

## Supporting Information

### Two-Dimensional composite of D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub> (MXene) as Cathode Material for Aluminum-ion Batteries

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### Experimental Section

#### Preparation of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

Firstly, weighed 30mL of 40% HF acid in a ventilated kitchen, and placed it in a 100mL Teflon reactor. Then weighed 2g of Ti<sub>3</sub>AlC<sub>2</sub> powder, and added it to HF acid with a plastic key slowly. Stirring reaction by magnetic stirring at room temperature for 12 h, then the solid-liquid phase was centrifuged by a centrifuge (10000 rpm, 5 min), and centrifuged with deionized water (3500 rpm, 5 min) until the pH of the supernatant was close to 6, then transferred the solid-liquid mixed phase to a vacuum pumping flask and washed it with 1000 mL of deionized water again. Finally, placed it in a vacuum drying oven, and dried at 80 °C for 12 h, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> powder was obtained.

#### Preparation of D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

Firstly, weighed 200 mg of prepared Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> powder, and placed it in 4 mL of DMSO solution. Stirring reaction by magnetic stirring at room temperature for 18 h, then the solid-liquid phase was centrifuged by a centrifuge (10000 rpm, 5 min), followed washed 2-3 times by absolute ethanol to remove excess DMSO. Then the sample was placed in 2 mL absolute ethanol and sonicated for 3 h under high power conditions,

and transferred the solid-liquid mixed phase to a vacuum pumping flask and washed it with 500 mL of deionized water. Finally, placed it in a vacuum drying oven, and dried at 80 °C for 12 h, D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> powder was obtained.

### Preparation of D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S

The stripped D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and elemental sulfur were weighed according to a mass ratio of 1:1, and ground uniformly with an agate mortar, then placed it in a tube furnace with a quartz boat as carrier. Firstly, under the condition that argon gas is shielding gas, the temperature was raised to 600 °C and kept for 2 h (heating rate is 5 °C min<sup>-1</sup>).

### Preparation of D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>

The stripped D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and elemental sulfur were weighed according to a mass ratio of 1:1, and ground uniformly with an agate mortar, then placed it in a tube furnace with a quartz boat as carrier. Firstly, under the condition that argon gas is shielding gas, the temperature was raised to 600 °C and kept for 2 h (heating rate is 5 °C min<sup>-1</sup>). Secondly, under the condition that oxygen gas is shielding gas, and kept for 2 h at 200 °C. Finally, the material was cooled to room temperature, and obtained D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>.

### Battery assembly

The as-prepared active material (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>), conductive carbon black, and polytetrafluoroethylene (PTFE) binder were ground evenly at a mass ratio of 8:1:1 for 15 minutes. After that, the mixture was added to 3 ml of organic solvent N-methyl-2-pyrrolidone (NMP) and then sonicated for 1 h to form a homogeneous slurry. The slurry was casted onto a molybdenum (Mo) foil current collector, and then dried at 60 °C for 12 h in an oven to obtain the cathode. A room-temperature ionic liquid electrolyte was made by mixing anhydrous aluminum chloride (AlCl<sub>3</sub>) and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) at a molar ratio of 1.3:1 in a glove box filled with high purity argon gas. The mixture was then homogeneously stirred and mixed to give a pale yellow ionic liquid, which was used as the rechargeable aluminum batteries electrolyte. The high purity aluminum foil after ethanol cleaning was used as the anode, and a Whatman glass fiber (GF/C) was

