

## Supporting Information

### Thiophene-functionalized porphyrin complexes as high performance electrodes for sodium ion batteries

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## Experimental Procedures

### 1.1 Materials

All reagents and solvents were obtained from Alfa Aesar and Chemical Great-wall. Polyvinylidene fluoride (PVDF), acetylene black, stainless steel (316 L, 12 mm in diameter), and *N*-methyl-2-pyrrolidone (NMP), Glass microfiber filters (Whatman, GF/D) were purchased commercially and used as received without further purification. The use of all glassware was needed in the synthetic were conducted in oven-dried (70 °C).

### 1.2 Material characterization

Mass spectrometry (MS) were performed on a Bruker Aupoflflex III MALDI-TOF Analyzer using CCA as matrix. The morphology of samples was carried out using field emission scanning electron microscope (SEM, JSM-6610LV). The attenuated total reflectance-fourier transformation infrared (ATR-FTIR) spectroscopy was obtained on a Thermo Fisher Nicolet IS50 ATR-FTIR spectrometer from 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. UV-Vis spectra of porphyrins were measured on a Perkin-Elmer Cary 60 spectrometer. X-ray photoelectron Spectroscopy was recorded on a Escalab250Xi (Thermo Scientific), using monochromatized Al K $\alpha$  radiation (1486 eV). The pass energy for survey spectra was 100 eV, for detail spectra the energy was 30 eV. The thermogravimetry-differential scanning (TGA) was recorded on a Netzsch TG 209 (Netzsch). CV and electrochemical impedance using electrochemical workstation (DH7000C, Jiangsu Donghua Analytical Instruments Co. Ltd.)

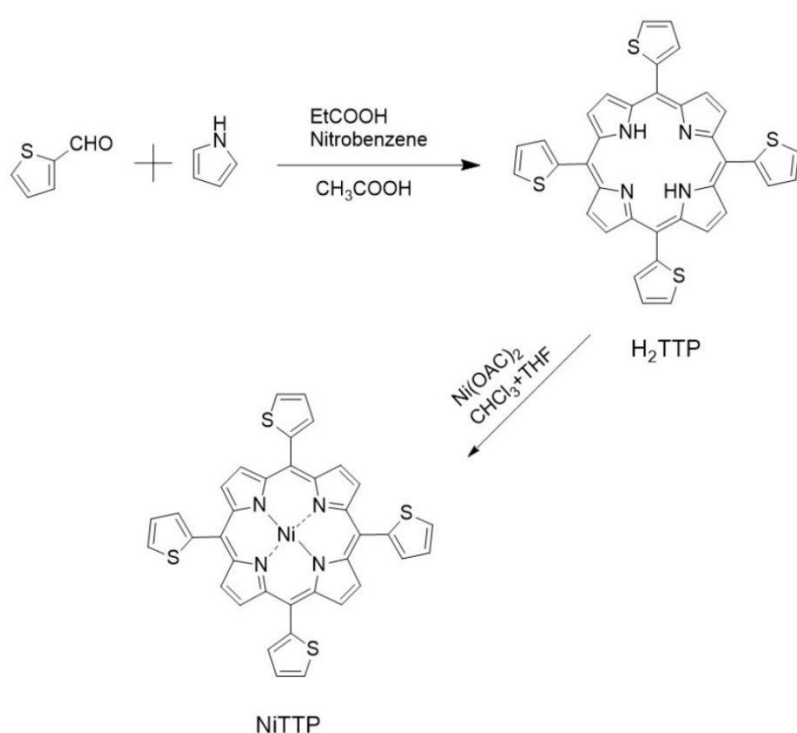
### 1.3 Synthesis of [5, 10, 15, 20-Tetrathienylporphyrin (H<sub>2</sub>TTP)

A mixture of 10 mL propionic acid, 10 mL nitrobenzene, and 15 mL acetic acid were stirred at 138 °C and refluxed for 10 minutes. A mixed liquid (10 mL propionic acid and 1.35 mL thiophene-2-carbaldehyde) was slowly injected. Next, a mixture of 10 mL acetic acid and 1.35 mL pyrrole was slowly added. After stirred for 90 min, the reaction mixture was poured into 100 mL MeOH and stirred at room temperature for 12 h in air. Afterward, the solid was obtained by filtration and washed with a copious amount of ethanol and water. After removal of solvents in vacuum, a dark

purple solid H<sub>2</sub>TTP (1 g, 20%) was obtained. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): -2.63 (s, 2H), 7.51 (dd, *J* = 3.2, 5.2 Hz, 4H), 7.86 (dd, *J* = 0.8, 5.2 Hz, 4H), 7.92 (dd, *J* = 0.8, 3.2 Hz, 4H), 9.04 (s, 8H); MALDI-TOF-MS Calc. for C<sub>36</sub>H<sub>22</sub>N<sub>4</sub>S<sub>4</sub>: [M+H]<sup>+</sup>, 638.85; Found: *m/z* 639.29.

#### 1.4 Synthesis of [5, 10, 15, 20-Tetrathienylporphinato] Nickel (II) (NiTTP)

Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.623 g, 2.5 mmol) was added to a solution of compound H<sub>2</sub>TTP (0.319 g, 0.5 mmol) in a mixture of 50 mL chloroform (CHCl<sub>3</sub>) and 10 mL THF. Then it was heated at 60 °C for 36 h. After it was cooled to room temperature, it was poured into 150 mL water and extracted by DCM (150 mL). The DCM solution was concentrated under reduced pressure. After removal of solvents in vacuum, a purple solid NiTTP (0.332 g, 95 %) was obtained. Uv-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 423, 537. IR (KBr, cm<sup>-1</sup>) 3099, 1552, 1430, 1330, 1301, 1235, 1168, 1075, 1035, 991, 860, 808, 793, 700. MALDI-TOF-MS Calc. for C<sub>36</sub>H<sub>20</sub>NiN<sub>4</sub>S<sub>4</sub>: [M+H]<sup>+</sup>, 694.097; Found: *m/z* 694.07.



