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Supercapacitive study for the electrode materials around the framework-collapsed point of Ni-based coordination polymer

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Experimental section：

Materials. All chemicals (analytical grade) were purchased from commercial sources and directly used as received. Water was purified with the Millipore system (18.2 MΩ cm).

Synthesis of Ni-TATB. 4,4',4''-*s*-triazine-2,4,6-triyl-tribenzoic acid (H_3TATB, 2.2052 g, 5 mmol) and H_2O (50 mL) were mixed at 90 °C. Then slowly added the prepared 3 mol L^{-1} NaOH solution dropwise until pH≈7, 0.1mol L^{-1} sodium triazine solution was successfully prepared. The sodium triazine solution (0.1 mol L^{-1}, 4 mL), nickel acetate solution (0.1 mol L^{-1}, 6 mL), ultrapure water (5 mL) and absolute ethanol (5 mL) were introduced into a stainless steel autoclave at 120 °C for 12 h. After cooling down to room temperature, washed with deionized water and absolute ethanol, and vacuum lyophilized to obtain Ni-TATB in a green powder state. FT-IR (KBr pellet, cm^{-1}): 3300(s), 2287(w), 1593(s), 1471.5(m), 1313.29(m), 1274(m), 846(w), 796(w), 674(w).

Preparation of Ni-TATB derivatives. The Ni-TATB precursor was separately decomposed to the selected calcination temperature at a heating rate of 2 °C min^{-1} under N_2 atmosphere for 2 h, and the calcination temperature (300 °C, 365 °C, 375 °C, 400 °C) was selected according to the thermogravimetric curve of Ni-TATB. The obtained samples were denoted as Ni-TATB-X (X = 300, 365, 375, 400 correspond to the temperature).

Material characterization. The thermogravimetric curve of Ni-TATB was measured by a microcomputer thermogravimetric balance (HTG-1, China), and the heating rate was 10 °C min^{-1}. The microscopic morphology of the samples was observed by scanning electron microscope (SEM, QUANTA FEG 450, FEI, USA). Ni-TATB was tested by Fourier transform infrared spectrometer (FT-IR, Nicolet 380, Thermo Fisher) in the range of 500 cm^{-1}-4000 cm^{-1} with background subtraction using potassium bromide. The chemical composition of the material was measured by X-ray powder diffractometer (XRD, MiniFlex600, CuKa, λ=0.154 nm). X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher, USA) uses two independent systems equipped with a monochromatic Al Kα source to explore the composition, content, chemical state, molecular structure, and chemical bonds of elements in a sample. The micro-regions of the samples were qualitatively and quantitatively analyzed by X-ray energy dispersive analysis (EDS). Gas adsorption-desorption isotherms were measured using a specific surface and porosity analyzer (BET, ASAP 2460, USA) at 77 K using a relative pressure P/P_0 of 0–0.99 and nitrogen as the adsorbate. Pore volume and pore size distribution were estimated by density functional theory (DFT) models, and specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method. Before the BET test, the Ni-MOFs were evacuated in a closed container and heated at a constant temperature of 80 °C for 4 h. The calcined samples were evacuated in a closed container and heated at a constant temperature of 120 °C for 4 h to remove the surface of the sample. The physical adsorption material was introduced into a closed container with nitrogen gas for 10-15 s.

Electrochemical tests. In this experiment, an electrochemical workstation (CHI660E, Shanghai Chenhua) was used to characterize the electrochemical performance in 6M KOH electrolyte, including cyclic voltammetry (CV), galvanostatic charge-discharge curve (GCD) and electrochemical impedance spectroscopy (EIS, a frequency range of 0.01 to 100 kHz.). The electrochemical properties of Ni-TATB and its derivatives as the working electrode were investigated by a three-electrode configuration, respectively. In the three-electrode test, the platinum wire electrode was used as the counter electrode, the Hg/HgO electrode was used as the reference electrode, and Ni-TATB and its derivatives were used as the positive electrode material [positive electrode active material, acetylene black and polytetrafluoroethylene (PTFE) with 75:15:10 weight ratio, isopropanol as solvent]. The electrochemical properties of the materials were further studied by assembling asymmetric supercapacitors, Ni-TATB and its derivatives were used as the positive material, and commercial activated carbon was used as the negative electrode [negative active material, acetylene black and polyvinylidene fluoride (PVDF) at 75:15:10 weight ratio, N-methyl-2-pyrrolidone (NMP) as solvent], the loading of the positive and negative electrodes should be based on the equation: $m_{positive} \times C_{positive} \times V_{positive} = m_{negative} \times C_{negative} \times V_{negative}$ [m is the mass of the active material on the electrode (g), C is the specific capacitance (F g^{-1}), V is the potential window (V)]. [1]

