

Supporting Information for

## Ultra-Low-Dose Pre-Metallation Strategy Served for Commercial Metal-Ion Capacitors

Zirui Song<sup>1</sup>, Guiyu Zhang<sup>1</sup>, Xinglan Deng<sup>1</sup>, Kangyu Zou<sup>1</sup>, Xuhuan Xiao<sup>1</sup>, Roya Momen<sup>1</sup>, Abouzar Massoudi<sup>2</sup>, Wentao Deng<sup>1</sup>, Jiugang Hu<sup>1</sup>, Hongshuai Hou<sup>1</sup>, Guoqiang Zou<sup>1,\*</sup>, and Xiaobo Ji<sup>1,3</sup>

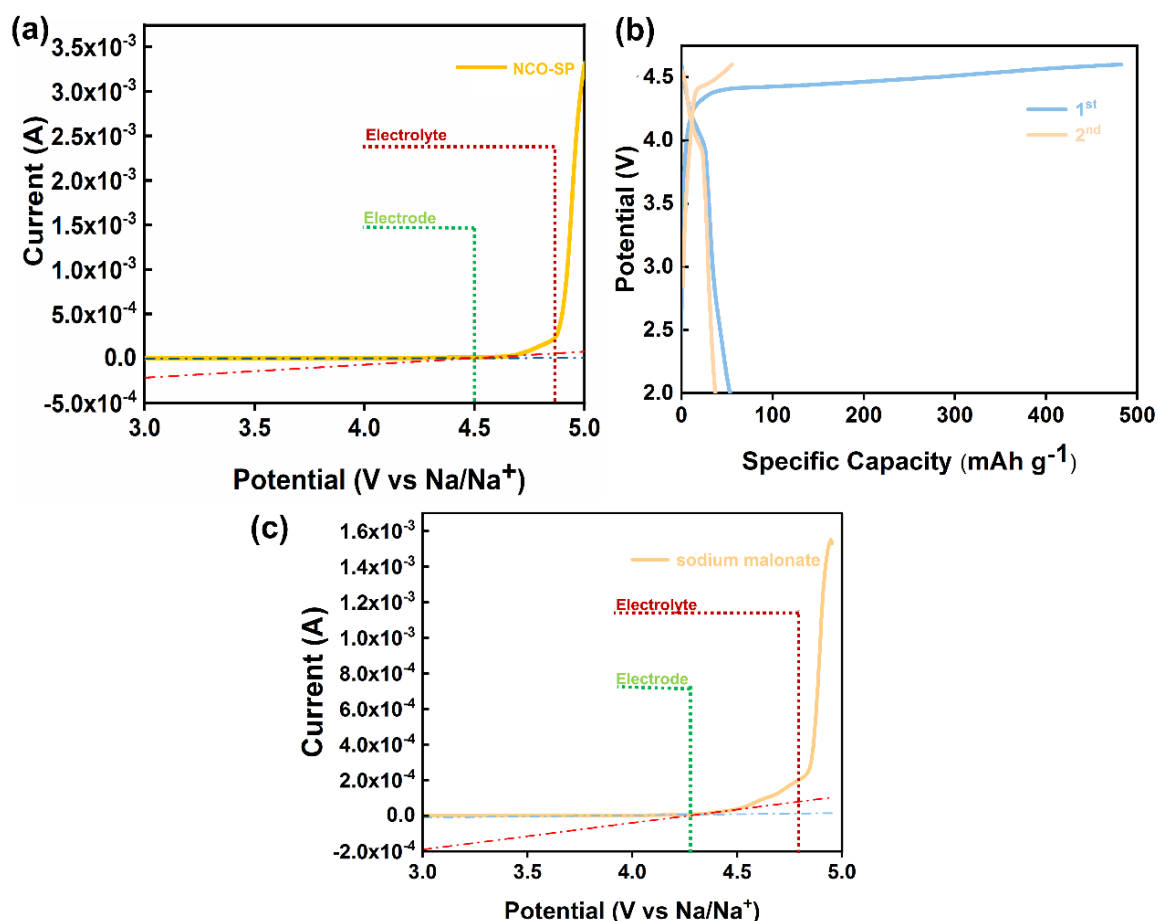
<sup>1</sup>College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, P. R. China