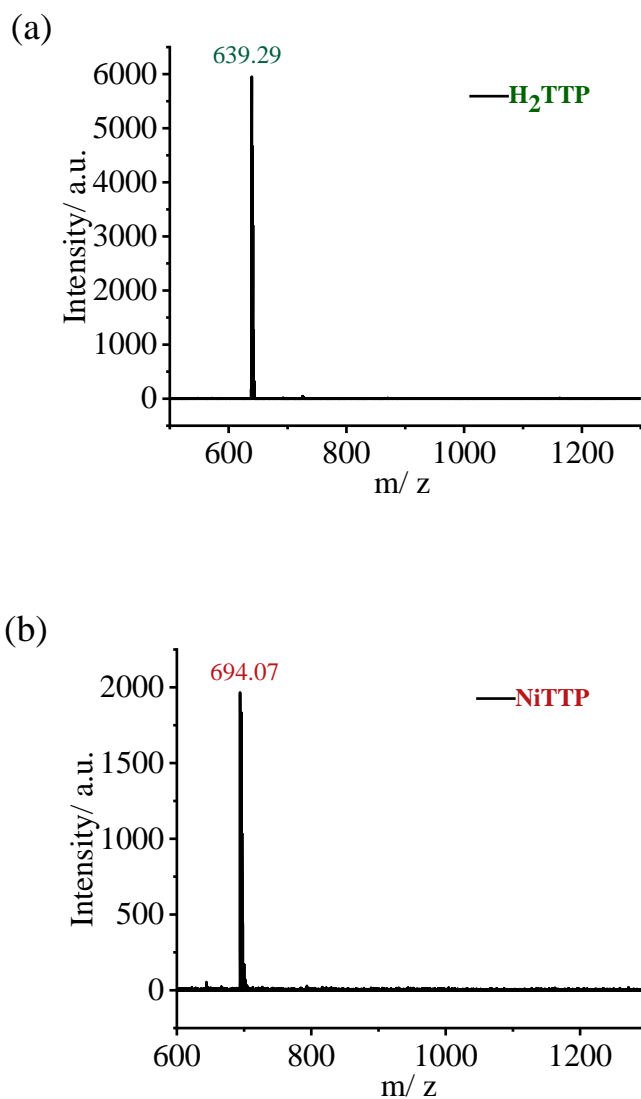
**Scheme S1.** Synthetic route and structure of MTTP (M = 2H, Ni).

#### 1.5 Electrochemical measurements

All the electrochemical performance of cell was performed by using CR2032 coin-type cells in an Ar-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1ppm Mikrouna). For the MTTP (M = 2H, Ni) electrode was prepared by mixing 50 wt% MTTP (M=2H, Ni), 40 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) (the ratio electrode was used to test long term cycle at 1000 mAh g<sup>-1</sup>). In addition, for the current density of 25 mA g<sup>-1</sup> test, 80 wt% MTTP (M = 2H, Ni), 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF), 70 wt% MTTP (M = 2H, Ni), 20 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF). For IR, Raman test, the MTTP (M = 2H, Ni) electrode was prepared by mixing 80 wt% MTTP, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF). The mass loading of MTTP electrode was about 1 mg cm<sup>-2</sup>. Sodium foil with 12 mm in diameter was directly used as the counter. 1 M NaPF<sub>6</sub> in mixture solvent of propylene carbonate (PC) and 5% fluoroethylene carbonate (FEC) was

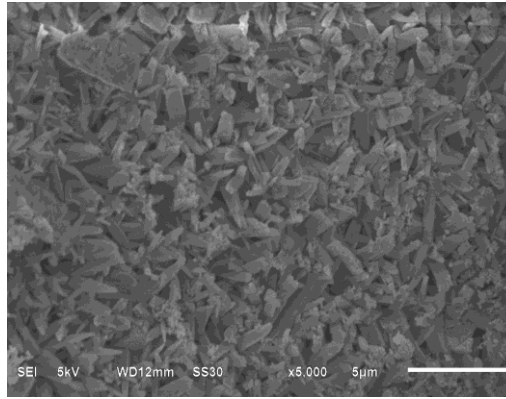
used as electrolyte when MTTP was used as cathode materials. Furthermore, 1 M NaPF<sub>6</sub> in mixture solvent of methoxymethane (DME) was used as electrolyte when MTTP was used as anode materials. All capacities are calculated based on the active material of the electrode.

For the full cell, the cathode electrode and anode was prepared similarly and the capacity ratio of negative/positive (N/P) electrodes was set to slightly higher than 1.0. The specific capacity of full cell was based on the mass of the cathode. Both cathode and anode were electrochemically pre-sodiated for five cycles (at 100 mA g<sup>-1</sup>). 1 M NaPF<sub>6</sub> in ethylene carbonate (EC) and diethyl carbonate (DEC) was used as electrolyte.