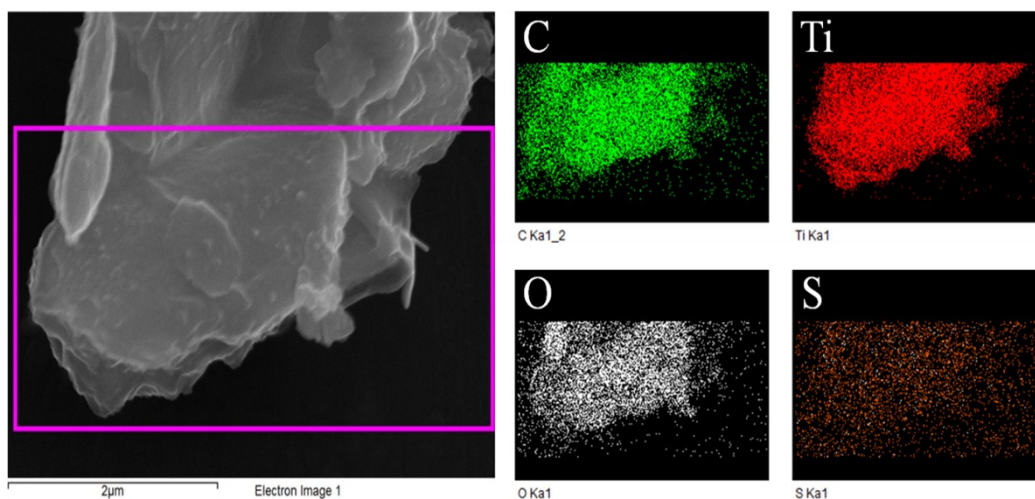
used as the separator. In addition, the assembly process of the battery is carried out in a glove box.

## Electrochemical tests

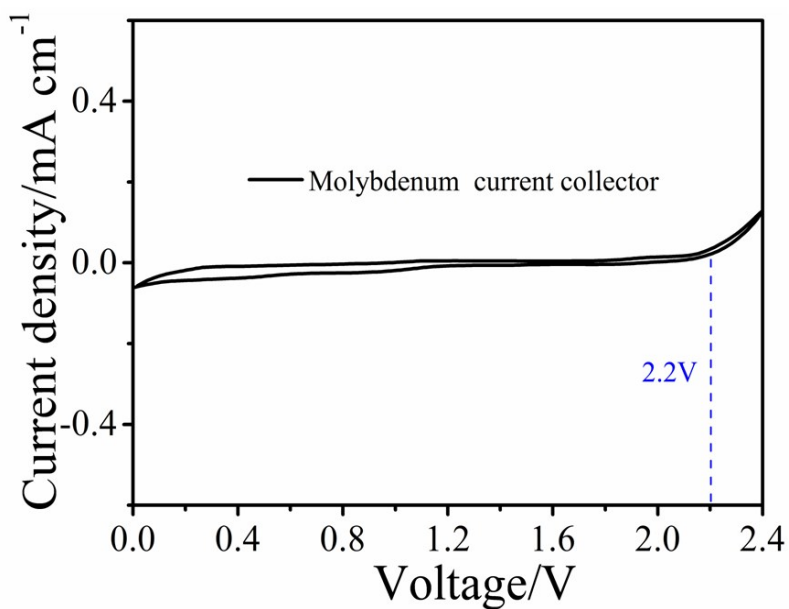
The galvanostatic charge/discharge performance of the cells were executed in the range of 0.45 V-2.2 V using a Land battery test system (CT2001A Wuhan, China), and the cycling tests were conducted at the current density of 100 mA g<sup>-1</sup> for 120 cycles. The cyclic voltammetry (CV) tests were performed by VMP2 electrochemical workstation at the scan rate of 0.2 mV s<sup>-1</sup> in the voltage range of 0.45-2.2 V (vs. Al). The electrochemical impedance spectroscopy (EIS) measurements were carried out by VMP2 electrochemical system with amplitude of 10.0 mV in the frequency range of 100 kHz to 10 mHz. All tests were carried out at room temperature.

## Characterization

The field-emission scanning electron microscopy (FESEM, Zeiss SUPRATM 55), energy-dispersive energy dispersive X-ray spectrometry (EDS) mapping and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30) determined the detailed morphology and microstructure of the as-prepared material (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>). The phase composition of the as-prepared powders was determined by power X-ray diffraction (XRD, Rigaku RINT2400) within the 2θ range 5-60° using Cu Kα radiation (λ=0.154056 nm) at a scan rate of 5°·min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements and analyses of the samples were performed with a Kratos AXIS UltraDLD X-ray Photoelectron Spectrometer equipped with an Al anode (Al K=α1486.6 eV). The thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) was performed under Ar<sub>2</sub> atmosphere with the heating rate of 10 °C /min.