<sup>2</sup>Department of Semiconductors Materials and Energy Research Center P.O. Box 14155/4777, Tehran, Iran

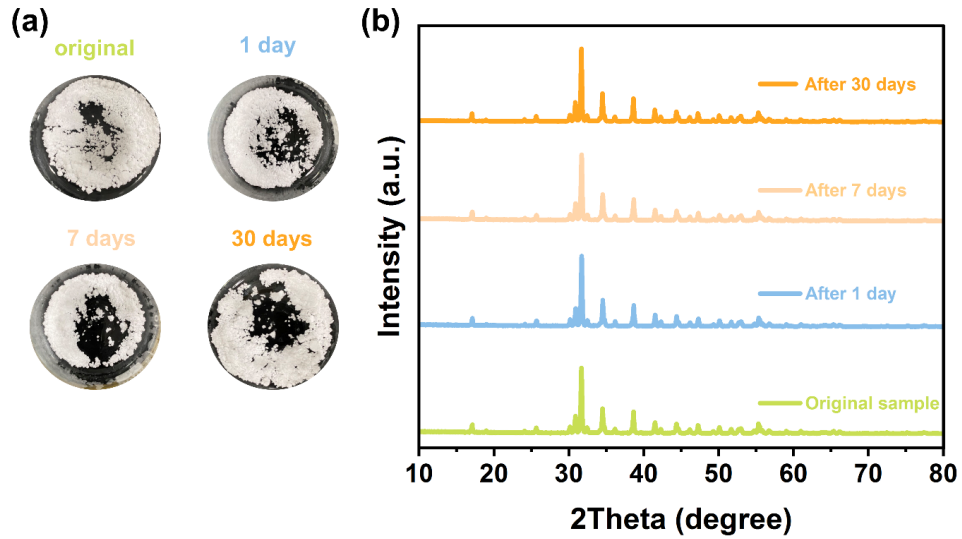
<sup>3</sup>College of Material Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China

\*Corresponding author. E-mail: [gq-zou@csu.edu.cn](mailto:gq-zou@csu.edu.cn) (Guoqiang Zou)

