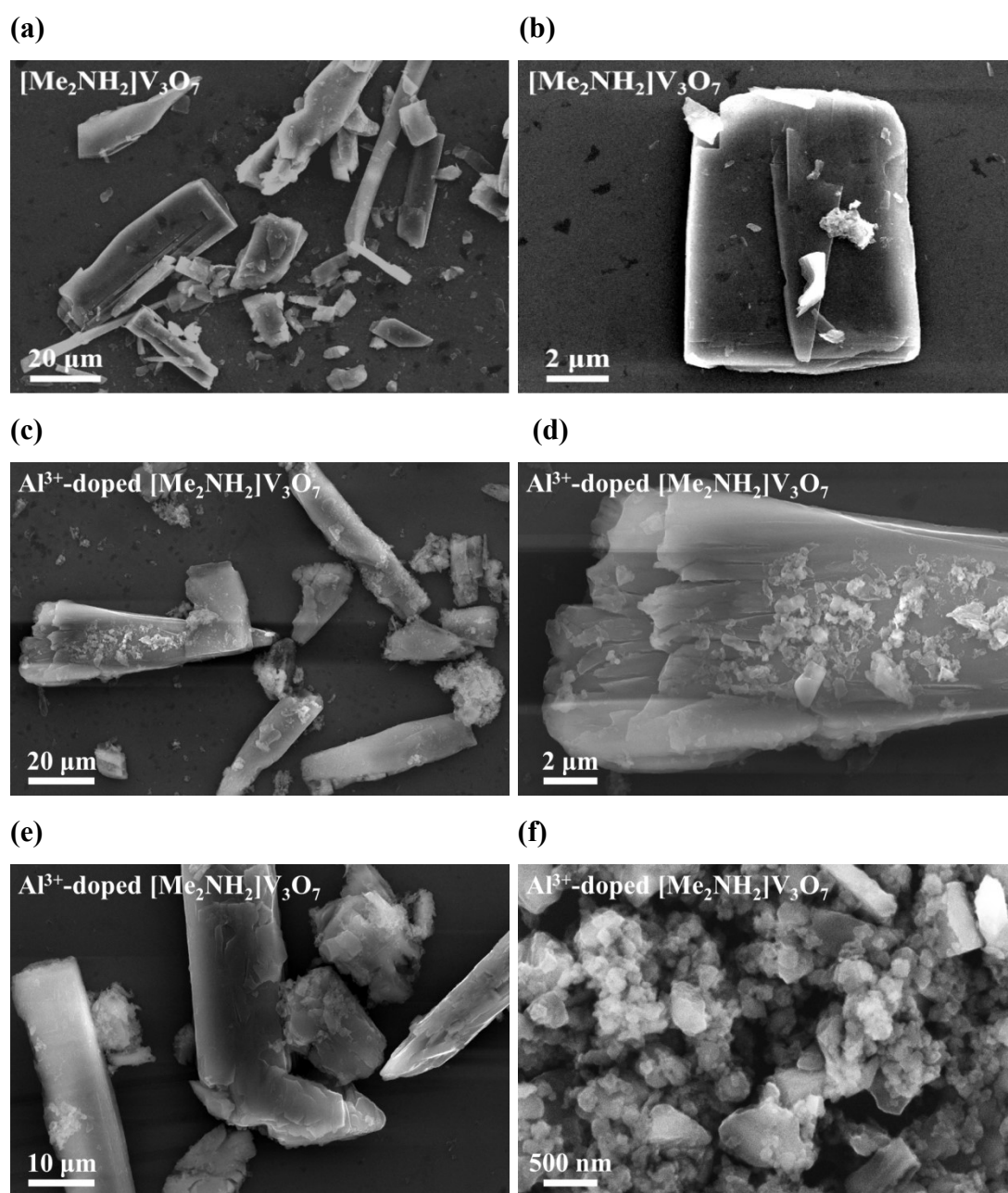


## Supporting Information

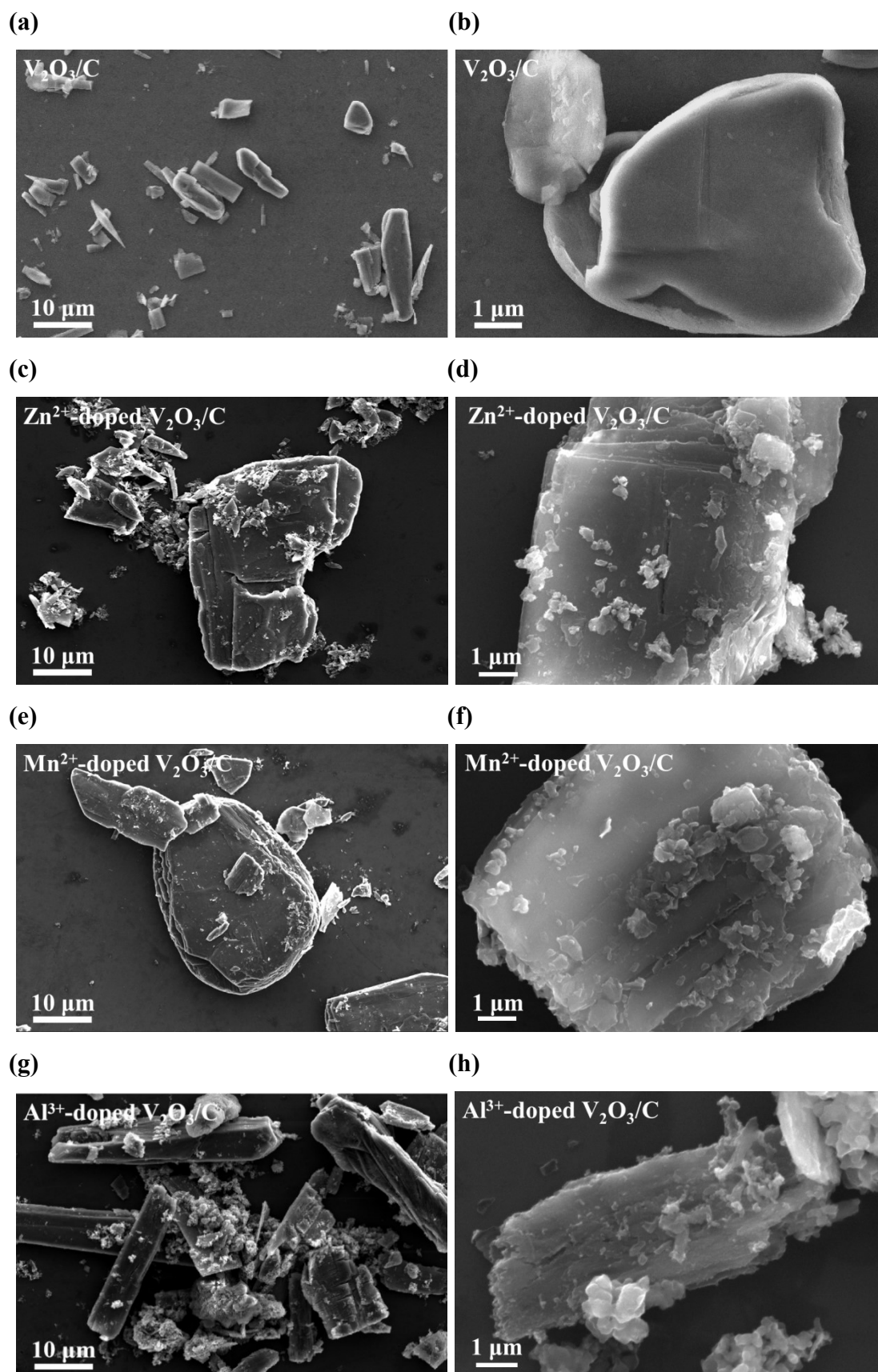
### Coordination polymer-derived Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C with rich oxygen vacancies for advanced aqueous zinc-ion battery with ultrahigh rate capability

Chang Lin Liu, Yang Liu, Xing Liu and Yun Gong\*

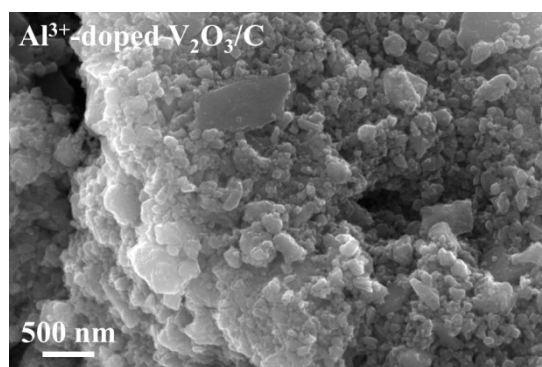
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**Figure S1** SEM images of (a, b)  $[\text{Me}_2\text{NH}_2]\text{V}_3\text{O}_7$  and (c-f)  $\text{Al}^{3+}$ -doped  $[\text{Me}_2\text{NH}_2]\text{V}_3\text{O}_7$ .

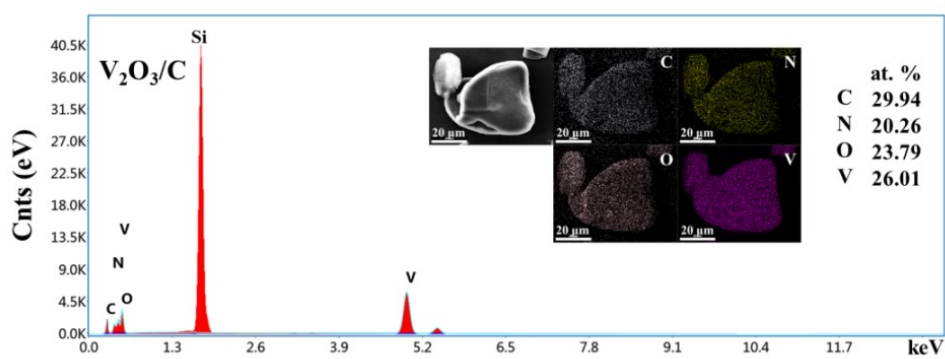


(i)

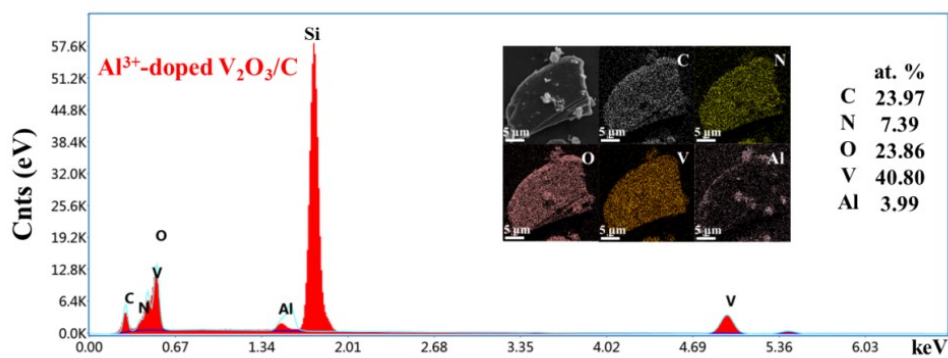


**Figure S2** SEM images of (a, b)  $\text{V}_2\text{O}_3/\text{C}$ , (c, d)  $\text{Zn}^{2+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$ , (e, f)  $\text{Mn}^{2+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$  and (g-i)  $\text{Al}^{3+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$ .