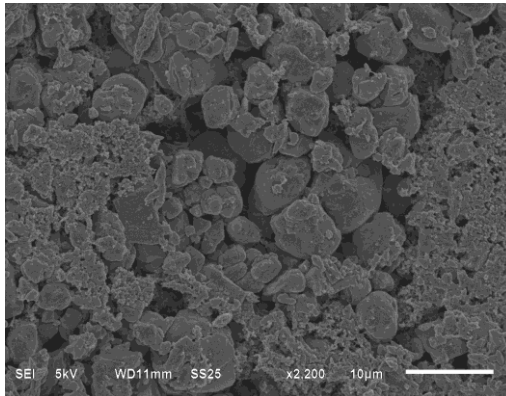


**Figure S1.** The flight mass spectrum of the H<sub>2</sub>TTP and NiTTP.

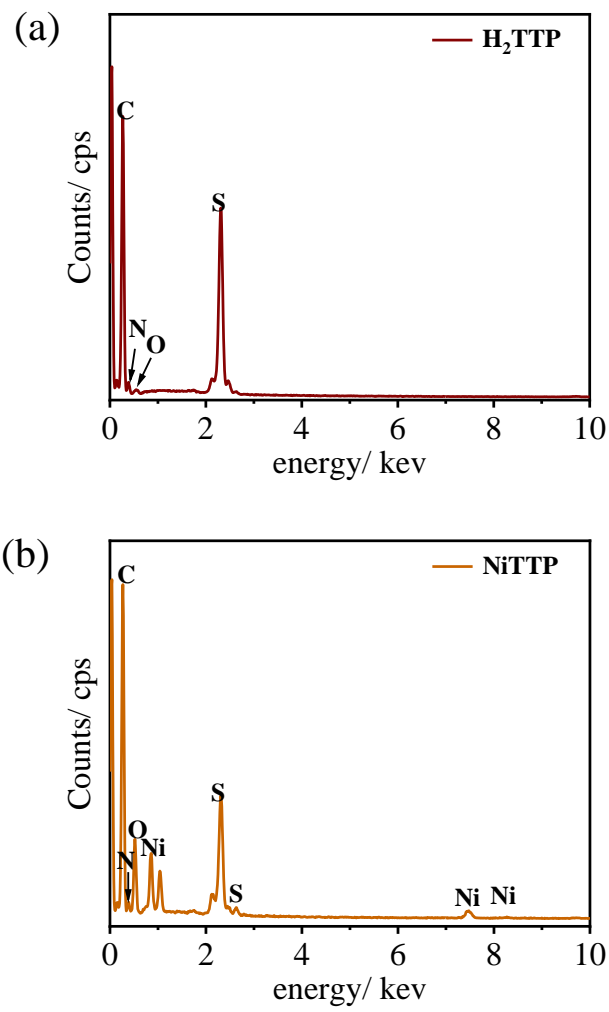
(a)



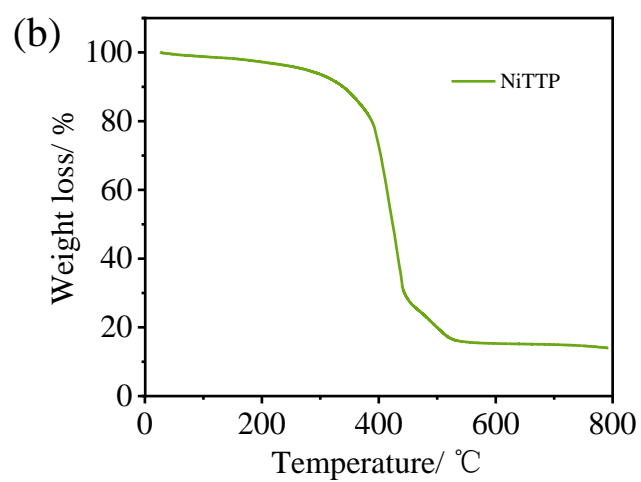
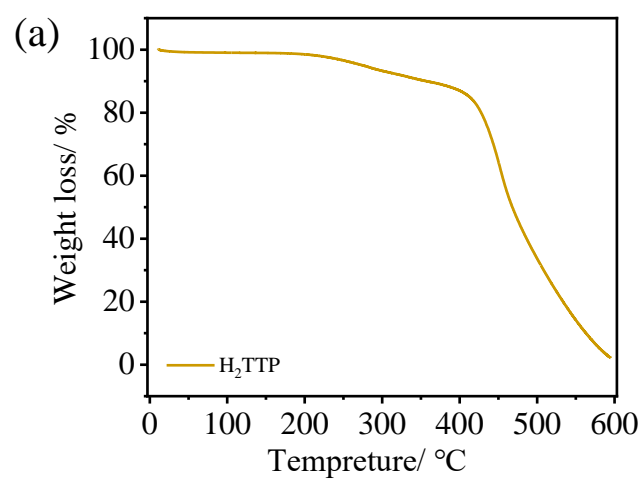
(b)



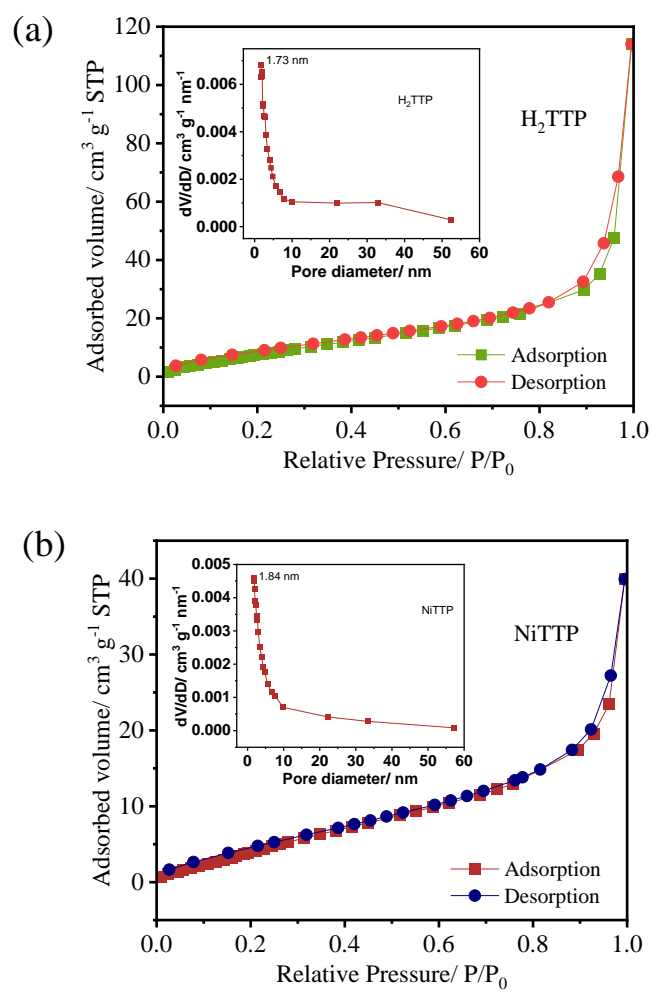
**Figure S2.** SEM images of (a) H<sub>2</sub>TTP and (b) NiTTP.