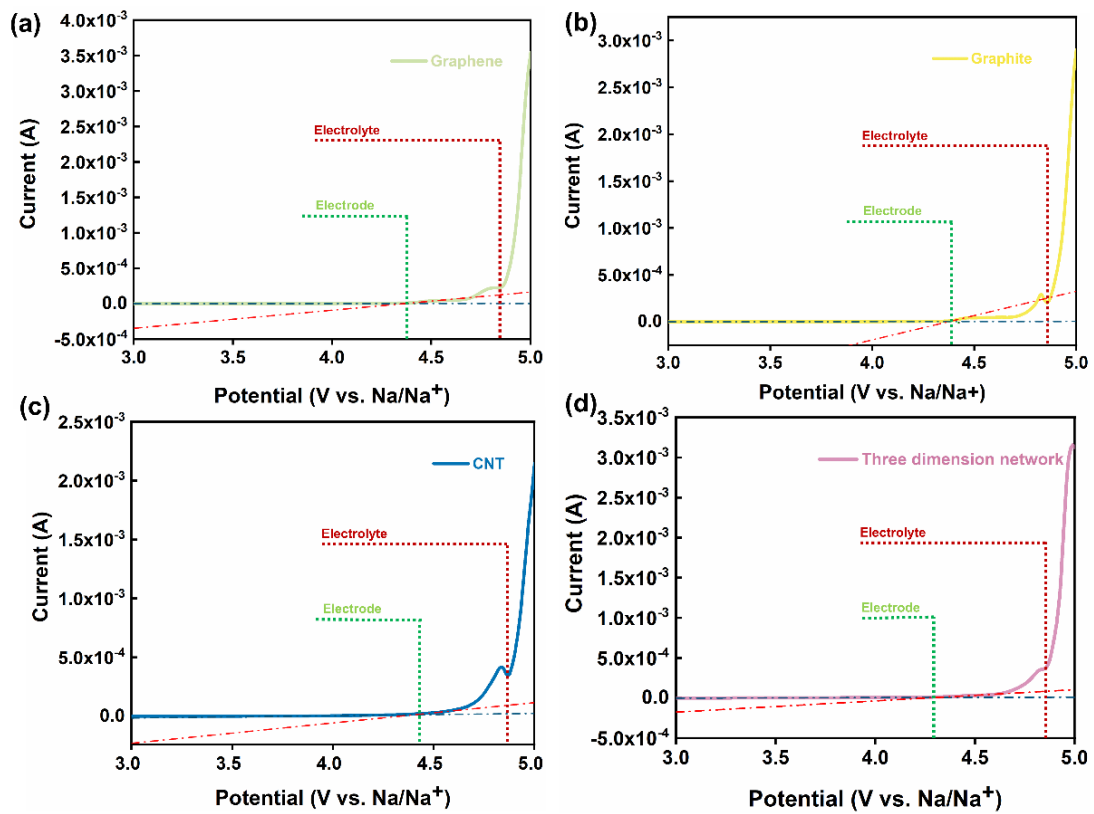
### Supplementary Figures and Tables



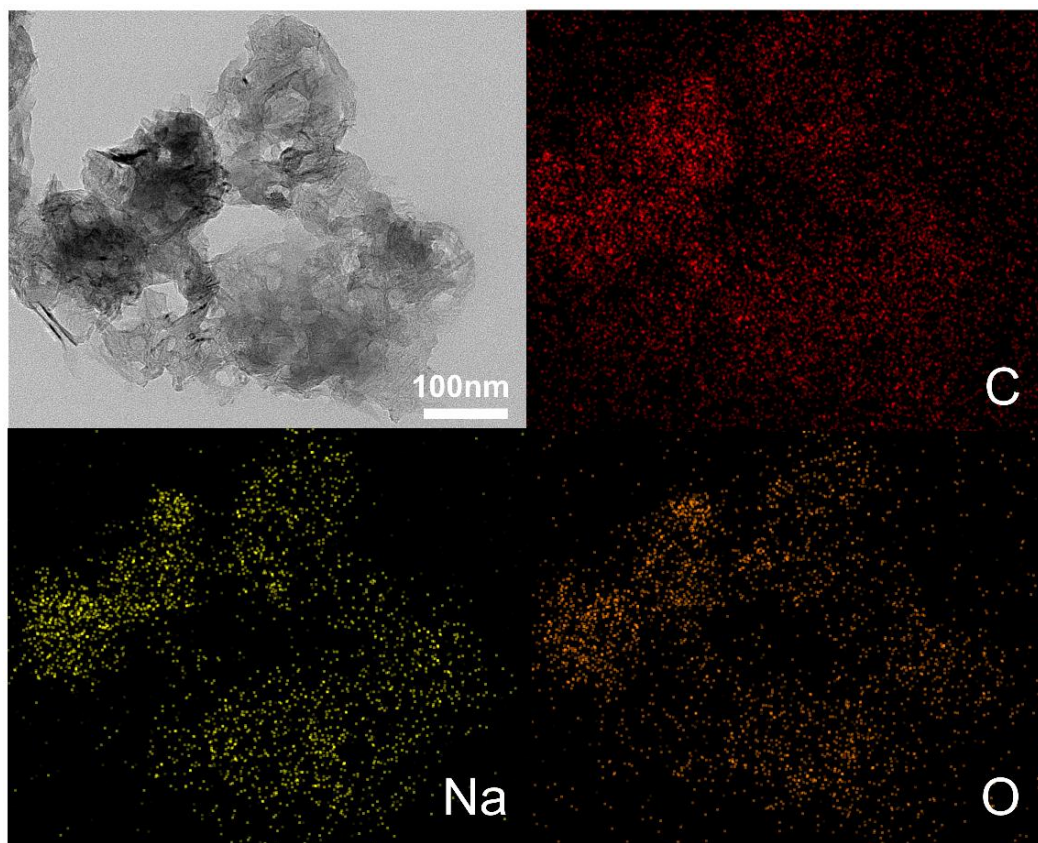
**Fig. S1** Electrochemical decomposition performance of NCO-SP electrode investigated by (a) CV curves at 0.25 mV s<sup>-1</sup>. (b) GCD curves of NCO-SP at the current density of 0.1C within the potential range of 4.6-2 V. (c) CV curves of Na<sub>2</sub>H<sub>2</sub>C<sub>3</sub>O<sub>4</sub>-SP at 0.25 mV s<sup>-1</sup>