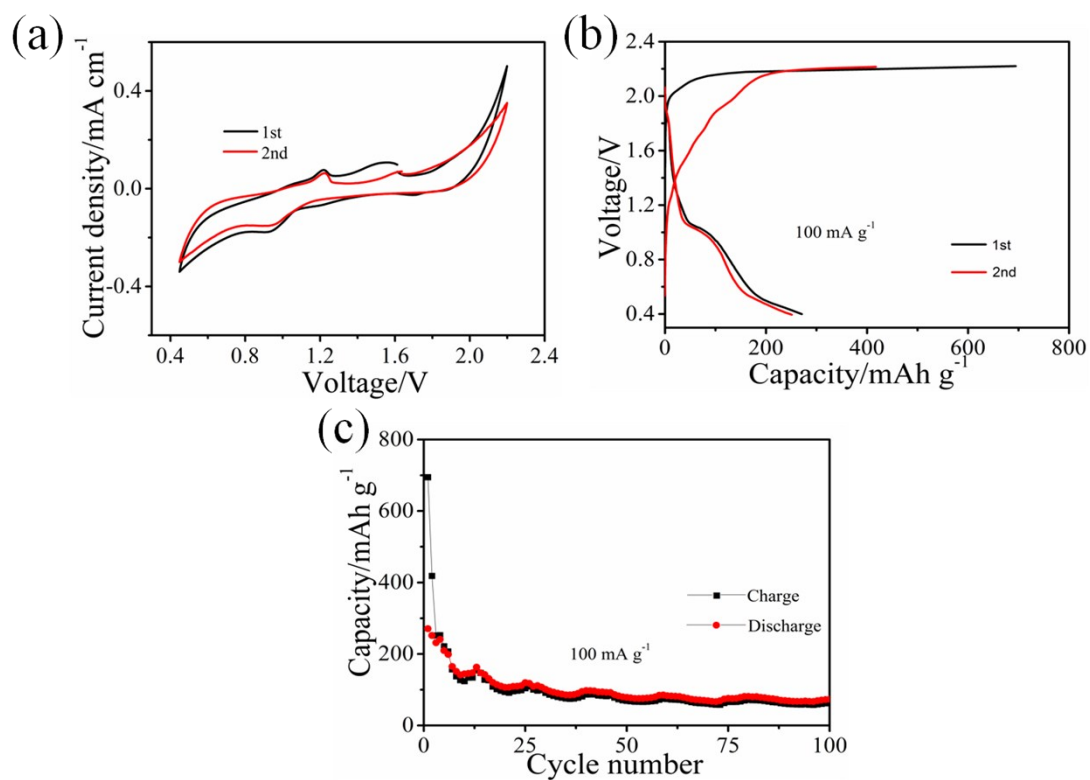
**Fig. S1** The mapping diagrams of D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>.



**Fig. S2** CV curve of molybdenum current collector.

**Table S1** The cycle performance with Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> as cathode materials in aluminum-ion batteries.