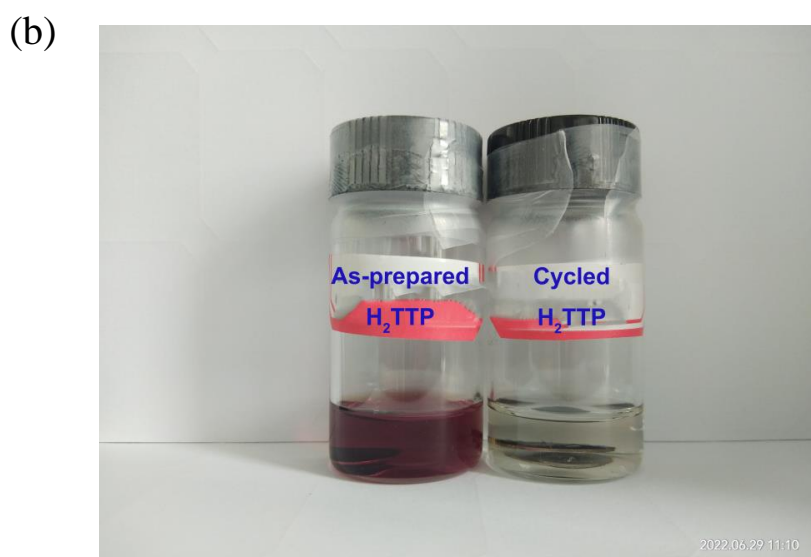
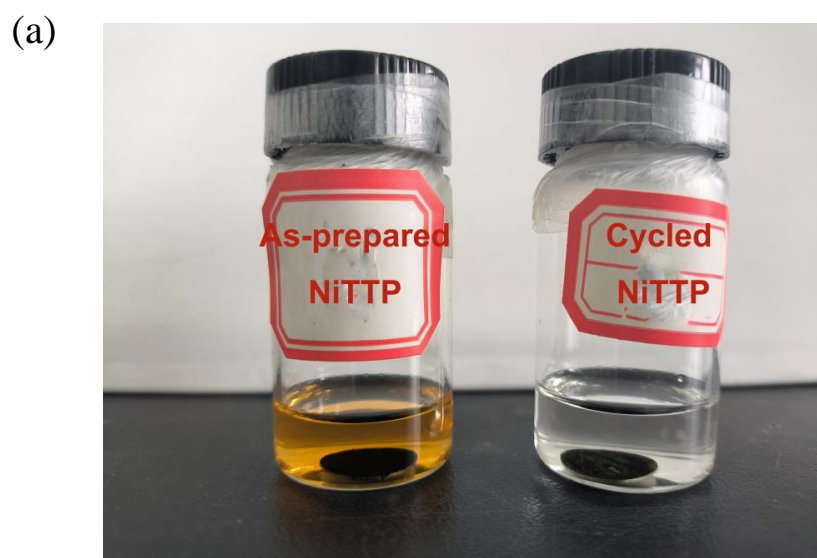
**Figure S3.** The EDX spectra of (a) H<sub>2</sub>TTP and (b) NiTTP.



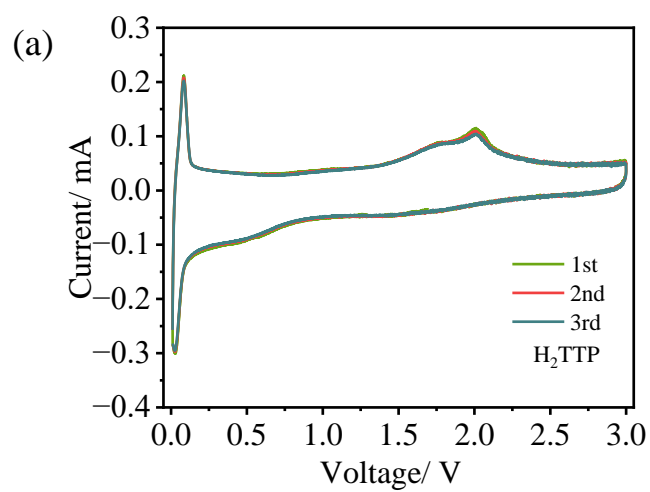
**Figure S4.** The TG curves of (a) H<sub>2</sub>TTP and (b) NiTTP.