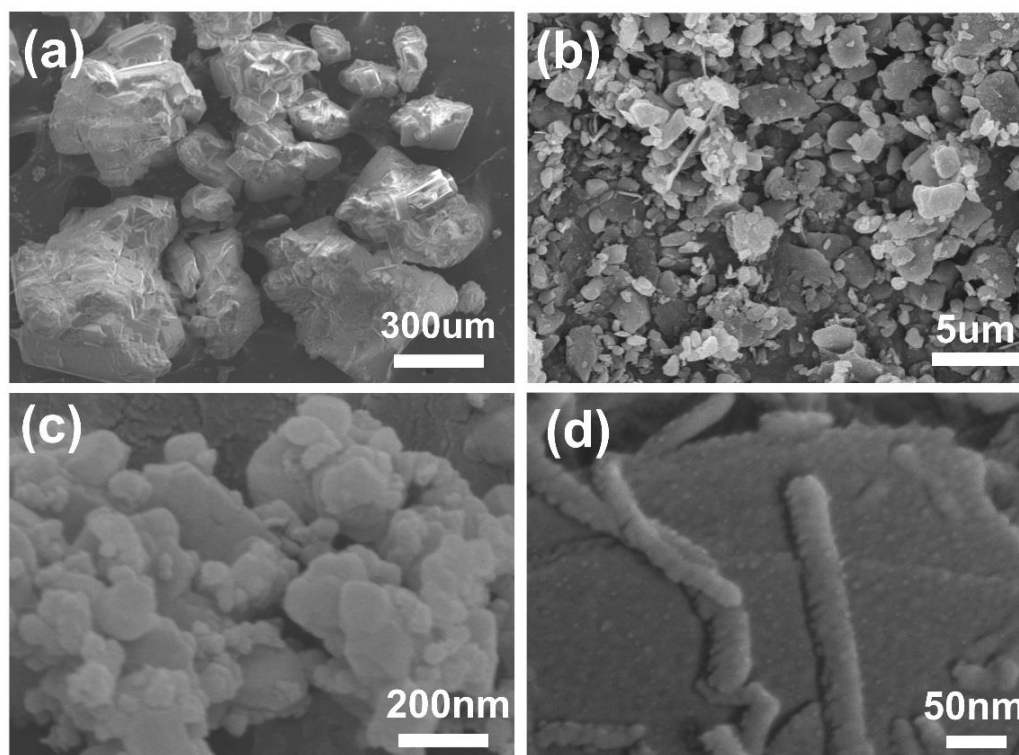
**Fig. S2** Status of sodium oxalate after being exposed in ambient environment for certain days. (a) Optical photos. (b) XRD patterns