Preparation of button battery. The active material was coated on a carbon cloth with a diameter of 14 mm (the carbon cloth was pretreated with HNO_3 for 2 h at 80 °C), and Ni-TATB and its derivatives were used as the positive electrode material and activated carbon as the negative electrode material. It consists of a positive electrode shell, positive electrode sheet, two filter paper separators with a diameter of 19 mm, negative electrode sheet, stainless steel gasket, shrapnel, negative electrode shell, 6 mol L^{-1} KOH electrolyte, and is sealed by a sealing machine. The specific capacity, energy density and power density of the three-electrode and two-electrode can be calculated according to the electrochemical performance calculation formulas in the literature. [2]

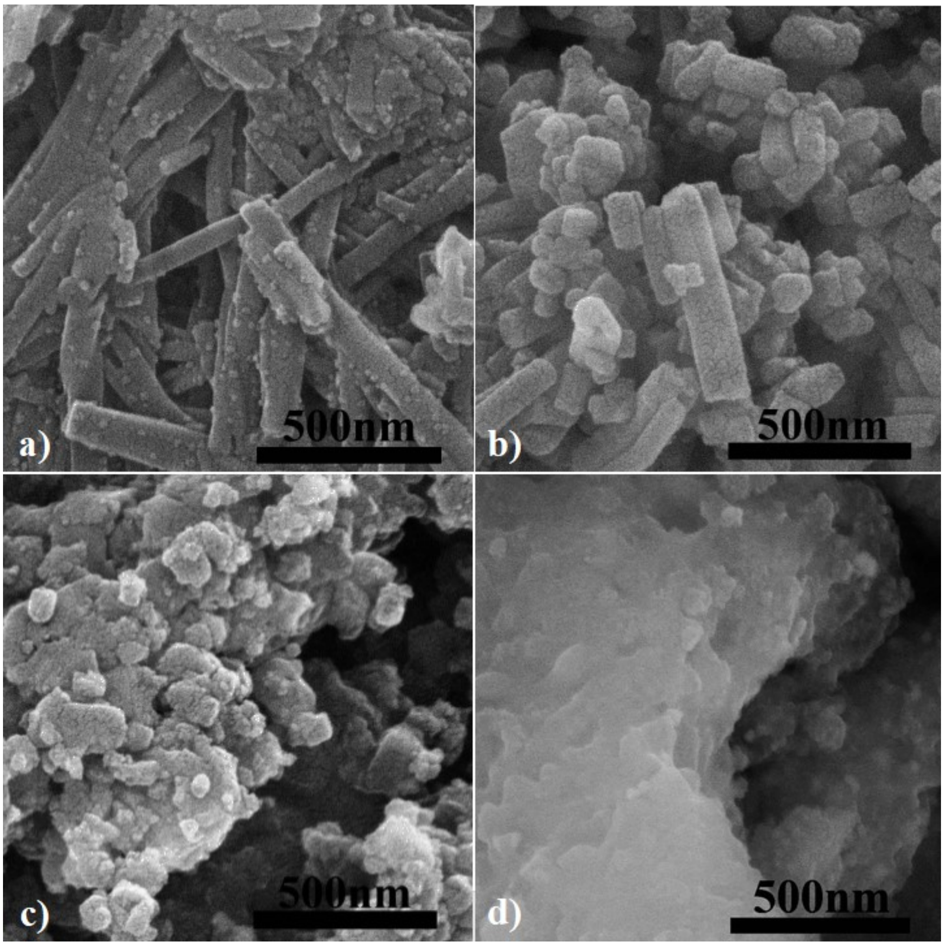


Figure S1 SEM of a) Ni-TATB -300, b) Ni-TATB-365, c) Ni-TATB-375, d) Ni-TATB-400.