**Figure S5.** The  $\text{N}_2$  absorption-desorption diagrams of (a)  $\text{H}_2\text{TTP}$  (b)  $\text{NiTTP}$

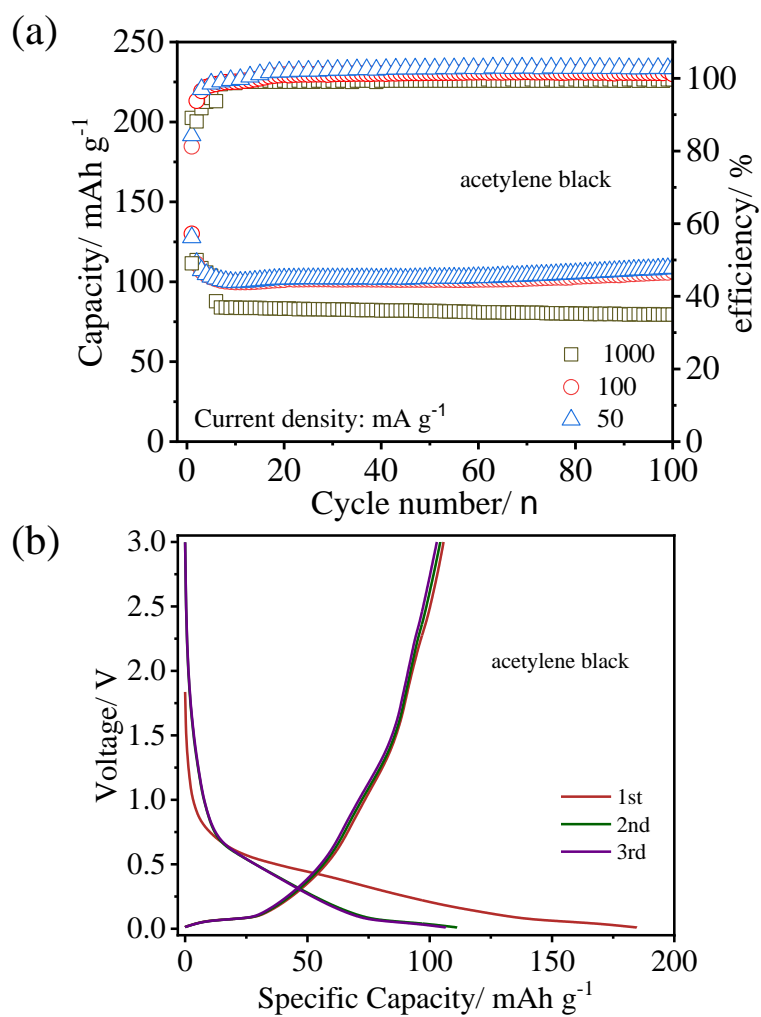


**Figure S6.** The pictures of (a) NiTTP anode (b) H<sub>2</sub>TTP anode soak in THF.

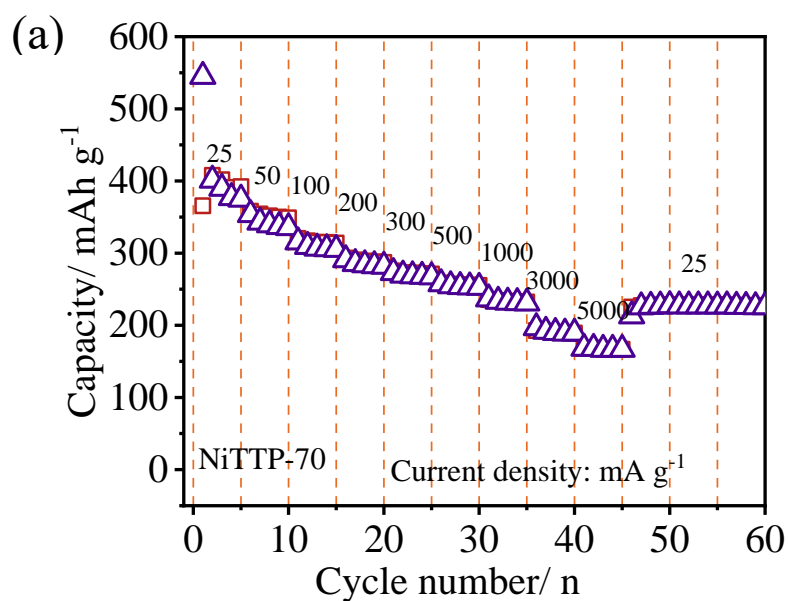


**Figure S7.** CV curves of the H<sub>2</sub>TTP after stabilization process at a scanning rate of 0.2 mV s<sup>-1</sup>.

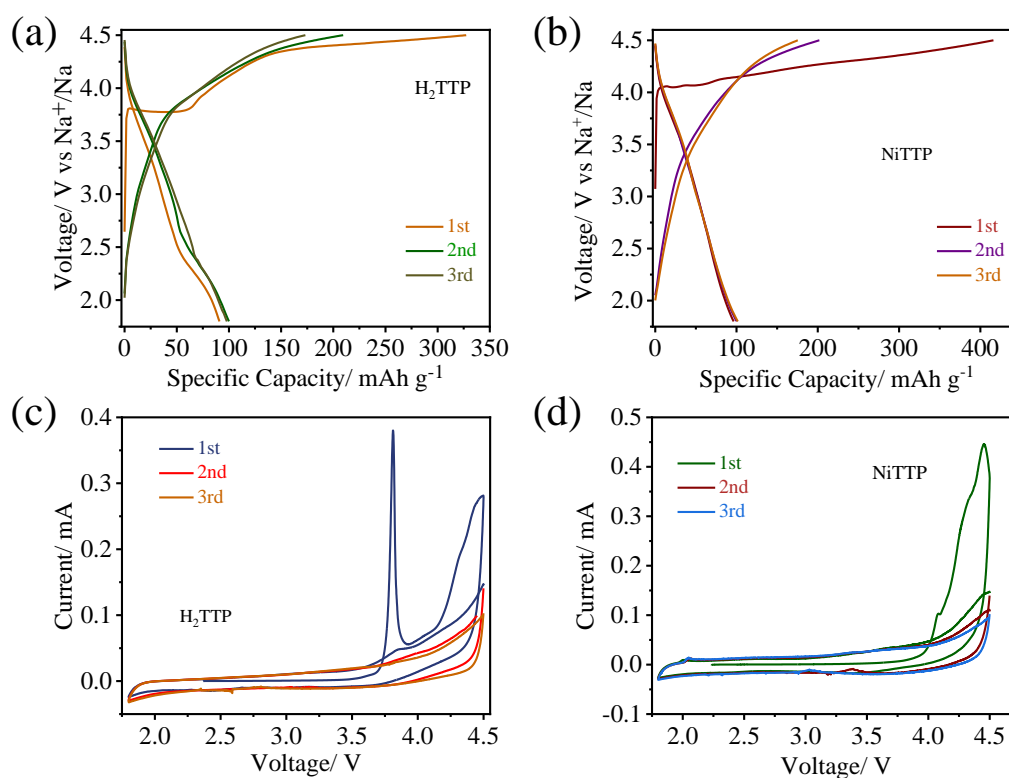




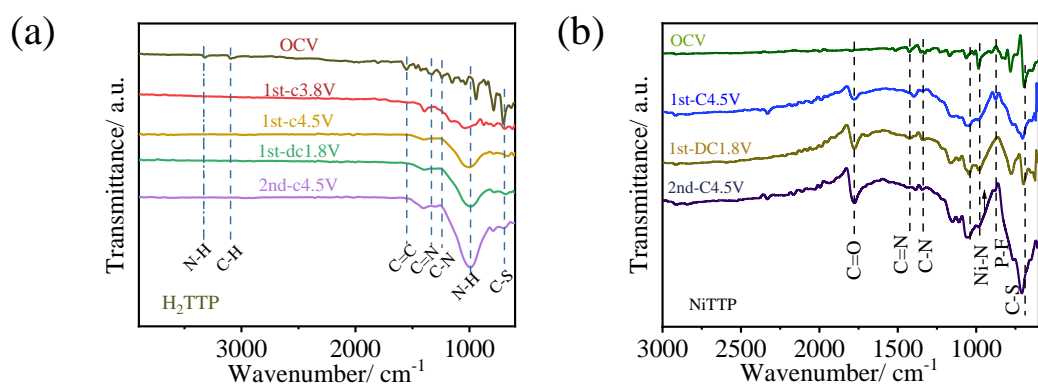
**Figure S8.** (a) The different current density of the discharge capacity of acetylene black electrode (the electrode was prepared by mixing 90 wt% acetylene black, and 10 wt% PVDF). (b) The initial three cycles of acetylene black electrode at 100 mA g<sup>-1</sup>.