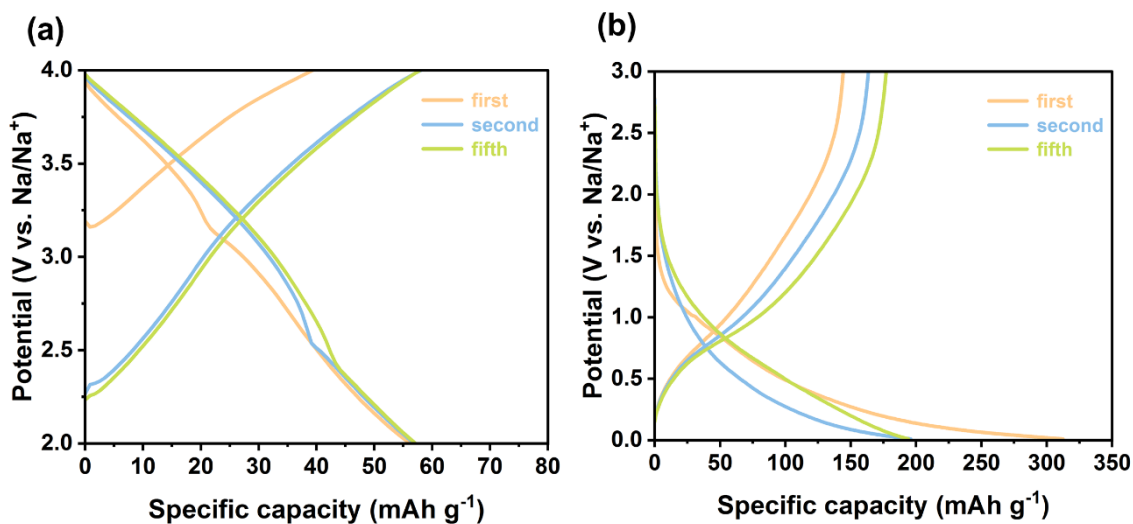
**Fig. S3** CV curves of  $\text{Na}_2\text{C}_2\text{O}_4$  in various conductive additive systems at  $0.25 \text{ mV s}^{-1}$ . (a) graphene system. (b) graphite system. (c) carbon nanotube system. (d) 3D conductive network system



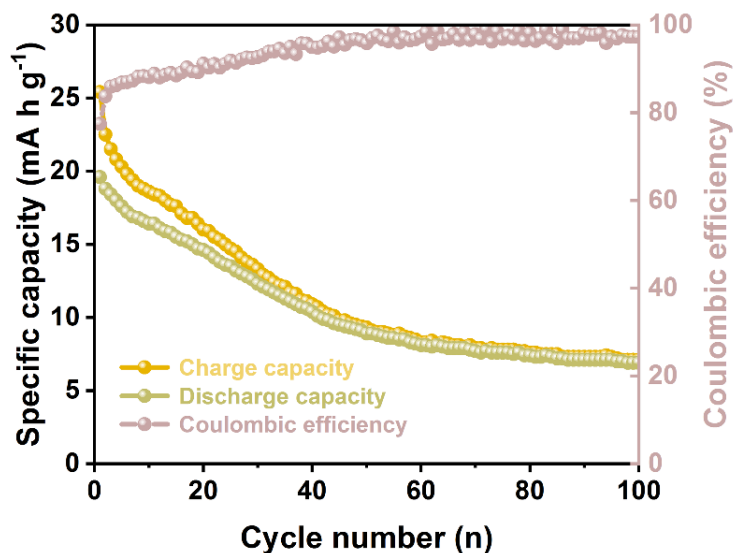
**Fig. S4** TEM image of NCO-S-3D and corresponding EDS elemental mapping



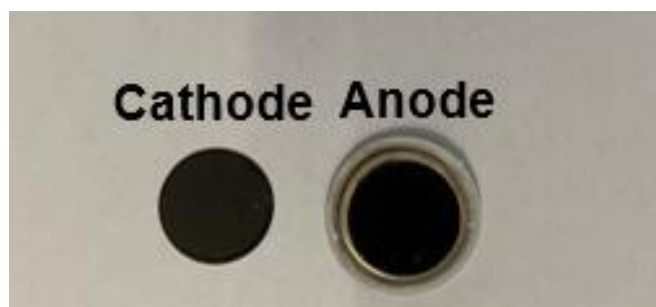
**Fig. S5** SEM images of (a) pristine sodium oxalate and (b-d) after being ball milled with 3D conductive network



**Fig. S6** Charge and discharge profiles of (a) activated carbon and (b) TiO<sub>2</sub> at the current density of 100 mA g<sup>-1</sup>