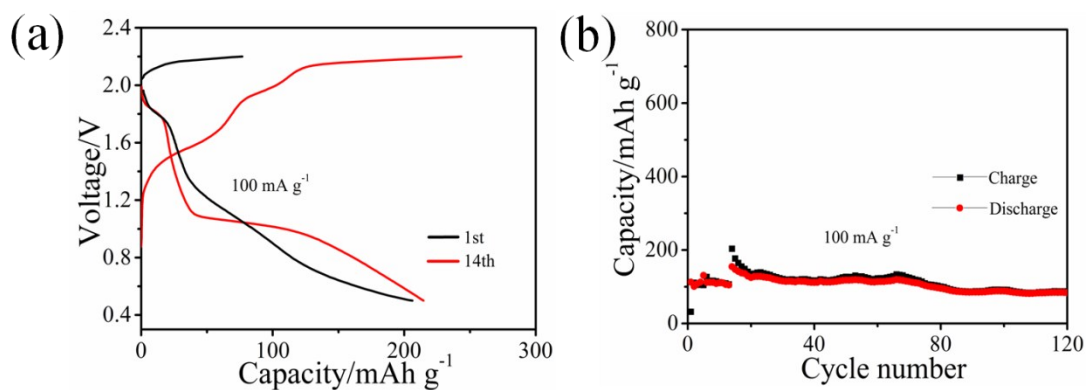
Cycle	Discharge (mAh g <sup>-1</sup> )	Charge (mAh g <sup>-1</sup> )
1 <sup>st</sup>	245.5	775
2 <sup>nd</sup>	204	224
5 <sup>th</sup>	174	177
50 <sup>th</sup>	74	64
100 <sup>th</sup>	65	56



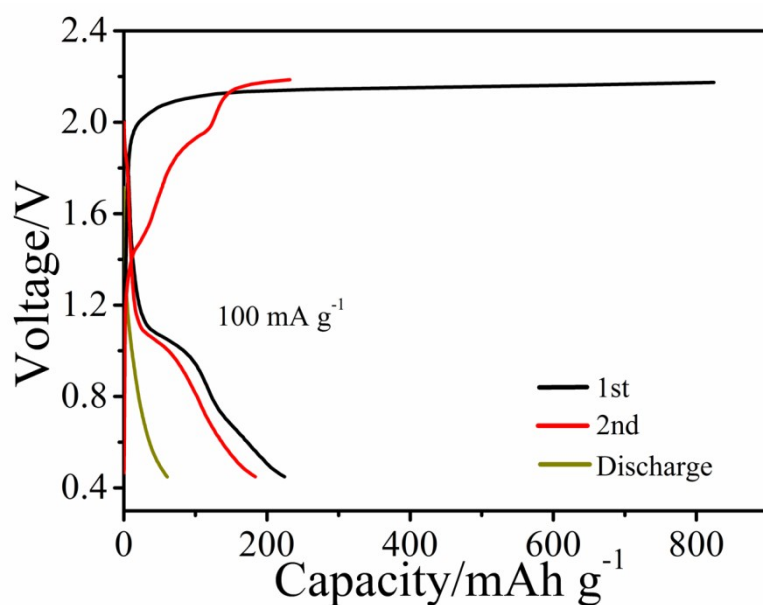
**Fig. S3** The electrochemical performance with D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> as cathode materials in aluminum-ion batteries.

**Table S2** The cycle performance with D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> as cathode materials in aluminum-ion batteries.

Cycle	Discharge (mAh g <sup>-1</sup> )	Charge (mAh g <sup>-1</sup> )
1 <sup>st</sup>	270.8	694.4
2 <sup>nd</sup>	251.8	418.2
5 <sup>th</sup>	231.4	251.6
50 <sup>th</sup>	68.8	78.5
100 <sup>th</sup>	73.5	62.8



**Fig. S4** The electrochemical performance with D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S as cathode materials in aluminum-ion batteries



**Fig. S5** The electrochemical performance when first discharged

**Table S3** The proportion of Ti-C bonds, Ti<sup>2+</sup>, Ti<sup>3+</sup> and Ti<sup>4+</sup> for Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> before charging/discharging, after full charging and after full discharging.

	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>
Ti-C	20.3 %	29.3 %	29.4 %
Ti <sup>2+</sup>	46.7%	37.3 %	27.7 %
Ti <sup>3+</sup>	33.0%	32.8 %	19.3 %
Ti <sup>4+</sup>	--	--	23.6 %

**Table S4** The stable adsorption position of  $Ti_3C_2S$  for  $[AlCl_4]^-$ 

O17S1	energy(sigma->0)	O17S1	energy(sigma->0)
O-surface1	-605.87115673	O-surface2	-605.78593683
C-surface1	-605.79478784	C-surface2	-605.78470740
Ti-surface1	-605.84634918	Ti-surface2	-605.78258008
S-surface1	-605.66239189	S-surface2	-605.77209921
C-Osurface1	-605.82793724	C-Osurface2	-605.69819642
Ti-Osurface1	-605.80524840	Ti-Osurface2	-605.66406706