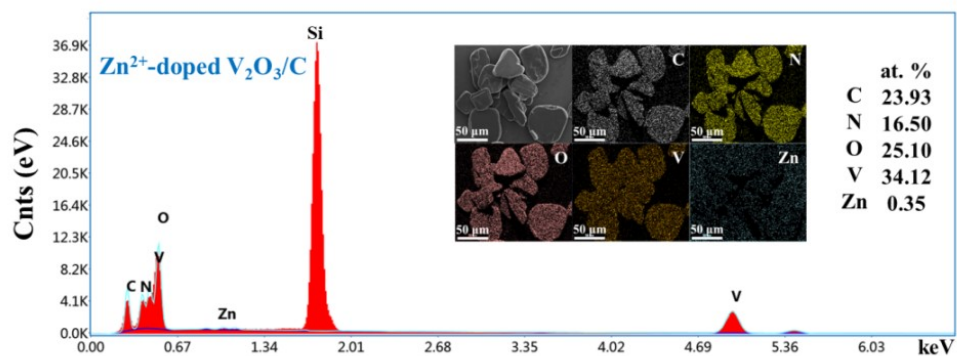
(a)



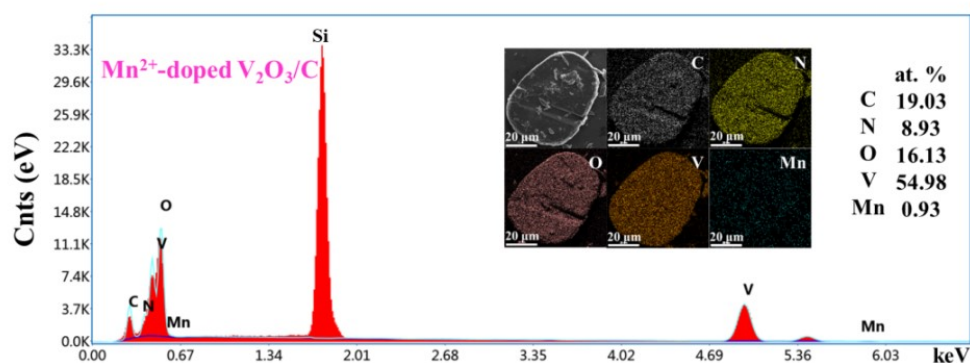
(b)



(c)



(d)

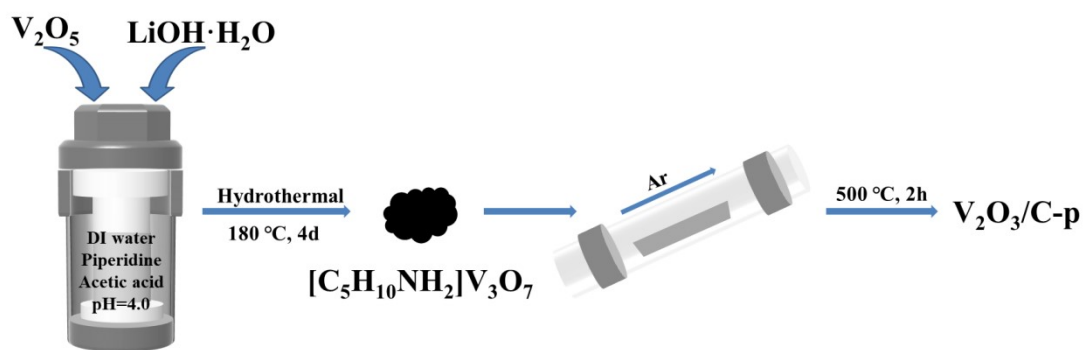


**Figure S3** EDS and elemental mappings (inset) of (a)  $V_2O_3/C$ , (b)  $Al^{3+}$ -doped  $V_2O_3/C$ , (c)  $Zn^{2+}$ -doped  $V_2O_3/C$  and (d)  $Mn^{2+}$ -doped  $V_2O_3/C$ .

## S1 Syntheses, compositions and morphologies of $[C_5H_{10}NH_2]V_3O_7$ and $V_2O_3/C-p$

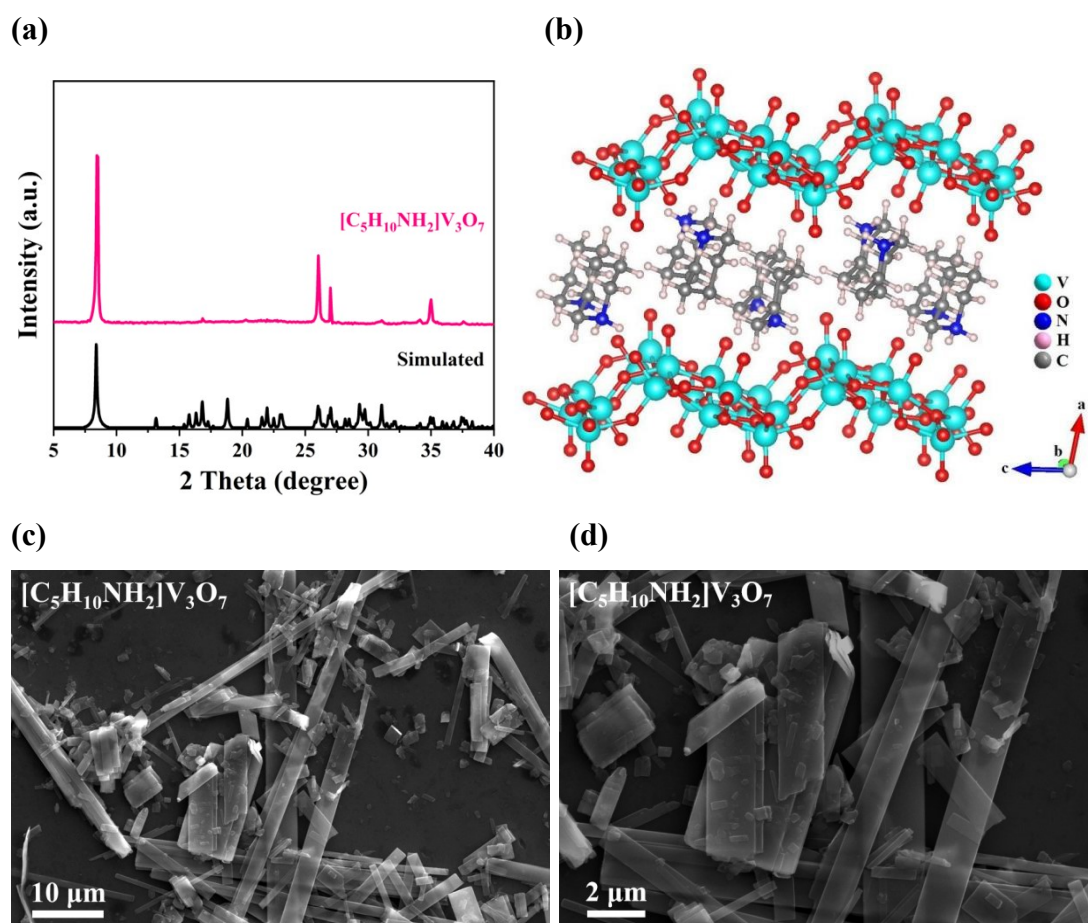
### S1.1 Syntheses of $[C_5H_{10}NH_2]V_3O_7$ and $V_2O_3/C-p$

The  $[C_5H_{10}NH_2]V_3O_7$  precursor was prepared under the same condition except that piperidine ( $C_5H_{10}NH$ ) (0.375 mL, 2.5 mmol) was used instead of DMF (1 mL) in the synthesis of  $[Me_2NH_2]V_3O_7$ .<sup>1</sup> And  $V_2O_3/C-p$  was obtained via the same annealing method except that 100 mg  $[C_5H_{10}NH_2]V_3O_7$  precursor was annealed instead of  $[Me_2NH_2]V_3O_7$  in the synthesis of  $V_2O_3/C$  (**Scheme S1**).



**Scheme S1** The synthesis procedures of  $[C_5H_{10}NH_2]V_3O_7$  and  $V_2O_3/C-p$ .

### S1.2 Structure and morphology of $[C_5H_{10}NH_2]V_3O_7$



**Figure S4** (a) XRD pattern of  $[C_5H_{10}NH_2]V_3O_7$  and the simulated profile; (b)  $[V_3O_7]^{4-}$  anionic layers and lamellar  $[C_5H_{10}NH_2]^+$  cations in  $[C_5H_{10}NH_2]V_3O_7$ ; (c, d) SEM images of  $[C_5H_{10}NH_2]V_3O_7$ .

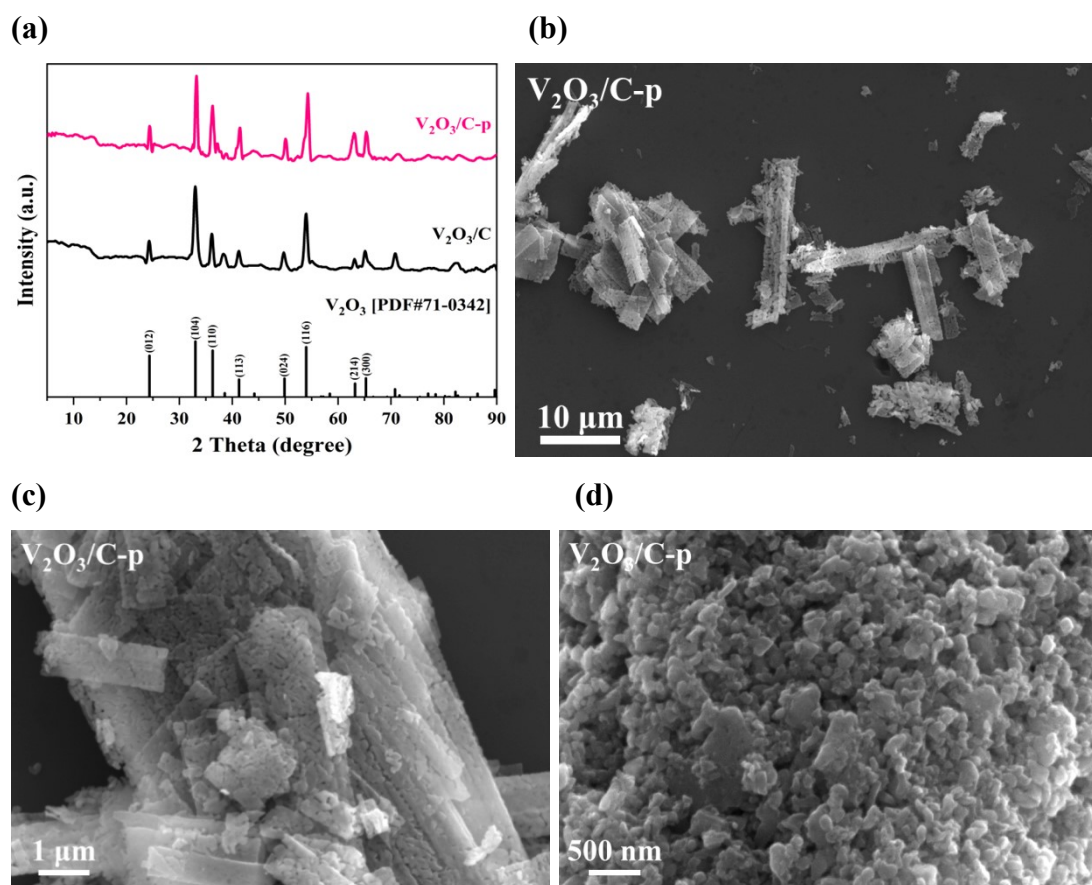
The XRD pattern of  $[C_5H_{10}NH_2]V_3O_7$  is shown in **Figure S4a**, which meets well with the simulated profile based on the single crystal diffraction data (CCDC No.