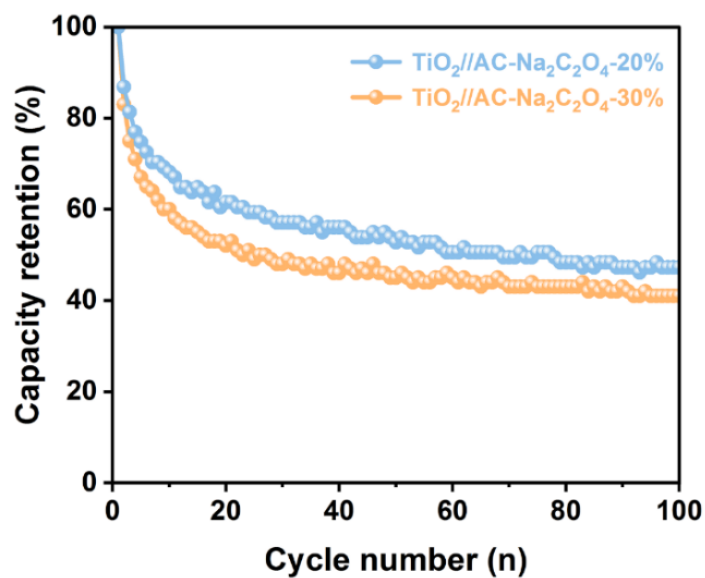
**Fig. S7** Cycling performance and CE of TiO<sub>2</sub>//AC-NCO-15% with traditional slurry method under 1C at 4-0 V after presodiation



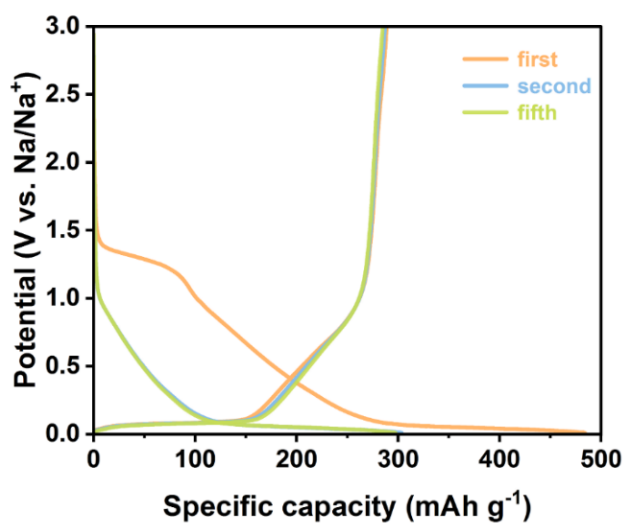
**Fig. S8** Optical photos of electrodes in disassembled SIC system after cycling for 100 cycles



**Fig. S9** Optical photos of separators disassembled SIC system after cycling for 100 cycles

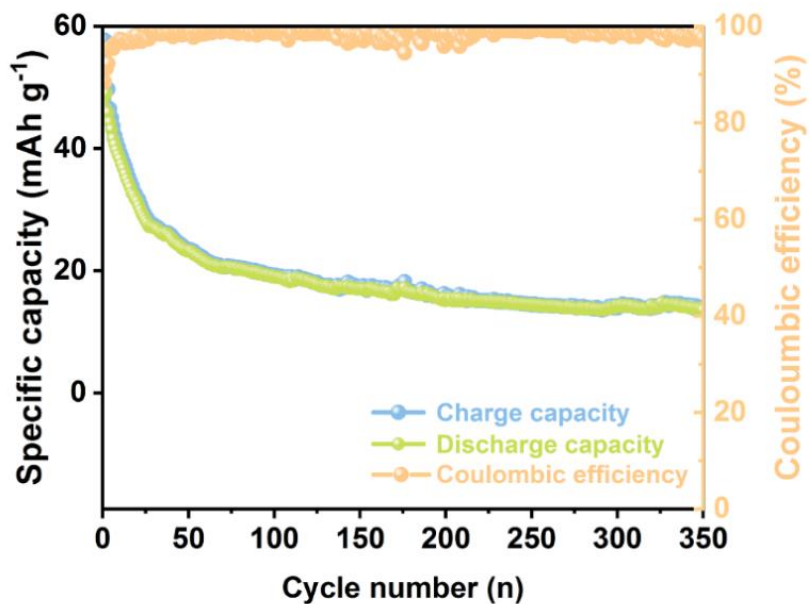


**Fig. S10** Cycling stability of TiO<sub>2</sub>//AC-NCO-S-3D-20% and TiO<sub>2</sub>//AC-NCO-S-3D-30% SICs at 1C within 4-0 V after presodiation