**Table S5** The stable adsorption position of  $Ti_3C_2OH$  for  $[AlCl_4]^-$ .

OH	energy(sigma->0)	OH	energy(sigma->0)
OH-surface1	-676.09069122	OH-surface2	-676.08343549
C-surface1	-676.01896919	C-surface2	-675.99085864
Ti-surface1	-676.01293297	Ti-surface2	-675.99232052

**Table S6** The fitting data after different cycles.

Cycle (n)	1	10	120
$R_s (\Omega)$	41.7	43.3	64.3
$R_{ct} (\Omega)$	151.6	83.9	193.1

$R_{sf}(\Omega)$	102.4	84.3	144.5
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**Table S7** The proportion of different bonds for Ti 2p, C 1s and S 2p in D-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@S@TiO<sub>2</sub>.

D-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> @S@TiO <sub>2</sub>						
Ti 2p	Ti-O	Ti-S	Ti-C	--		
	20.8%	38.7%	40.5%	--		
C 1s	C-F	C-O	C-S	C-C	C=C	C-Ti
	8.7%	14.2%	18.6%	24.4%	28.1%	5.9%
S 2p	S-O	S-Ti-C	--	--		
	26.2%	76.9%	--	--		

**Table S8** The specific parameters of electrochemical performance for other cathode in aluminum-ion batteries.

Primary cathode	electrolyte	Cycle number/n	Capacity/mAh g <sup>-1</sup>	Discharge voltage/V	Current density/mA g <sup>-1</sup>
Graphitic-foam <sup>1</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	7500	70	2.0	4000
Carbon paper <sup>2</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	70	1.8	--
3D Graphene <sup>3</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	10000	120	2.0	5000
Graphene <sup>4</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	4500	80	2.0	300
Graphite <sup>5</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	6000	60	2.0	660
Advanced	AlCl <sub>3</sub> /[EMIm]Cl	25000	97	1.95	50000



Graphene <sup>6</sup>	(1.3:1)				
Graphene microflower <sup>7</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	5000	100	--	20000
3D graphene <sup>8</sup>	Al(ClO <sub>4</sub> ) <sub>3</sub>	400	100	1.0	2000
V <sub>2</sub> O <sub>5</sub> <sup>9</sup>	□ AlCl <sub>3</sub> /[EMIm]Cl 1 (1.1:1)	20	273	0.5	--
V <sub>2</sub> O <sub>5</sub> <sup>10</sup> □ □	AlCl <sub>3</sub> -[BMI]Cl (1.1:1)	5	180/--	0.6	116
TiO <sub>2</sub> <sup>11</sup> □ □	1M aqueous AlCl <sub>3</sub> solution	13	75	0.9	--
VO <sub>2</sub> <sup>12</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.1:1)	100	116/50	0.5	C
WO <sub>3-x</sub> <sup>13</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	65	1.0	100
Co <sub>3</sub> O <sub>4</sub> <sup>14</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	122.1	0.6	200
CuO <sup>15</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	121	0.6	100
FeS <sub>2</sub> <sup>16</sup>	AlCl <sub>3</sub> /[EMIm]Cl (2:1)	--	--	0.5	--
Ni <sub>3</sub> S <sub>2</sub> <sup>17</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	60	1.0	100
NiS <sup>18</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	104	1.0	200
CuS <sup>19</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	90	1.0	20
SnS <sub>2</sub> <sup>20</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	70	0.68	200

MoS <sub>2</sub> <sup>21</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	66.7	0.6	40
Co <sub>9</sub> S <sub>8</sub> <sup>22</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	6000	87	0.9	1000
V <sub>2</sub> CT <sub>x</sub> (MXene) <sup>23</sup>	AlCl <sub>3</sub> /[EMIm]Cl (1.3:1)	100	90	1.0	200

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