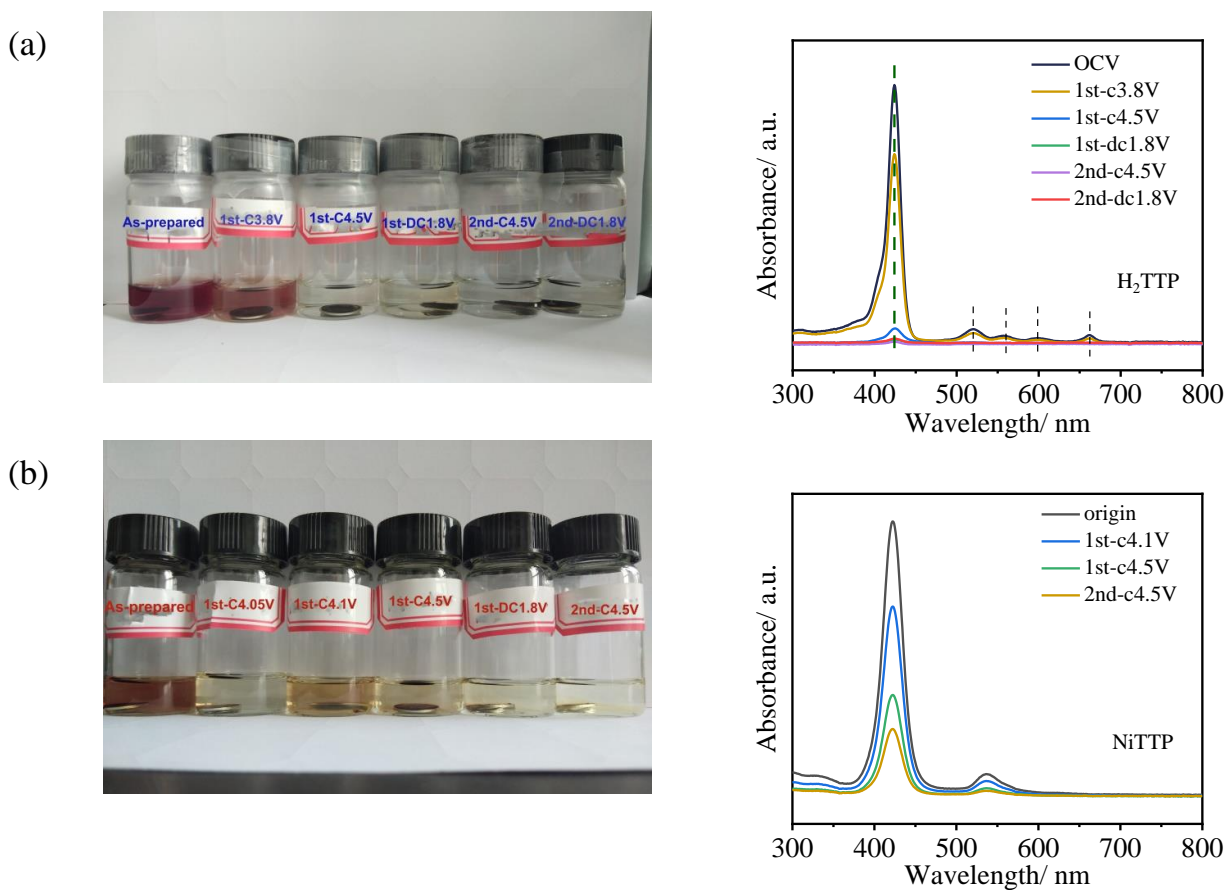
**Figure S9.** (a) The rate performance of NiTTP-70.



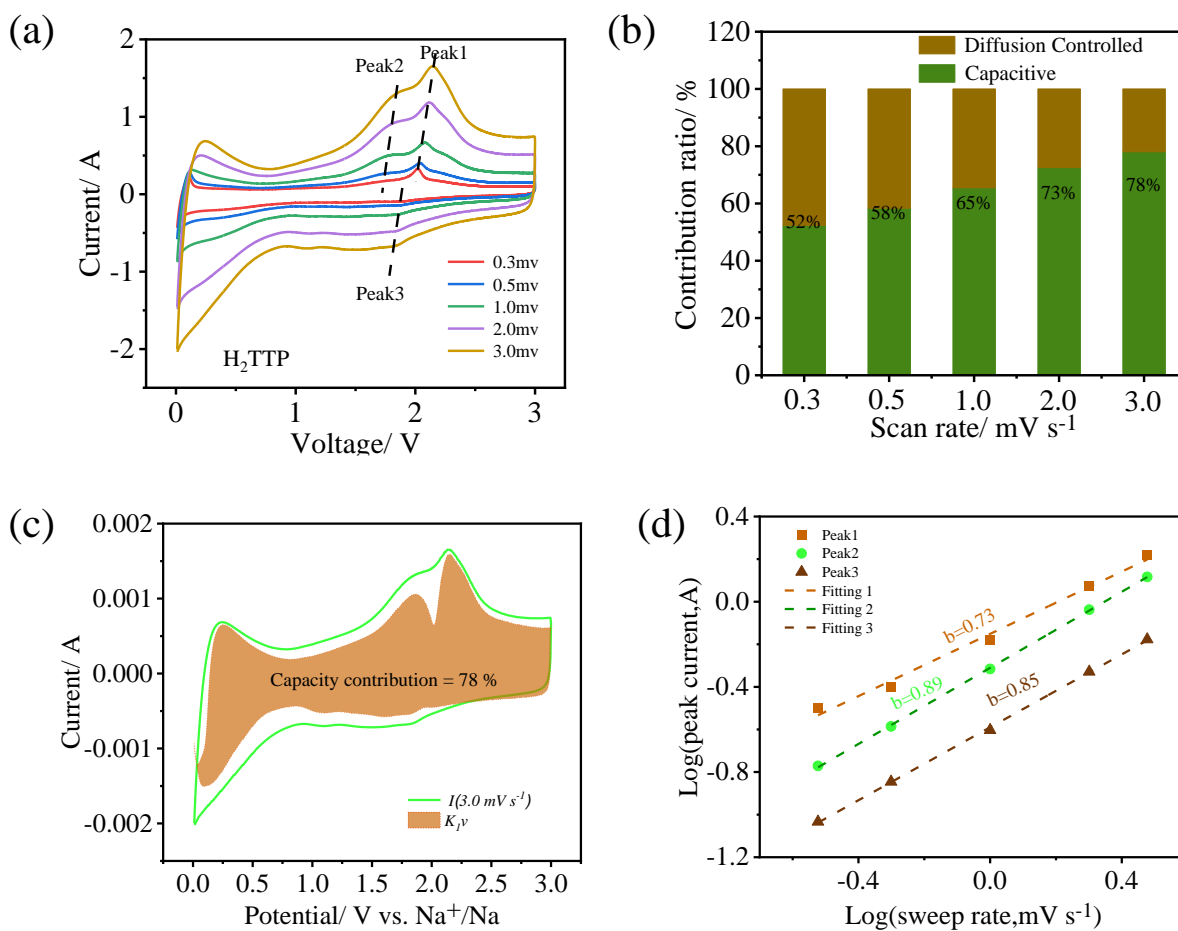
**Figure S10.** (a, b) Initial charge–discharge curves of MTTP (M = 2H, Ni) cathode for sodium-organic batteries at  $200 \text{ mA g}^{-1}$ . (c, d) Cyclic voltammetry (CV) test of MTTP (M = 2H, Ni) as cathode in SIBs.