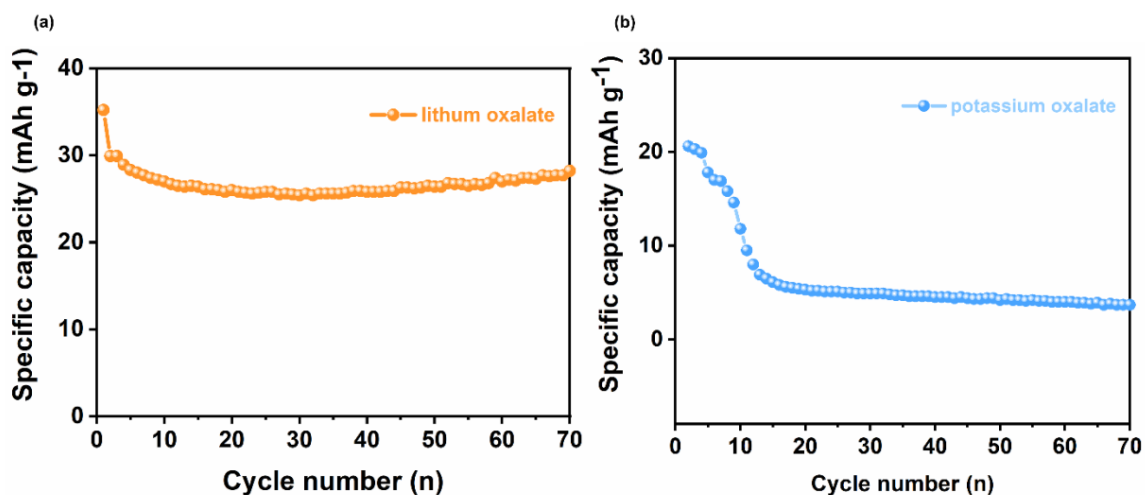


**Fig. S11** Charge and discharge profiles of hard carbon at the current density of 100 mA g<sup>-1</sup>

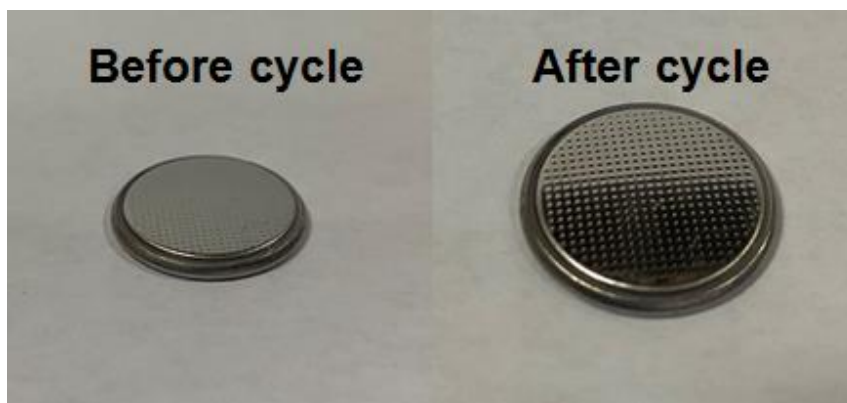




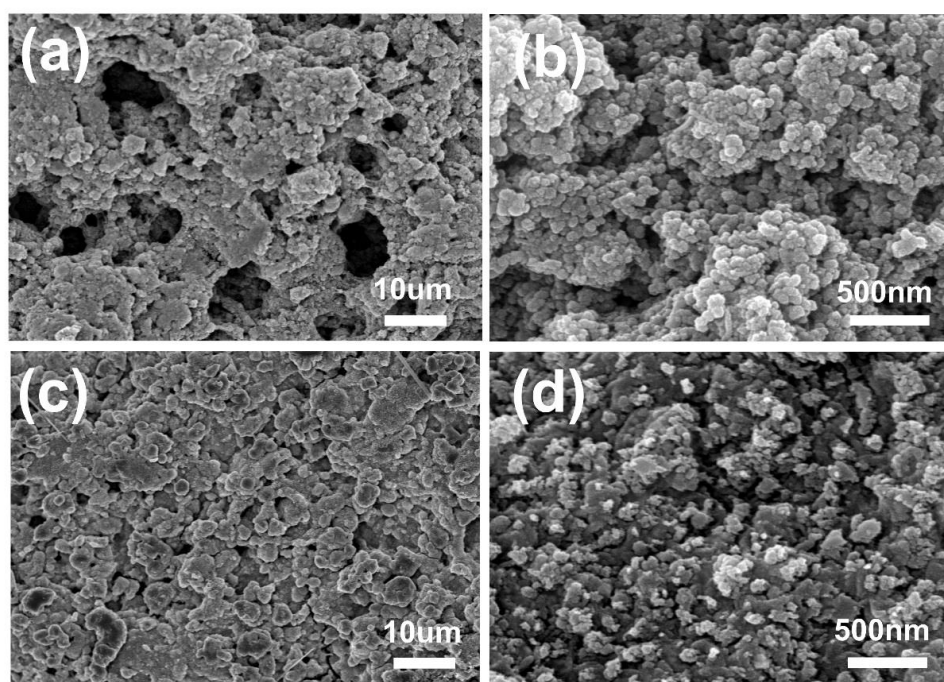
**Fig. S12** Cycling performance and CE of HC//AC-NCO-30% under 1C at 4-0 V after presodiation



**Fig. S13** Cycling performance of (a) TiO<sub>2</sub>//AC-Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-15% and (b) TiO<sub>2</sub>//AC-K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-15% under 1C at 4-0 V after premetallation



**Fig. S14** Observation of coin-type SIC before and after cycling



**Fig. S15** Surface images of TiO<sub>2</sub> anode before (a, b) and after (c, d) cycles

**Table S1** Properties of sacrificial cathode additives currently applied in sodium ion capacitors

Sacrificial additives	Decomposition product	Theoretical capacity (mA h g <sup>-1</sup> )	Dosage (compared to active cathode)	Cost (CNY kg <sup>-1</sup> )	Purity
Na <sub>2</sub> S	S	687	100%	50000	95%
Na <sub>2</sub> C <sub>4</sub> O <sub>4</sub>	CO <sub>2</sub> /C	339	80%	Lab-synthesis	Lab-synthesis