235654),<sup>1</sup> indicating the successful preparation of the sample without impurity. As shown in **Figure S4b**,  $[\text{C}_5\text{H}_{10}\text{NH}_2]\text{V}_3\text{O}_7$  possesses the same 2D  $[\text{V}^{\text{IV}}_2\text{V}^{\text{V}}\text{O}_7]^-$  anionic skeleton, however, the interlayer uncoordinated cation is the protonated piperidine cation  $[\text{C}_5\text{H}_{10}\text{NH}_2]^+$ . The result elucidates the generality for the synthesis of the  $[\text{V}_3\text{O}_7]^-$ -based coordination polymer.

As shown in **Figure S4(c, d)**, the morphology of  $[\text{C}_5\text{H}_{10}\text{NH}_2]\text{V}_3\text{O}_7$  displays regular nanobelts, demonstrating that the different interlayer cations lead to different morphologies.

### S1.3 Composition and morphology of $\text{V}_2\text{O}_3/\text{C-p}$

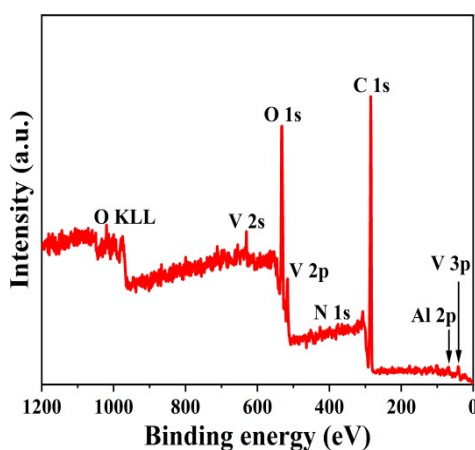


**Figure S5** (a) XRD pattern and (b-d) SEM images of  $\text{V}_2\text{O}_3/\text{C-p}$ .

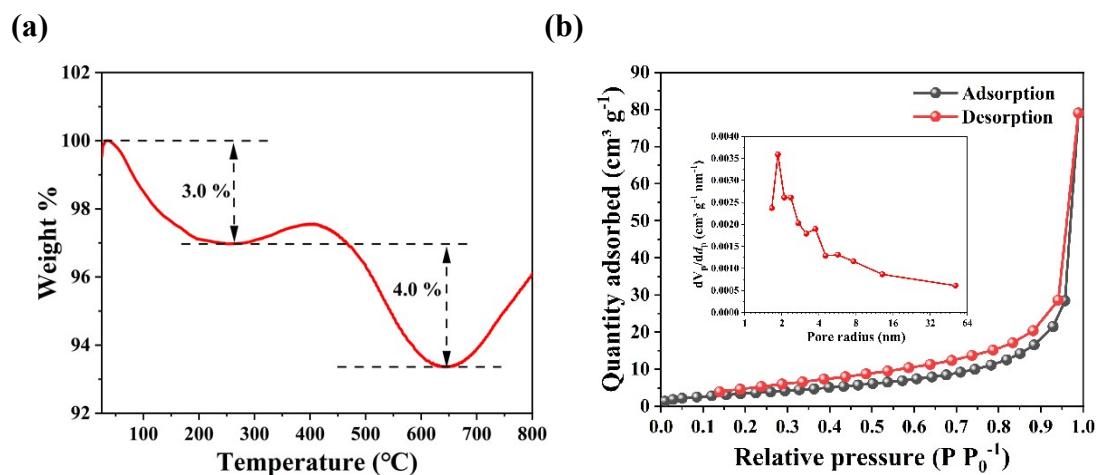
$\text{V}_2\text{O}_3/\text{C-p}$  was synthesized via calcination of  $[\text{C}_5\text{H}_{10}\text{NH}_2]\text{V}_3\text{O}_7$ . The XRD pattern of  $\text{V}_2\text{O}_3/\text{C-p}$  is shown in **Figure S5a**, which meets well with that of the hexagonal  $\text{V}^{\text{III}}_2\text{O}_3$  (PDF#71-0342). Similarly, the broad peak in the range of  $10 \sim 15^\circ$  is attributed to amorphous carbon, which originates from the decomposition of  $[\text{C}_5\text{H}_{10}\text{NH}_2]^+$  cations during annealing, inferring the formation of  $\text{V}_2\text{O}_3/\text{C}$  composite. The result depicts that regardless of  $[\text{Me}_2\text{NH}_2]\text{V}_3\text{O}_7$  and  $[\text{C}_5\text{H}_{10}\text{NH}_2]\text{V}_3\text{O}_7$ , their

annealed products are both  $V_2O_3/C$  composites, which is probably because they possess the same 2D  $[V_3O_7]^-$  anionic skeleton.

As shown **Figure S5(b-d)**, similar to the  $[C_5H_{10}NH_2]V_3O_7$  precursor,  $V_2O_3/C-p$  preserves a nanobelt-like contour, which is composed of numerous nanoparticles (NPs). It is expected that the *in situ*-yielded carbon can combine oxygen to release  $CO_2$  ( $C + O_2 \rightarrow CO_2$ ) during the high temperature annealing process, leading to the formation of the porous nanobelt and the reduction of  $[V^{IV}_2V^V O_7]^-$  into  $V^{III}_2O_3$ .



**Figure S6** The survey spectrum of  $Al^{3+}$ -doped  $V_2O_3/C$ .



**Figure S7** (a) TG analysis of  $Al^{3+}$ -doped  $V_2O_3/C$ ; (b) Nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution curve (inset) of  $Al^{3+}$ -doped  $V_2O_3/C$ .

**Table S1** The electrochemical performances of Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C in comparison with some vanadium-based materials

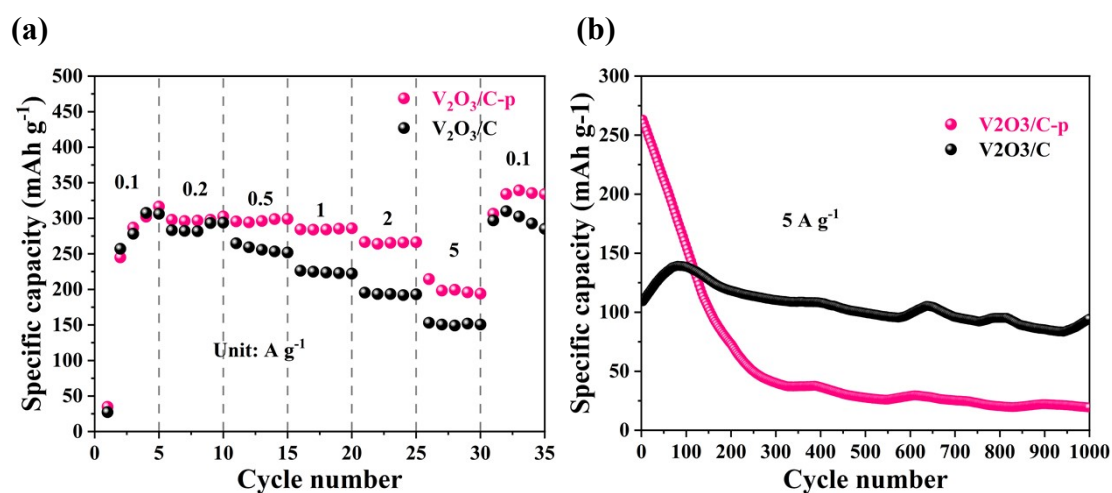
Cathode	Electrolyte	Voltage window	Specific capacity	Cycle performance	Ref
Mg <sub>0.34</sub> V <sub>2</sub> O <sub>5</sub> ·0.8H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.1-1.8 V	353 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup>	97 % retained after 2000 cycles at 5 A g <sup>-1</sup>	2
VO <sub>2</sub>	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.3-1.5 V	357 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	91.2 % retained after 300 cycles at 0.75 A g <sup>-1</sup>	3
VO <sub>2</sub> /rGO	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.3-1.4 V	276 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	99 % retained after 1000 cycles at 4 A g <sup>-1</sup>	4
V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	372 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup>	71 % retained after 900 cycles at 6 A g <sup>-1</sup>	5
V <sub>5</sub> O <sub>12</sub> ·6H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	354 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	94 % retained after 1000 cycles at 2 A g <sup>-1</sup>	6
Na <sub>2</sub> V <sub>6</sub> O <sub>16</sub> ·1.63H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	352 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup>	90 % retained after 6000 cycles at 5 A g <sup>-1</sup>	7
Mg <sub>0.1</sub> V <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> PAM gel	0.1-1.6 V	470 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	95 % retained after 3000 cycles at 5 A g <sup>-1</sup>	8
Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	1 M ZnSO <sub>4</sub>	0.2-1.4 V	248 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup>	85 % retained after 1000 cycles at 4 A g <sup>-1</sup>	9
H <sub>2</sub> V <sub>3</sub> O <sub>8</sub>	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	423.8 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	94.3 % retained after 1000 cycles at 5 A g <sup>-1</sup>	10
Ba <sub>1.2</sub> V <sub>6</sub> O <sub>16</sub> ·3H <sub>2</sub> O	2 M ZnSO <sub>4</sub>	0.3-1.4 V	321.2 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	95.6 % retained after 2000 cycles at 5 A g <sup>-1</sup>	11
NaV <sub>6</sub> O <sub>15</sub> /V <sub>2</sub> O <sub>5</sub>	2 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.8 V	390 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup>	92.3 % retained after 3000 cycles at 5 A g <sup>-1</sup>	12
Ca <sub>0.23</sub> V <sub>2</sub> O <sub>5</sub> ·0.95H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	355.2 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	97.7 % retained after 2000 cycles at 5 A g <sup>-1</sup>	13
Zn <sub>3</sub> V <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O	1 M ZnSO <sub>4</sub>	0.2-1.8 V	213 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup>	68 % retained after 300 cycles at 0.2 A g <sup>-1</sup>	14
V <sub>10</sub> O <sub>24</sub> ·12H <sub>2</sub> O	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.7-1.7 V	164.5 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	80.1 % retained after 3000 cycles at 10 A g <sup>-1</sup>	15
Al <sup>3+</sup> -doped V <sub>2</sub> O <sub>3</sub> /C	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.2-1.6 V	375 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	94.7 % retained after 1000 cycles at 5 A g <sup>-1</sup>	<b>This work</b>

## S2 Electrochemical performance of V<sub>2</sub>O<sub>3</sub>/C-p in comparison with that of V<sub>2</sub>O<sub>3</sub>/C