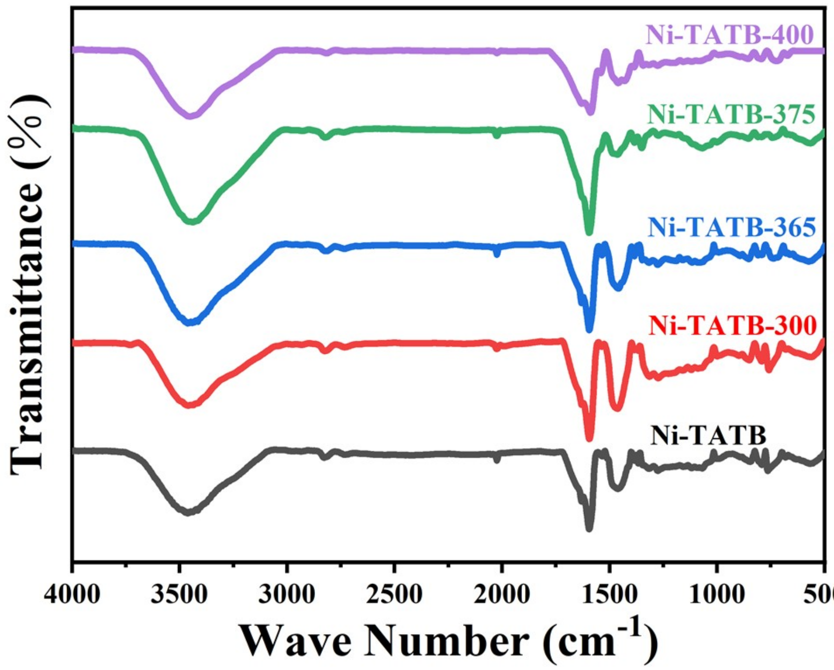
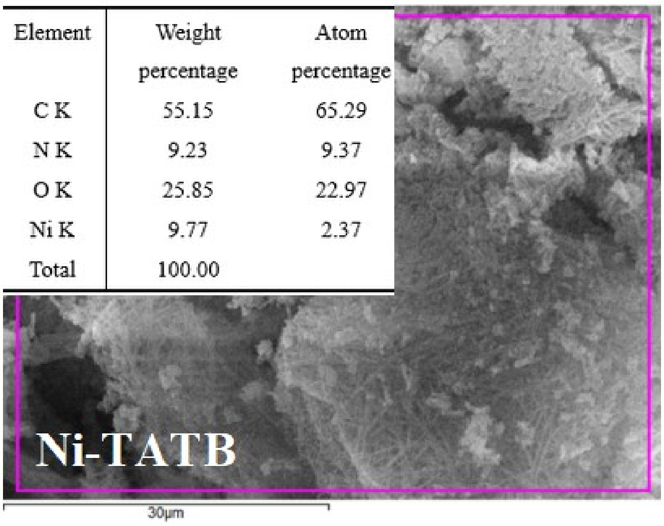


Figure S2 Comparison of the Infrared spectra of Ni-TATB and its calcined samples.

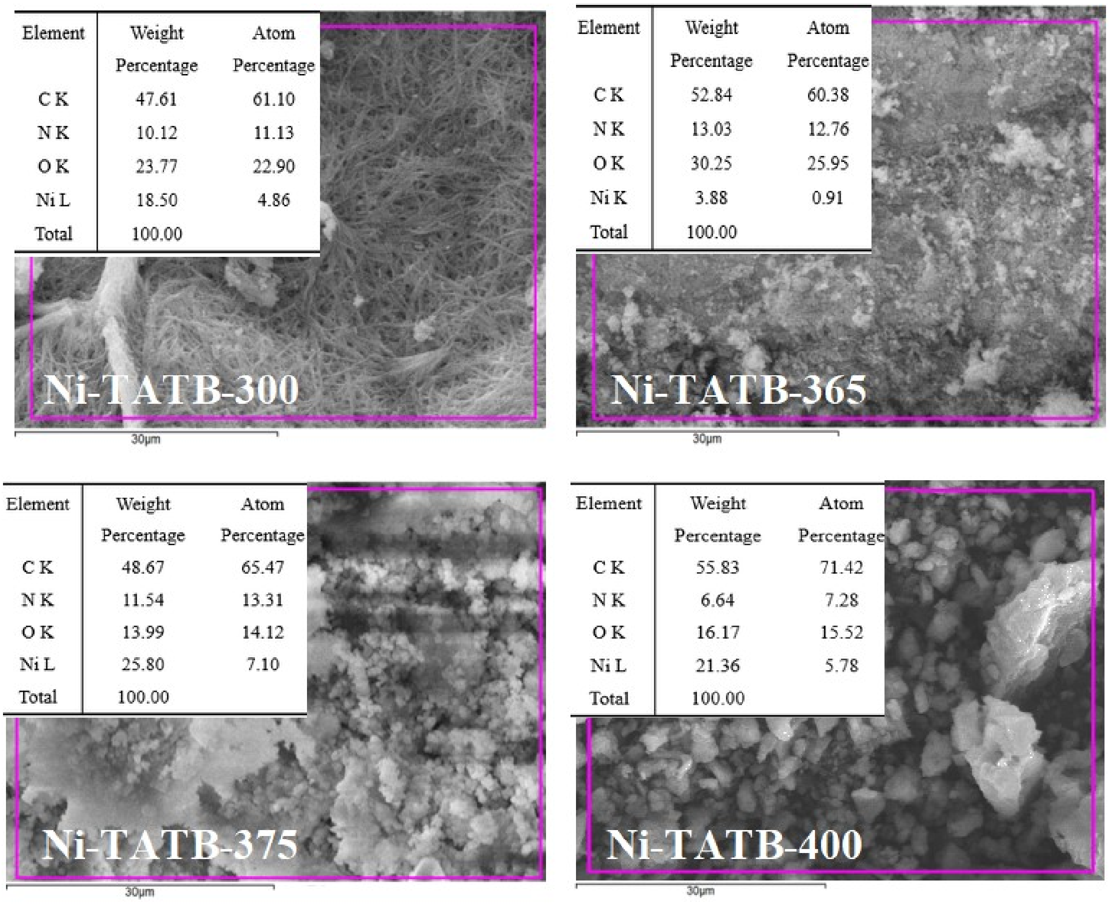
Table S1 Elemental composition analysis of Ni-MOF and its calcined samples based on the XPS survey spectra