Na <sub>2</sub> C <sub>4</sub> O <sub>4</sub>	CO <sub>2</sub> /CO/C	339	58%/220%	Lab-synthesis	Lab-synthesis
Na <sub>2</sub> C <sub>6</sub> O <sub>6</sub>	C <sub>6</sub> O <sub>6</sub>	250	60%/100%/167%	4400	Analytical Reagent
NaNH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub> /N <sub>2</sub> /H <sub>2</sub>	686	45%	328	95%
<b>Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (our work)</b>	<b>CO<sub>2</sub></b>	<b>400</b>	<b>15%/20%/30%</b>	<b>5</b>	<b>99.8%</b>

**Table S2** Summary of decomposition voltages of sacrificial cathode additives related to various amelioration methods

	NCO-SP	Na <sub>2</sub> H <sub>2</sub> C <sub>3</sub> O <sub>4</sub> -SP	NCO-graphene	NCO-graphite	NCO-carbon nanotube	NCO-3D	<b>NCO-S-3D</b>
<b>Decomposition potential (V)</b>	4.50	4.30	4.36	4.38	4.40	4.30	<b>3.95</b>

Abbreviations:

NCO: Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>;

3D: Three dimension conductivenetwork;

NCO-SP: Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with super p;

NCO-S-3D: size-reduced Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with 3D network.