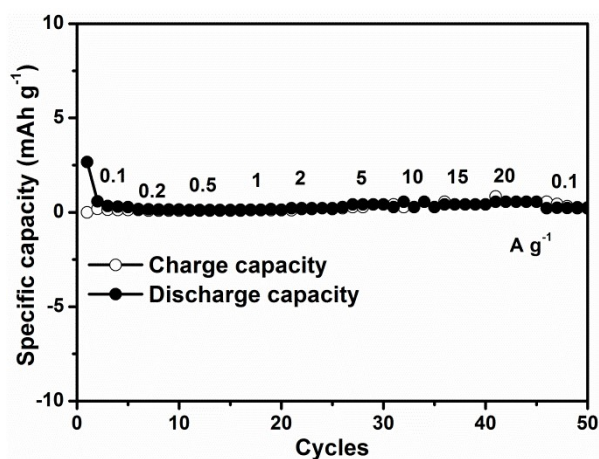
In order to explore the effect of the morphology on the electrochemical behavior, the rate and cycling performances of V<sub>2</sub>O<sub>3</sub>/C-p was also measured in comparison with V<sub>2</sub>O<sub>3</sub>/C. As shown in **Figure S8a**, V<sub>2</sub>O<sub>3</sub>/C-p can deliver an average capacity of 308,



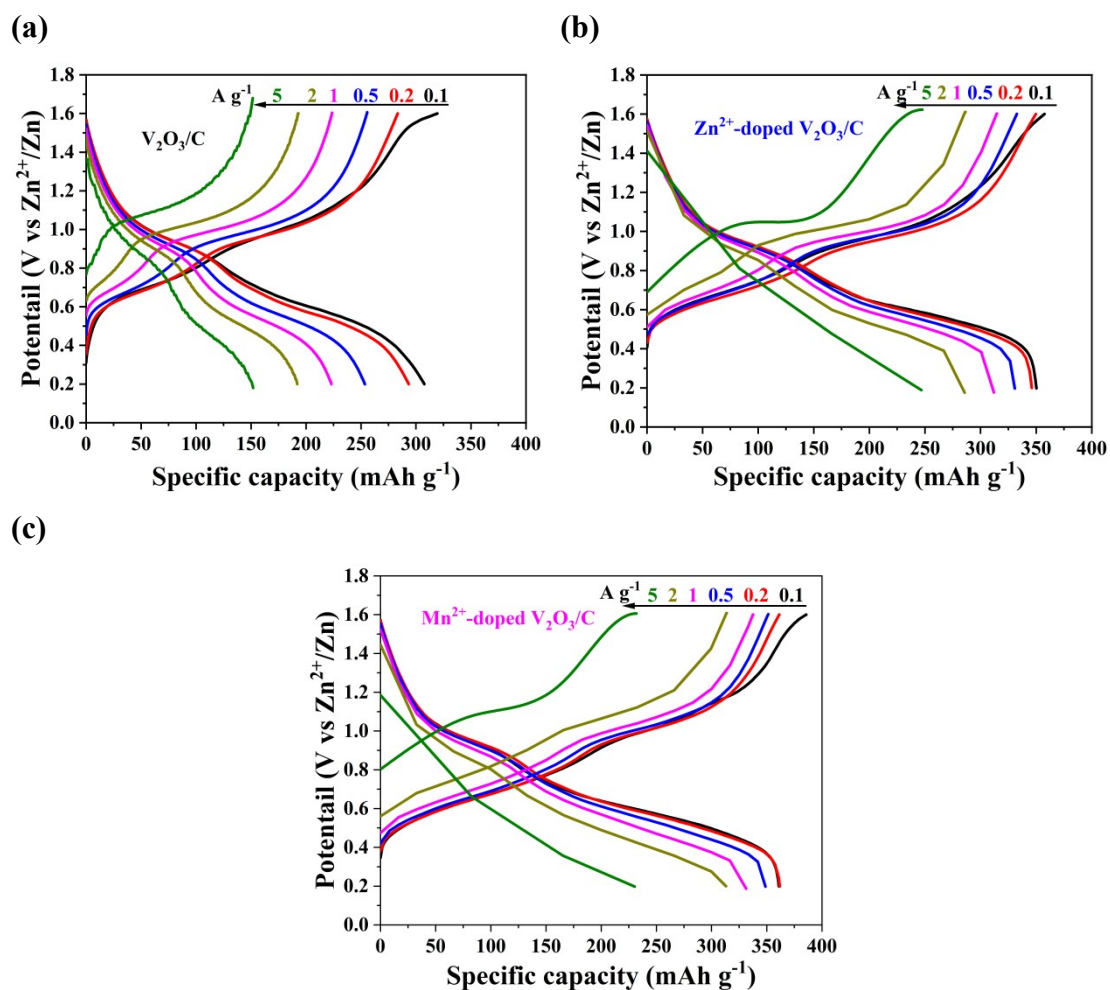
296, 298, 285, 265 and 195 mAh g<sup>-1</sup> at 0.1, 0.2, 0.5, 1, 2 and 5 A g<sup>-1</sup>, respectively, and recover to 335 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>, which are higher than those of V<sub>2</sub>O<sub>3</sub>/C. It is associated with the porous nanobelts built by numerous nanoparticles in V<sub>2</sub>O<sub>3</sub>/C-p, which is beneficial for the diffusion of electrolyte ions and facilitate the exposure of active sites, thus enhance the storage of Zn<sup>2+</sup>. However, the cycling performance of V<sub>2</sub>O<sub>3</sub>/C-p is inferior to that of V<sub>2</sub>O<sub>3</sub>/C though V<sub>2</sub>O<sub>3</sub>/C-p can provide a larger initial capacity of 263 mAh g<sup>-1</sup> at 5 A g<sup>-1</sup>, it sharply declines to 20 mAh g<sup>-1</sup> at the end of 1000 cycles with a capacity retention of only 7.6 % (**Figure S8b**), suggesting the porous nanobelts also favor for the capacity decay.



**Figure S8** (a) Rate capability and (b) long-life cycling performances of V<sub>2</sub>O<sub>3</sub>/C-p in comparison with V<sub>2</sub>O<sub>3</sub>/C.



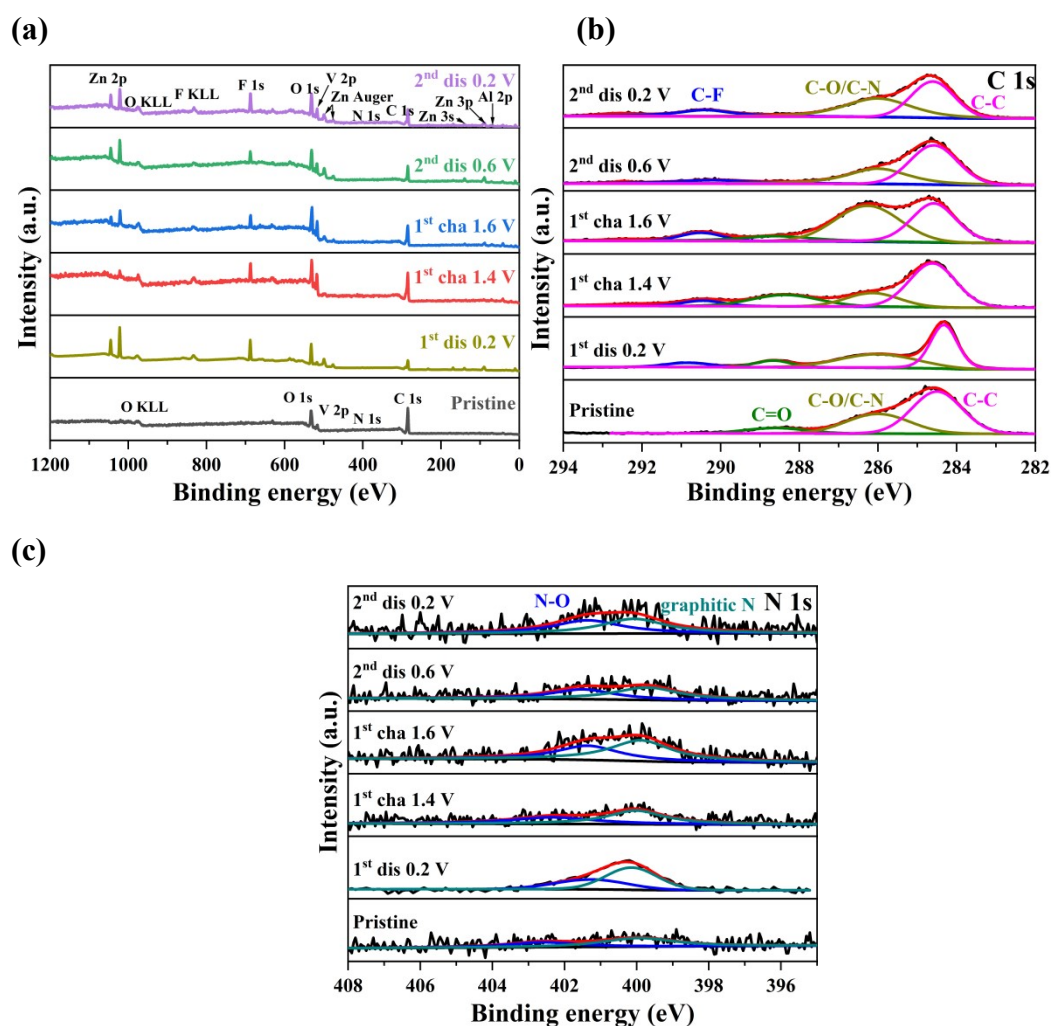
**Figure S9** Rate performance of the pure graphite



**Figure S10** Discharge-charge curves of (a) V<sub>2</sub>O<sub>3</sub>/C, (b) Zn<sup>2+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C and (c) Mn<sup>2+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C at various current densities from 0.1 to 5 A g<sup>-1</sup>.

**Table S2** The parameters in the simulated equivalent circuit for Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C and V<sub>2</sub>O<sub>3</sub>/C

	$R_s$ ( $\Omega$ cm <sup>-2</sup> )	$R_{ct}$ ( $\Omega$ cm <sup>-2</sup> )	CPE	$R_1$ ( $\Omega$ cm <sup>-2</sup> )
Al <sup>3+</sup> -doped V <sub>2</sub> O <sub>3</sub> /C	3.7	5.1	0.7	11.3
V <sub>2</sub> O <sub>3</sub> /C	2.2	13.5	0.6	8.9



**Figure S11** XPS spectra of (a) survey, (b) C 1s and (c) N 1s of the  $\text{Al}^{3+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$  electrode at different states.

## S2 *Ex situ* SEM, EDS and elemental mappings of the $\text{Al}^{3+}$ -doped $\text{V}_2\text{O}_3/\text{C}$ electrode

In order to obtain deeper insight into the compositional evolution during the discharge/charge process, *ex situ* SEM (Figure S12a-t), EDS and elemental mappings (Figure S13a-j) of the  $\text{Al}^{3+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$  electrode were performed. As shown in Figure S12(a, b), upon the 1<sup>st</sup> charge to 0.6 V, the sample exhibits stacked sheets with nanoparticles on the surfaces, which is similar to the morphology of the pristine sample (Figure S2g-i). The amount of carbon (64.15 at. %) (Figure S13a and Table S3) in the discharged cathode is larger than that in the pristine sample (23.97 at. %),

which is mainly due to the addition of conducting agent (graphite and acetylene black) for the fabrication of the electrode. As a result, the Al content is lowered to 1.68 at. % due to the dilution effect of the carbon additive. The F content (6.48 at. %) in the electrode mainly comes from the PVDF binder. Furthermore, the presence of Zn (1.73 at. %) in the discharged electrode illustrates the intercalation of  $\text{Zn}^{2+}$ . Upon further discharge to 0.2 V, the stacked sheets become loose and the electrode still keeps its original appearance because the 1<sup>st</sup> discharge process is short (ca. 40 min) (**Figure S12c, d**). Similarly, the morphologies of the  $\text{Al}^{3+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$  electrode are preserved upon the 1<sup>st</sup> charge to 0.6 (**Figure S12e, f**) and 1.0 V (**Figure S12g, h**). It is consistent with their XRD patterns, which are almost the same as the pristine sample, indicating they maintain the structural integrity of  $\text{V}_2\text{O}_3$ .