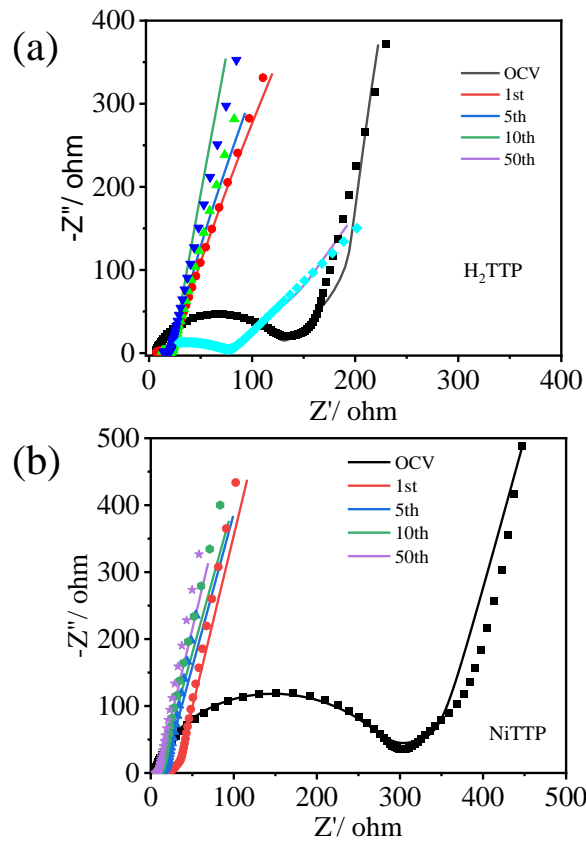
**Figure S11.** The ex-situ FTIR spectra of (a) H<sub>2</sub>TTP cathode (b) NiTTP cathode in different cycled states.



**Figure S12.** The electrode of (a) H<sub>2</sub>TTP and (b) NiTTP cathode soak in THF and corresponding to ex-situ UV-vis spectra.

