of S^{2-} and S . The 2D layered material $Ti_3C_2T_x$ has the function of not only a binder but also a conductive agent. In addition, DFT calculation results predict that $Ti_3C_2T_x$ has a stronger binding energy toward Al polysulfides compared with graphene, which means that it is

Figure 7 Schematic illustration of the electrochemical reactions of S@Ti₃C₂T_x film and S + Ti₃C₂T_x cathodes in working Al-S batteries.

a more promising host material for sulfur anchoring. This novel electrode material prepared by a simple and controllable method paves a new way for the development of high-performance Al-S batteries in the future.

Received 24 September 2021; accepted 29 November 2021;
published online 19 January 2022

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Acknowledgements This work was supported by the National Natural Science Foundation of China (51272155, 21875061, 21975066 and 21901157), the Open Research Fund Program of Science and Technology on Aerospace Chemical Power Laboratory (STACPL 120201B05), and the National Key R&D Program of China (2021YFC2100100).

Author contributions Zheng X and Wei L designed the project; Zheng X performed the main experiments and drafted the manuscript; Wang Z and Li J conducted the theoretical calculation. All authors participated in the manuscript revision.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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无粘结剂 $\text{S@Ti}_3\text{C}_2\text{T}_x$ 三明治结构薄膜作为铝硫电池的 稳定、高容量正极

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摘要 铝硫二次电池是一种具有高能量密度、廉价原材料、有前途的替代储能装置。然而, 铝硫电池面临着一些障碍, 尤其是穿梭效应。本工作设计了一种硫分散均匀的无粘结剂 $\text{S@Ti}_3\text{C}_2\text{T}_x$ 三明治结构薄膜。二维层状材料 $\text{Ti}_3\text{C}_2\text{T}_x$ 不仅具有粘结剂和导电剂的功能, 而且是一种很有前途的硫锚定载体。 $\text{S@Ti}_3\text{C}_2\text{T}_x$ 膜在 300 mA g^{-1} 时显示出初始容量为 489 mA h g^{-1} , 并在280圈稳定循环后保持为 415 mA h g^{-1} , 平均库仑效率约为95%。该薄膜的容量和稳定性均高于采用浆料涂覆法制备的 $\text{S} + \text{Ti}_3\text{C}_2\text{T}_x$ 正极(初始容量为 317 mA h g^{-1} , 循环160圈后衰减为 222 mA h g^{-1})。 $\text{S@Ti}_3\text{C}_2\text{T}_x$ 膜在铝硫电池中的容量主要来源于 S^{2-} 和 S 之间的可逆氧化还原反应。这种新颖的二维材料与可控的电极结构设计相结合, 为铝硫电池的发展铺平了道路。