However, upon the 1<sup>st</sup> charge to 1.4 V, XRD pattern discloses the formation of  $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  with the disappearance of  $\text{V}_2\text{O}_3$ , the morphological change of the electrode is minor, which still displays nanoparticles on the surface of sheets (**Figure S12i, j**), indicating the transformation of  $\text{V}_2\text{O}_3 \rightarrow \text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  occurs in the inner channel of corundum-type  $\text{V}_2\text{O}_3$ , which retains the original contour of the pristine sample. Although  $\text{V}_2\text{O}_3$  is nonporous, the oxygen vacancies in the structure can provide accessible sites for the binding of  $\text{Zn}^{2+}$ . That is to say, with the oxidation reaction proceeding, the valence state of V is increased, the high-valent V can combine the intercalated  $\text{Zn}^{2+}$  into  $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ . As a result, the amount of oxygen deficiencies is decreased, which is consistent with the O 1s spectra. Similar phenomenon is observed upon deeply charged to 1.6 V. Although the XRD pattern at the fully charged state suggests the further transformation of  $\text{V}_2\text{O}_3 \rightarrow \text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , there is not obvious morphological change of the electrode (**Figure S12k, l**). However, as shown in **Scheme 1**, the corundum-type  $\text{V}_2\text{O}_3$

possesses a nonporous 3D architecture without free inner space, it is expected the inner accessible sites of  $V_2O_3$  is associated with its rich oxygen vacancies.

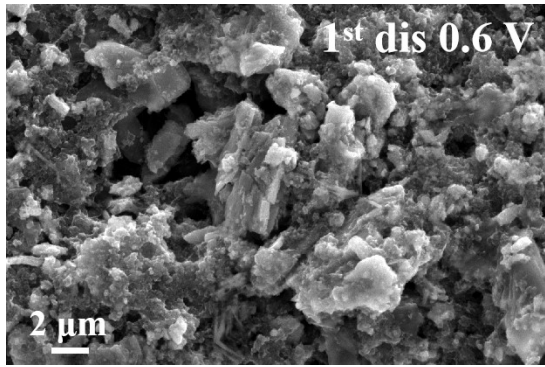
Based on XRD data, it is found  $Al^{3+}$ -doped  $V_2O_3/C$  has been replaced by  $Al^{3+}$ -doped  $Zn_3(OH)_2V_2O_7 \cdot 2H_2O/C$  after the 1<sup>st</sup> fully charged to 1.6 V, the subsequent discharge/charge process involves the redox reactions of  $Al^{3+}$ -doped  $Zn_3(OH)_2V_2O_7 \cdot 2H_2O/C$ . As a result, upon the 2<sup>nd</sup> discharge to 1.0 V, ultrathin nanosheets are observed on the outer surface of the  $Al^{3+}$ -doped  $Zn_3(OH)_2V_2O_7 \cdot 2H_2O/C$  sample (**Figure S12m, n**). The ultrathin nanosheets become more and more upon further discharge to 0.6 (**Figure S12o, p**) and 0.2 V (**Figure S12q, r**), which is the result of the  $H^+$  intercalation as evidenced by previous work,<sup>16-18</sup>. With the intercalation of  $H^+$  during the 2<sup>nd</sup> discharge process, the concentration of  $OH^-$  in the aqueous solution is excessive, which can combine  $Zn_x(CF_3SO_3)_y$  from the electrolyte solution into insoluble  $Zn_x(CF_3SO_3)_y(OH)_{2x-y} \cdot nH_2O$  on the outer surface of the electrode.<sup>17-19</sup> And the expectation can be proved by the *ex situ* EDS results. As shown in **Figure S13(g-i)** and **Table S3**, the F/S contents in the electrode increase from 5.43/0.15  $\rightarrow$  7.55/0.80  $\rightarrow$  9.18/1.85 at. % upon the 2<sup>nd</sup> discharge from 1.0  $\rightarrow$  0.6  $\rightarrow$  0.2 V. Furthermore, the (de)intercalation of  $H^+$  is almost reversible, upon the 2<sup>nd</sup> charge to 1.4 V, most of the ultrathin nanosheets have disappeared (**Figure S12s, t**) with the F/S contents drop to 6.36/0.24 at. % (**Figure S13j** and **Table S3**).

As for the content of Zn, it is increased from 2.96  $\rightarrow$  4.74  $\rightarrow$  6.68 at. % from the 2<sup>nd</sup> discharge to 1.0  $\rightarrow$  0.6  $\rightarrow$  0.2 V (**Figure S13g-i** and **Table S3**), which originate from the increase of the intercalated  $Zn^{2+}$  and adsorbed  $Zn^{2+}$  during the discharge process, agreeing with the Zn 2p spectra. And the Zn content drops to 6.68 at. % upon the 2<sup>nd</sup> charge to 1.4 V (**Figure S13j** and **Table S3**).

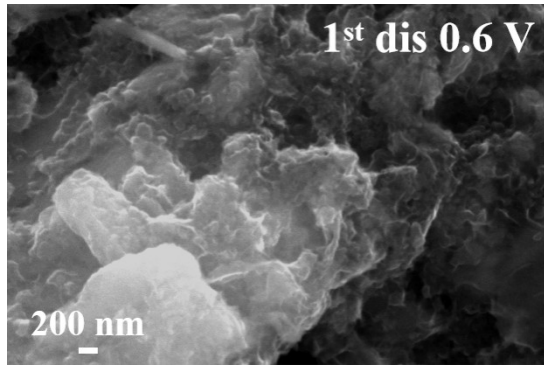
(a)

(b)

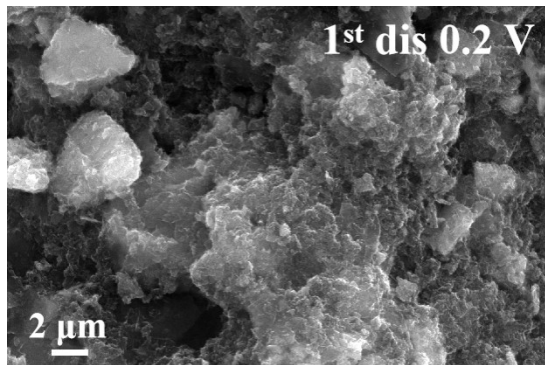




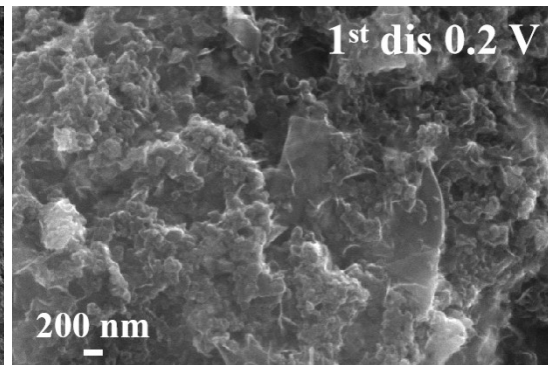
(c)



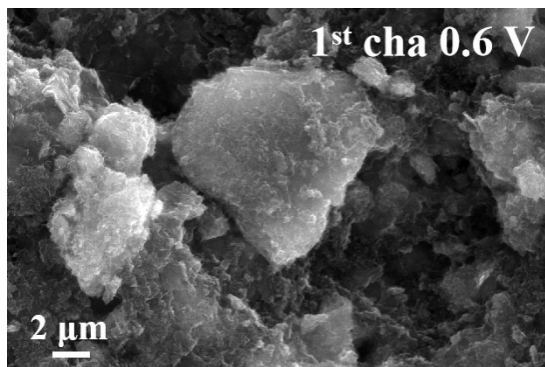
(d)



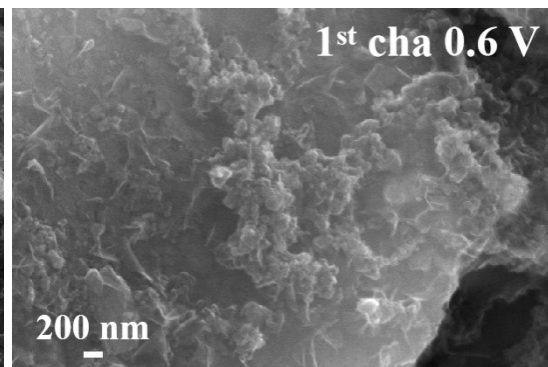
(e)



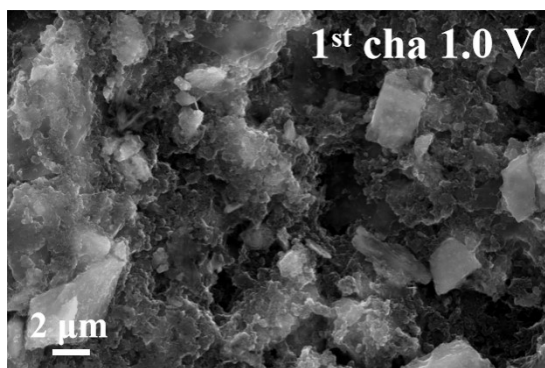
(f)



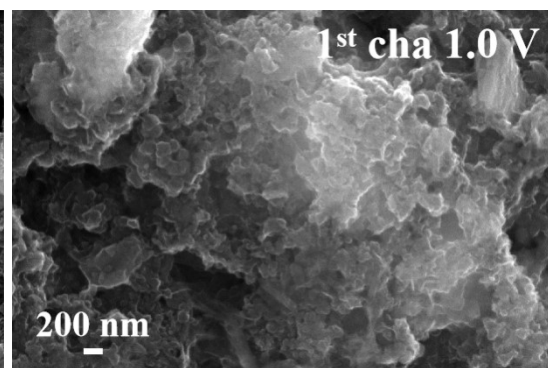
(g)



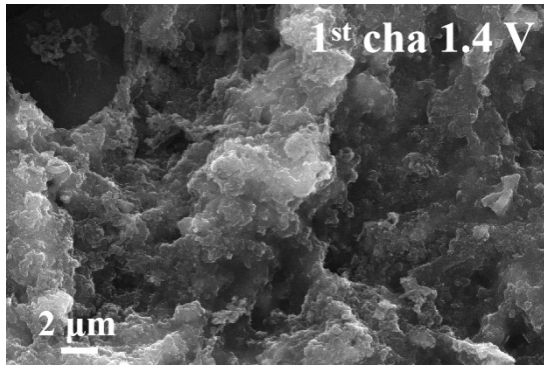
(h)



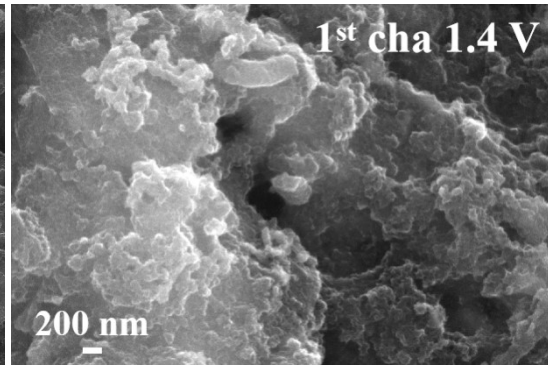
(i)