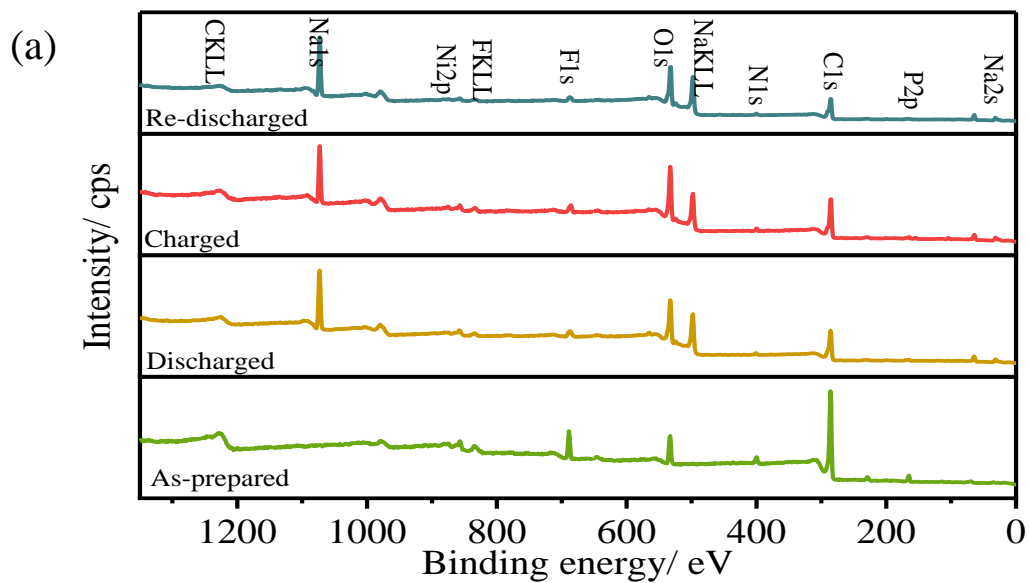


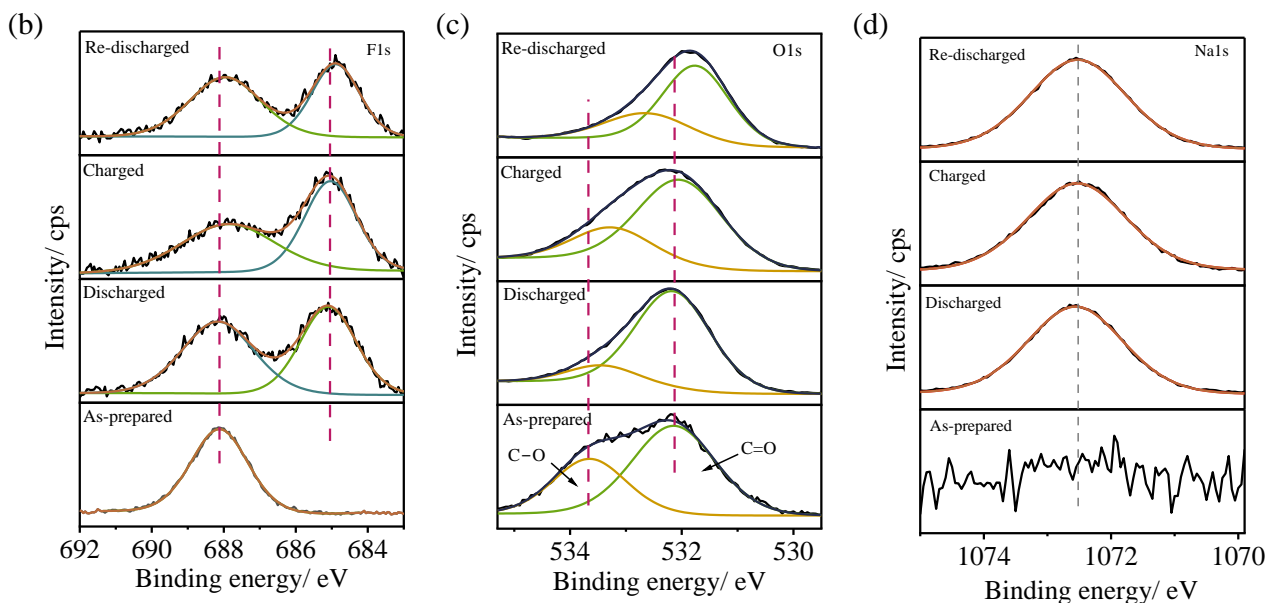
**Figure S13.** (a) The CV curves of H<sub>2</sub>TTP electrode obtained at various scan rates after initial three cycles between 0.01 and 3.0 V, (b) contribution ratio of the pseudocapacitance at various scan rates, (c) capacitive contributions (shaded area) to charge storage at a scan rate of 3 mV s<sup>-1</sup>, (d) log (*i*, current) versus log (*v*, scan rate) for determining the *b* values.



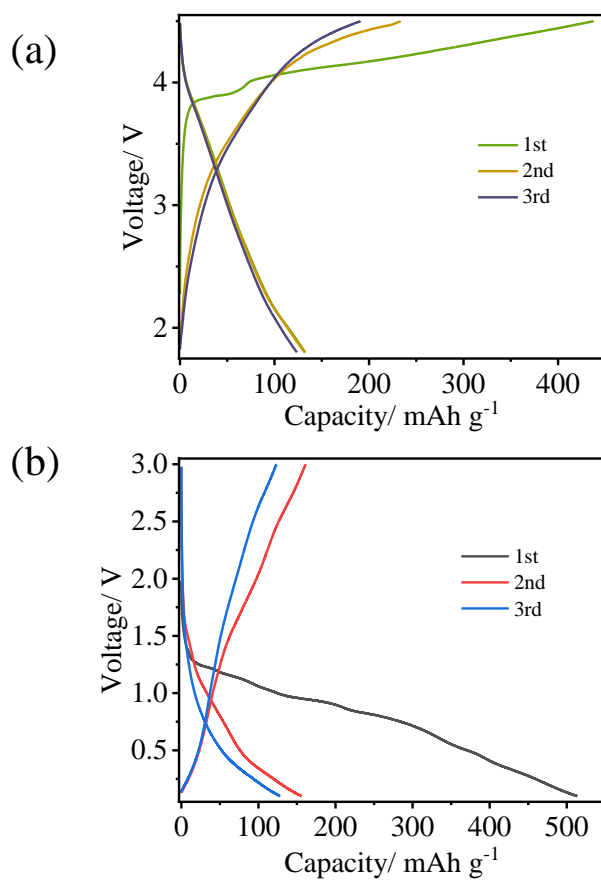
**Figure S14.** The EIS curves of (a) H<sub>2</sub>TTP (b) NiTTP at different cycles in SIBs.  
Time/h

**Figure S15.** The GITT test of (a) NiTTP-50 (b) H<sub>2</sub>TTP-50.

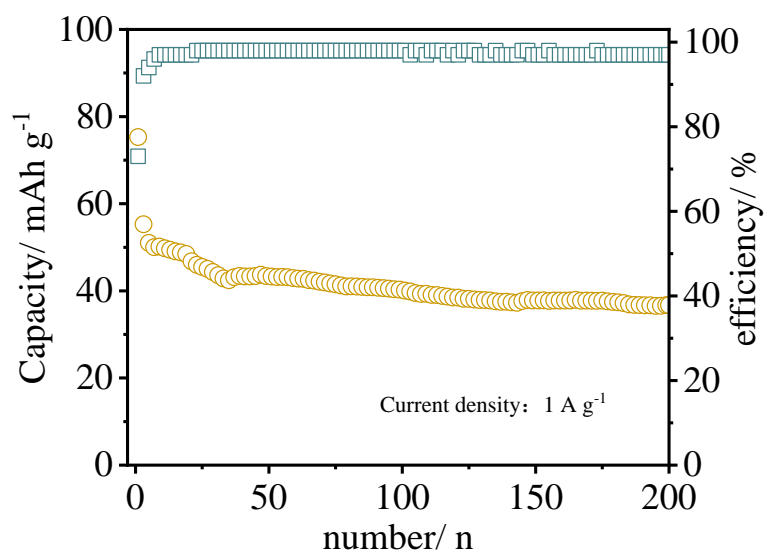




**Figure S16.** (a) Survey XPS spectra of NiTTP at as-prepared, discharged, charged and re-discharged states, (b) XPS spectra core level of fluorine, (c) oxygen, (d) sodium of NiTTP in different cycled states.



**Figure S17.** The initial three cycles of (a) NiTTP cathode, (b) NiTTP anode at  $0.1 \text{ A g}^{-1}$ .



**Figure S18.** The cycling performance of NiTTP/NaPF<sub>6</sub>/NiTTP in a voltage range of 0.1-4.0 V.