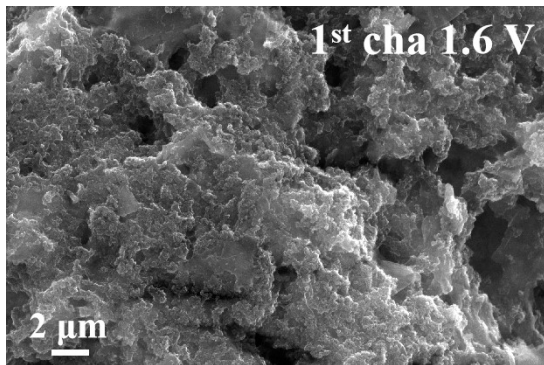
(j)



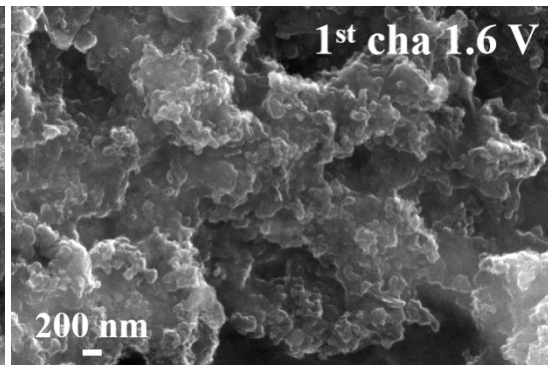
(k)



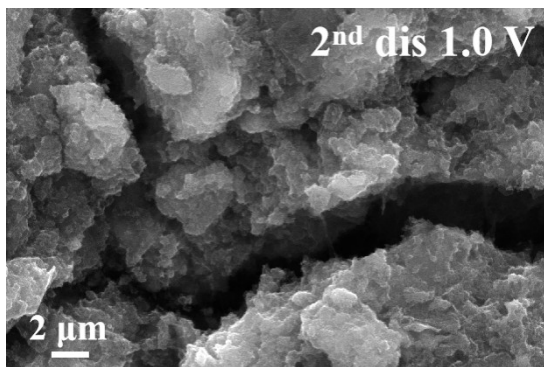
(l)



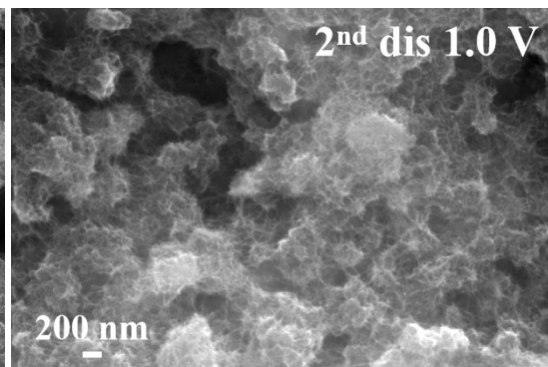
(m)



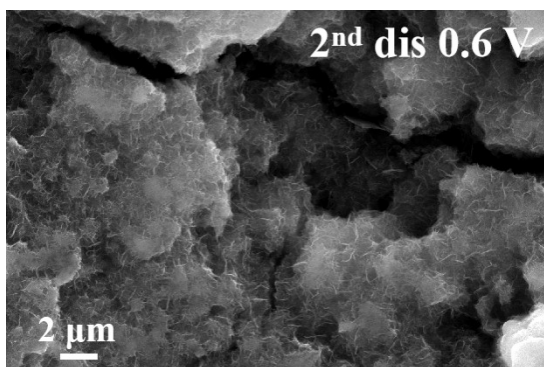
(n)



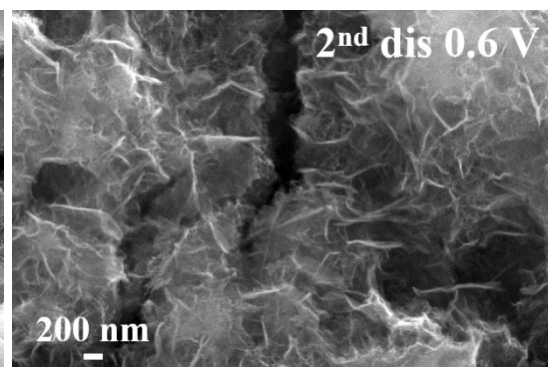
(o)



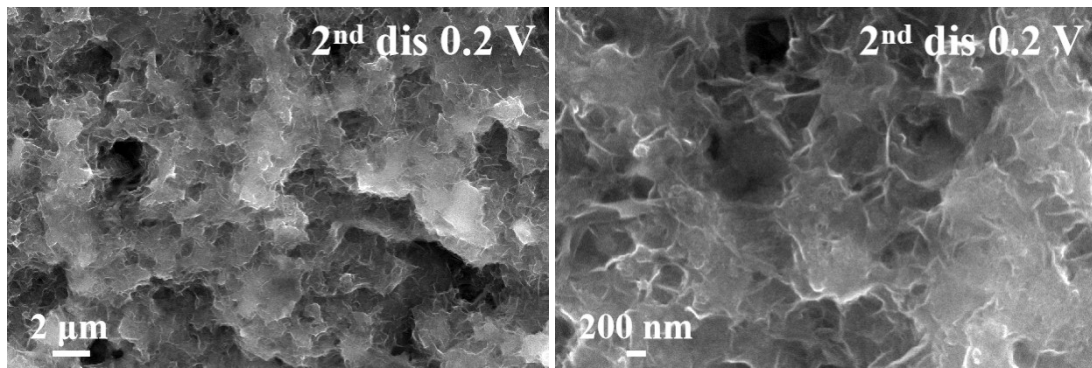
(p)



(q)

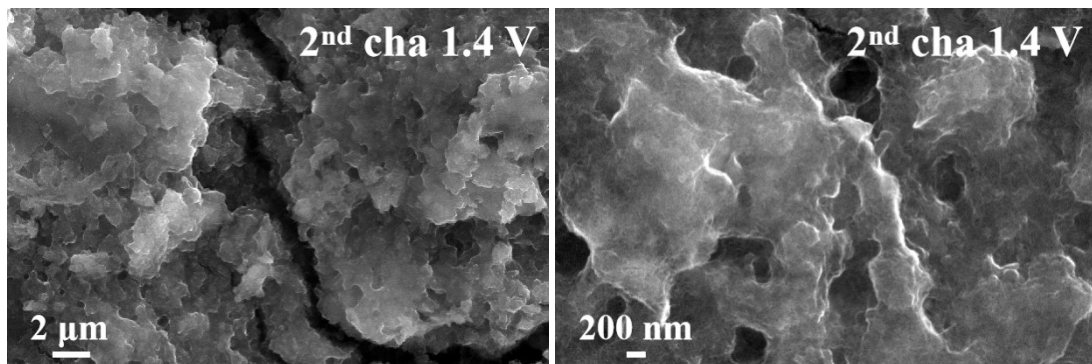


(r)



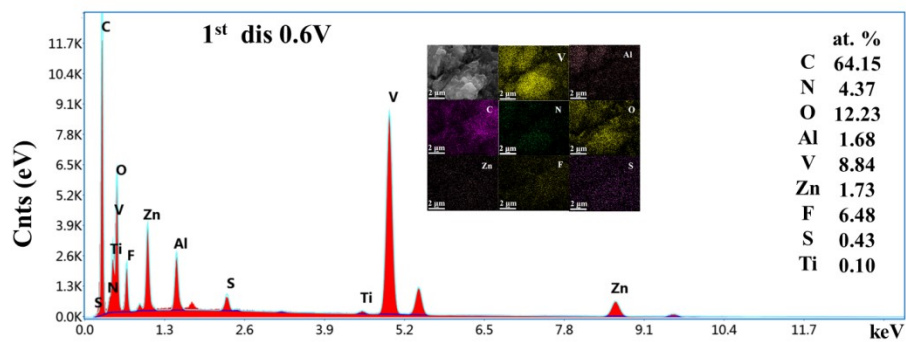
(s)

(t)

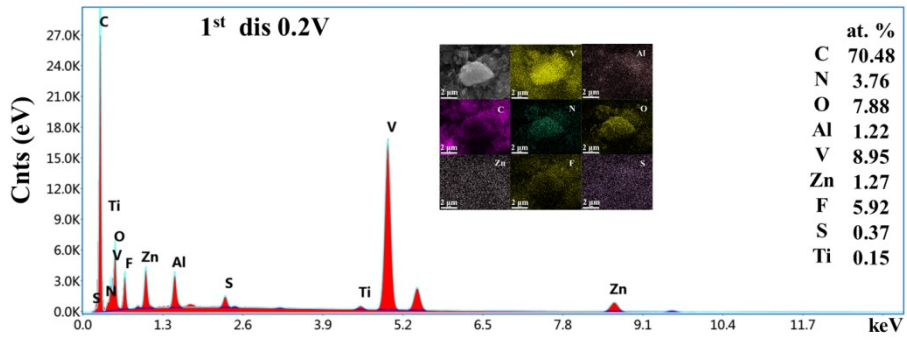


**Figure S12** *Ex situ* SEM images of the the Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C electrode at different states: 1<sup>st</sup> discharge to (a, b) 0.6 and (c, d) 0.2 V; 1<sup>st</sup> charge to (e, f) 0.6, (g, h) 1.0, (i, j) 1.4, and (k, l) 1.6 V; 2<sup>nd</sup> discharge to (m, n) 1.0, (o, p) 0.6 and (q, r) 0.2 V; (s, t) 2<sup>nd</sup> charge to 1.4 V.

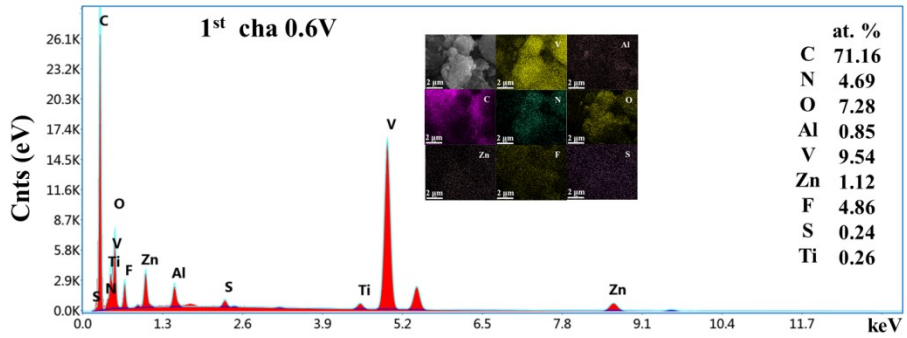
(a)



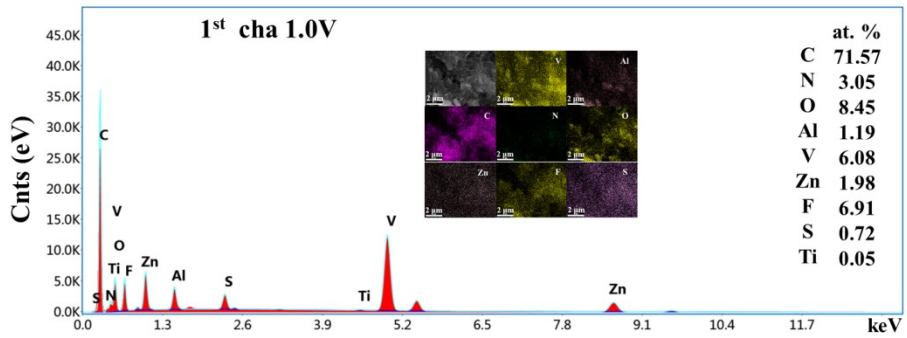
(b)



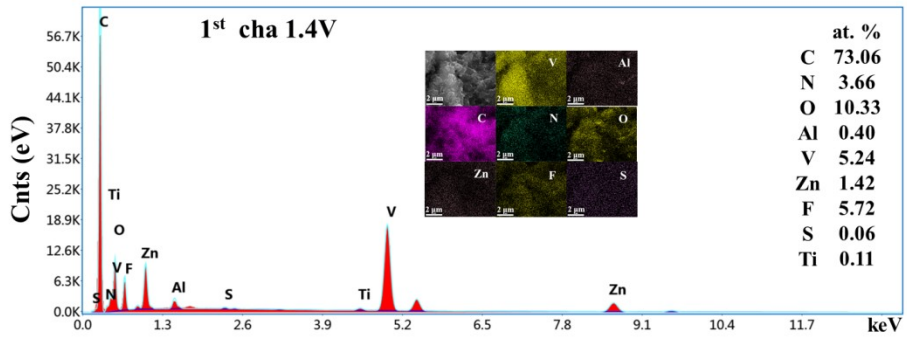
(c)



(d)

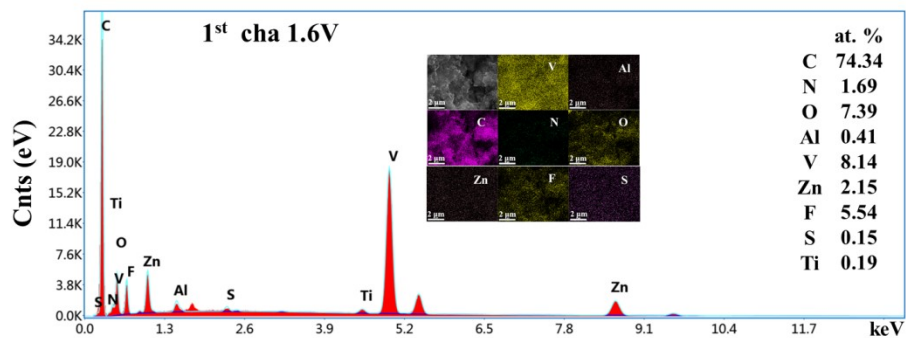


(e)

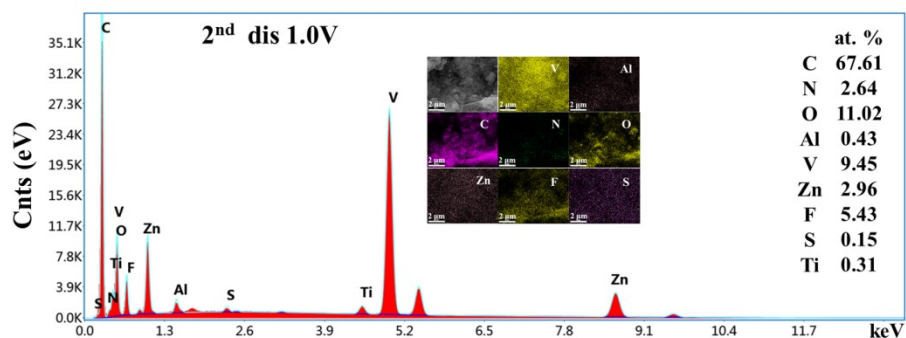


(f)

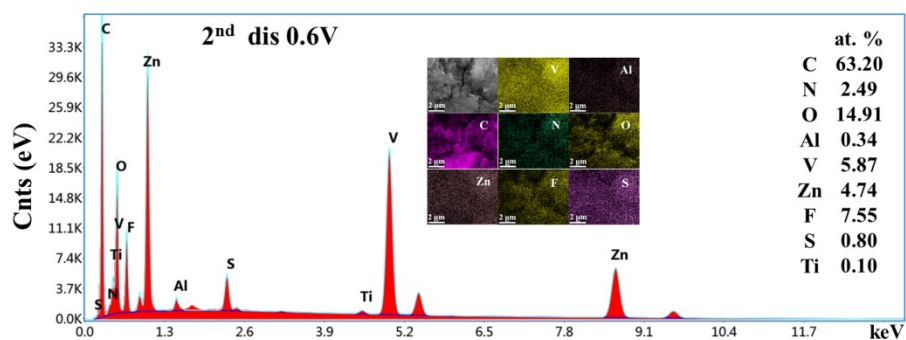




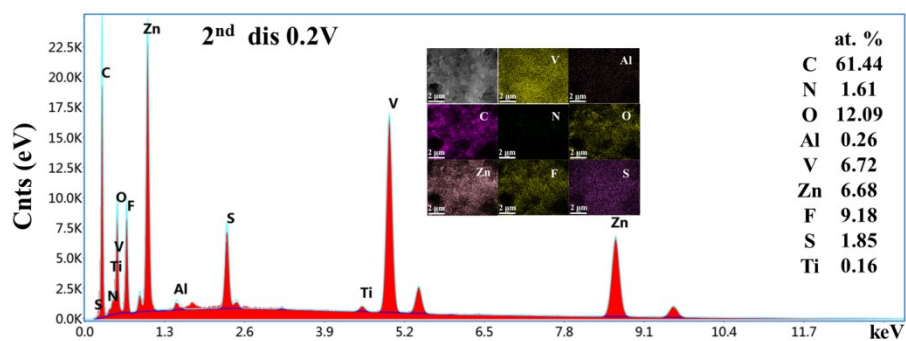
(g)



(h)

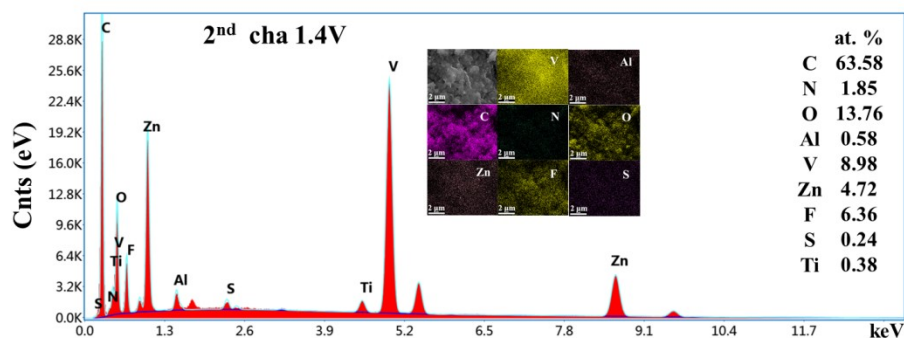


(i)



(j)



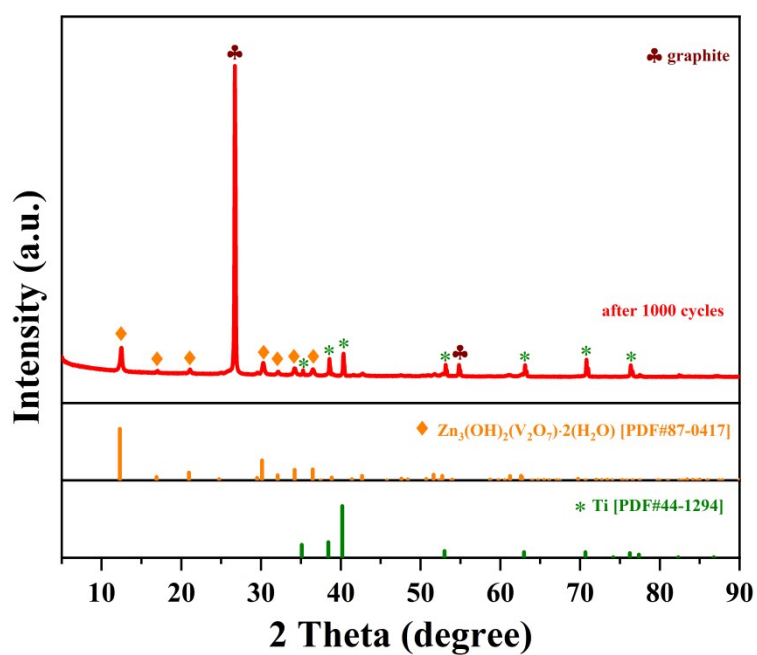


**Figure S13** *Ex situ* EDS and elemental mappings of the Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C electrode at different states: 1<sup>st</sup> discharge to (a) 0.6 and (b) 0.2 V; 1<sup>st</sup> charge to (c) 0.6, (d) 1.0, (e) 1.4 and (f) 1.6 V; 2<sup>nd</sup> discharge to (g) 1.0, (h) 0.6 and (i) 0.2 V, (j) 2<sup>nd</sup> charge to 1.4 V.

**Table S3** Comparison of the contents of C, N, O, Al, V, Zn, F, S and Ti elements in the Al<sup>3+</sup>-doped V<sub>2</sub>O<sub>3</sub>/C electrode at the different states

	C	N	O	Al	V	Zn	F	S	Ti
1 <sup>st</sup> dis 0.6 V	64.15	4.37	12.23	1.68	8.84	1.73	6.48	0.43	0.10
1 <sup>st</sup> dis 0.2 V	70.48	3.76	7.88	1.22	8.95	1.27	5.92	0.37	0.15
1 <sup>st</sup> cha 0.6 V	71.16	4.69	7.28	0.85	9.54	1.12	4.86	0.24	0.26
1 <sup>st</sup> cha 1.0 V	71.57	3.05	8.45	1.19	6.08	1.98	6.91	0.72	0.05
1 <sup>st</sup> cha 1.4 V	73.06	3.66	10.33	0.40	5.24	1.42	5.72	0.06	0.11
1 <sup>st</sup> cha 1.6 V	74.34	1.69	7.39	0.41	8.14	2.15	5.54	0.15	0.19
2 <sup>nd</sup> dis 1.0 V	67.61	2.64	11.02	0.43	9.45	2.96	5.43	0.15	0.31
2 <sup>nd</sup> dis 0.6 V	63.20	2.49	14.91	0.34	5.87	4.74	7.55	0.80	0.10
2 <sup>nd</sup> dis 0.2 V	61.44	1.61	12.09	0.26	6.72	6.68	9.18	1.85	0.16
2 <sup>nd</sup> cha 1.4 V	63.58	1.85	13.76	0.58	8.98	4.72	6.36	0.24	0.38

(a)



(b)

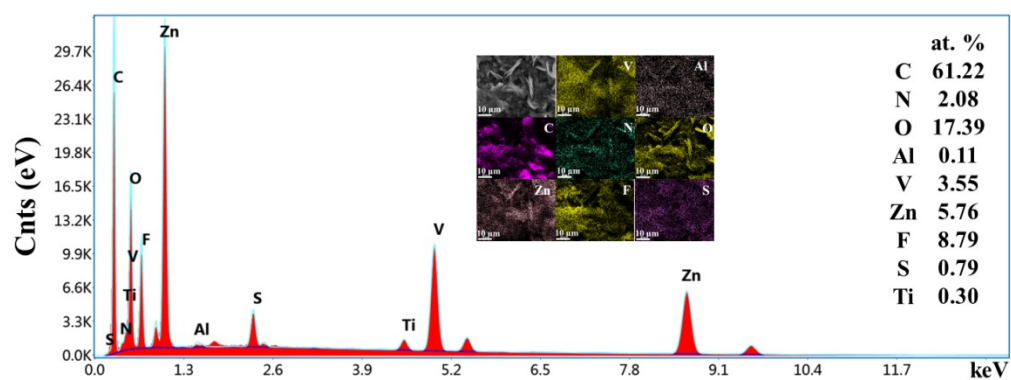
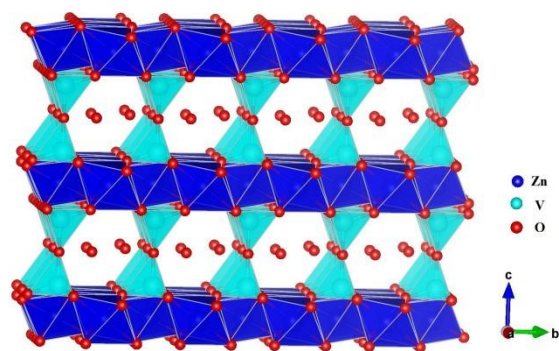
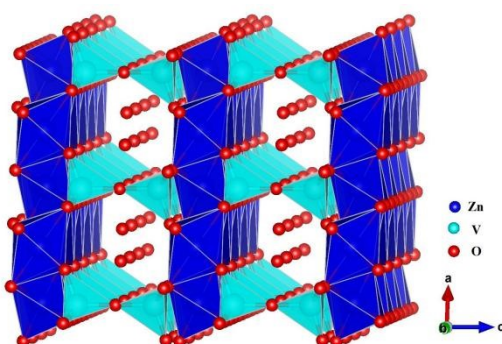


Figure S14 (a) XRD pattern and (b) EDS as well as elemental mappings (inset) of the  $\text{Al}^{3+}$ -doped  $\text{V}_2\text{O}_3/\text{C}$  electrode after 1000 discharge/charge cycles at  $5 \text{ A g}^{-1}$ .

(a)

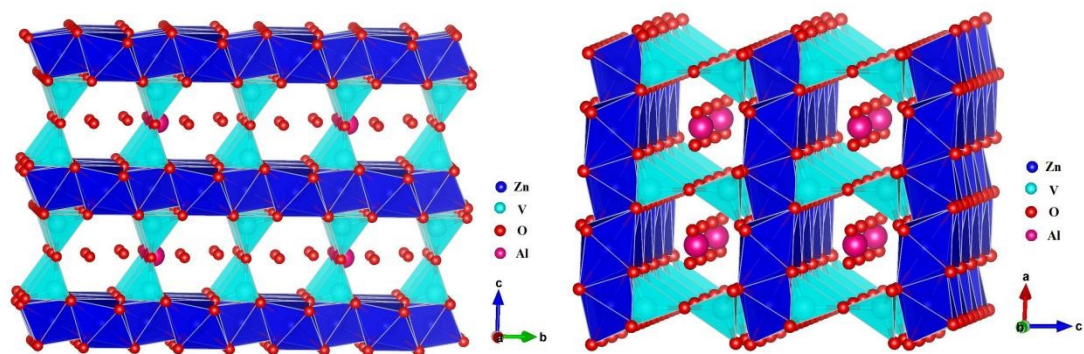


(b)

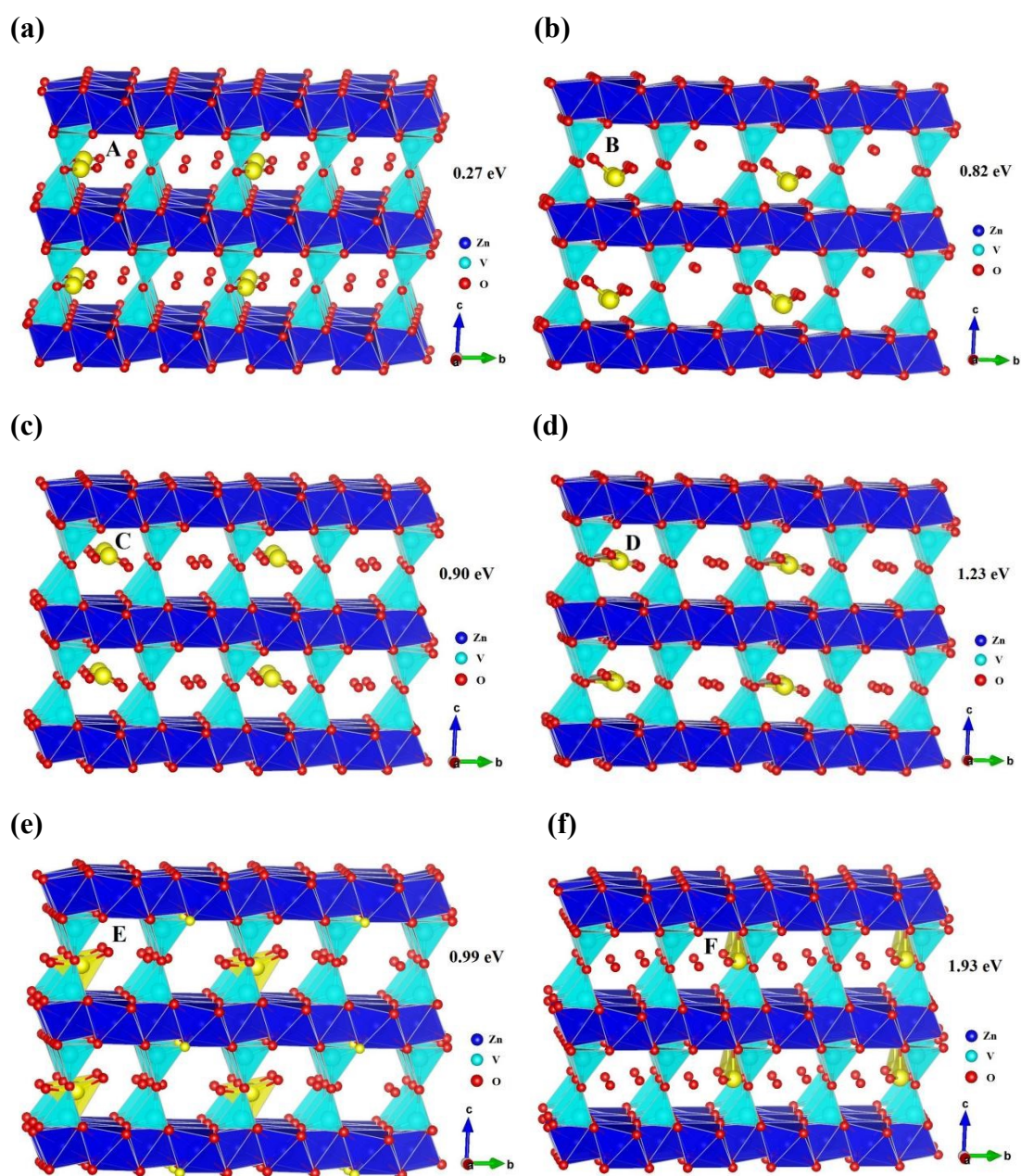


(c)

(d)



**Figure S15** 3D architectures of (a, b)  $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and (c, d) Al-doped  $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (H atoms omitted for clarity).



**Figure S16** The optimized configurations and the corresponding energies with  $\text{Zn}^{2+}$  adsorbed on sites (a) A, (b) B, (c) C, (d) D, (e) E and (f) F in  $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (H atoms omitted for clarity). The intercalated  $\text{Zn}^{2+}$  ions are denoted in yellow.

## Reference

1. S. T. Lutta, N. A. Chernova, P. Y. Zavalij and M. S. Whittingham, *J. Mater. Chem.*, 2004, **14**, 2922-2928.
2. F. Ming, H. Liang, Y. Lei, S. Kandambeth, M. Eddaoudi and H. N. Alshareef, *ACS Energy Lett.*, 2018, **3**, 2602-2609.
3. J. Ding, Z. Du, L. Gu, B. Li, L. Wang, S. Wang, Y. Gong and S. Yang, *Adv. Mater.*, 2018, **30**, e1800762.
4. X. Dai, F. Wan, L. Zhang, H. Cao and Z. Niu, *Energy Stor. Mater.*, 2019, **17**, 143-150.
5. M. Yan, P. He, Y. Chen, S. Wang, Q. Wei, K. Zhao, X. Xu, Q. An, Y. Shuang, Y. Shao, K. T. Mueller, L. Mai, J. Liu and J. Yang, *Adv. Mater.*, 2018, **30**, 1703725.
6. N. Zhang, M. Jia, Y. Dong, Y. Wang, J. Xu, Y. Liu, L. Jiao and F. Cheng, *Adv. Funct. Mater.*, 2019, **29**, 1807331.
7. P. Hu, T. Zhu, X. Wang, X. Wei, M. Yan, J. Li, W. Luo, W. Yang, W. Zhang, L. Zhou, Z. Zhou and L. Mai, *Nano Lett.*, 2018, **18**, 1758-1763.
8. W. Deng, Z. Zhou, Y. Li, M. Zhang, X. Yuan, J. Hu, Z. Li, C. Li and R. Li, *ACS Nano*, 2020, **14**, 15776-15785.
9. B. Sambandam, V. Soundharajan, S. Kim, M. H. Alfaruqi, J. Jo, S. Kim, V. Mathew, Y. K. Sun and J. Kim, *J. Mater. Chem. A*, 2018, **6**, 3850-3856.
10. P. He, Y. Quan, X. Xu, M. Yan, W. Yang, Q. An, L. He and L. Mai, *Small*, 2017, **13**, 1702551.
11. X. Wang, B. Xi, X. Ma, Z. Feng, Y. Jia, J. Feng, Y. Qian and S. Xiong, *Nano Lett.*, 2020, **20**, 2899-2906.
12. L. Fan, Z. Li, W. Kang and B. Cheng, *J. Energy Chem.*, 2021, **55**, 25-33.
13. W. Zhou, M. Chen, A. Wang, A. Huang, J. Chen, X. Xu and C. P. Wong, *J. Energy Chem.*, 2021, **52**, 377-384.
14. C. Xia, J. Guo, Y. Lei, H. Liang, C. Zhao and H. N. Alshareef, *Adv. Mater.*, 2018, **30**, 7.
15. T. Wei, Q. Li, G. Yang and C. Wang, *Electrochim. Acta*, 2018, **287**, 60-67.
16. L. L. Wang, K. W. Huang, J. T. Chen and J. R. Zheng, *Sci. Adv.*, 2019, **5**, 10.
17. L. Wang, K.-W. Huang, J. Chen and J. Zheng, *Sci. Adv.*, 2019, **5**, eaax4279.
18. M. Du, F. Zhang, X. Zhang, W. Dong, Y. Sang, J. Wang, H. Liu and S. Wang, *Sci China Chem*, 2020, **63**, 1767-1776.
19. W. Leng, L. Cui, Y. Liu and Y. Gong, *Adv. Mater. Interfaces*, 2021, **8**, 2101705.