	C 1s (%)	N 1s (%)	O 1s (%)	Ni 2p (%)
Ni-TATB	66.35	7.65	21.13	4.88
Ni-TATB-300	64.62	7.83	22.32	5.23
Ni-TATB-365	66.05	9.59	17.14	7.22
Ni-TATB-375	68.82	9.50	15.30	6.39
Ni-TATB-400	74.07	8.26	14.04	3.63



Element	Weight percentage	Atom percentage
C K	55.15	65.29
N K	9.23	9.37
O K	25.85	22.97
Ni K	9.77	2.37
Total	100.00	

Figure S3 EDS of Ni-TATB.



Ni-TATB-300:

Element	Weight Percentage	Atom Percentage
C K	47.61	61.10
N K	10.12	11.13
O K	23.77	22.90
Ni L	18.50	4.86
Total	100.00	

Ni-TATB-365:

Element	Weight Percentage	Atom Percentage
C K	52.84	60.38
N K	13.03	12.76
O K	30.25	25.95
Ni K	3.88	0.91
Total	100.00	

Ni-TATB-375:

Element	Weight Percentage	Atom Percentage
C K	48.67	65.47
N K	11.54	13.31
O K	13.99	14.12
Ni L	25.80	7.10
Total	100.00	

Ni-TATB-400:

Element	Weight Percentage	Atom Percentage
C K	55.83	71.42
N K	6.64	7.28
O K	16.17	15.52
Ni L	21.36	5.78
Total	100.00	

Figure S4 EDS of Ni-TATB -300, Ni-TATB-365, Ni-TATB-375 and Ni-TATB-400.

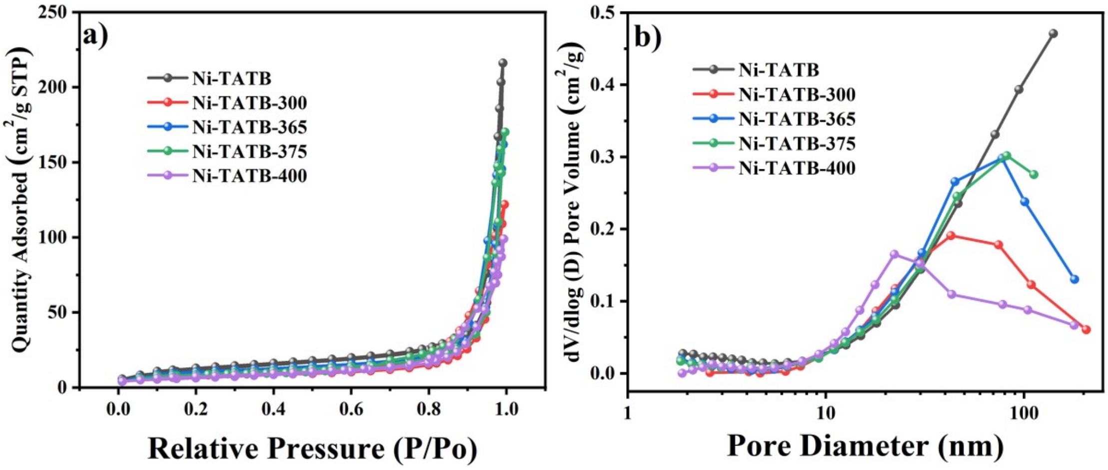


Figure S5 Nitrogen adsorption-desorption isotherm and pore-size distribution of Ni-TATB and its calcined samples.

Table S2 Comparison of specific surface area and pore-size of materials

	Ni-TATB	Ni-TATB-300	Ni-TATB-365	Ni-TATB-375	Ni-TATB-400
specific surface area (m^2 g^{-1})	42.47	23.78	38.51	31.08	22.79
Average pore size (nm)	33.74	24.21	19.70	27.27	23.43
Pore volume (cm^3 g^{-1},V_{total}-V_{mic})	0.337	0.185	0.168	0.258	0.1527

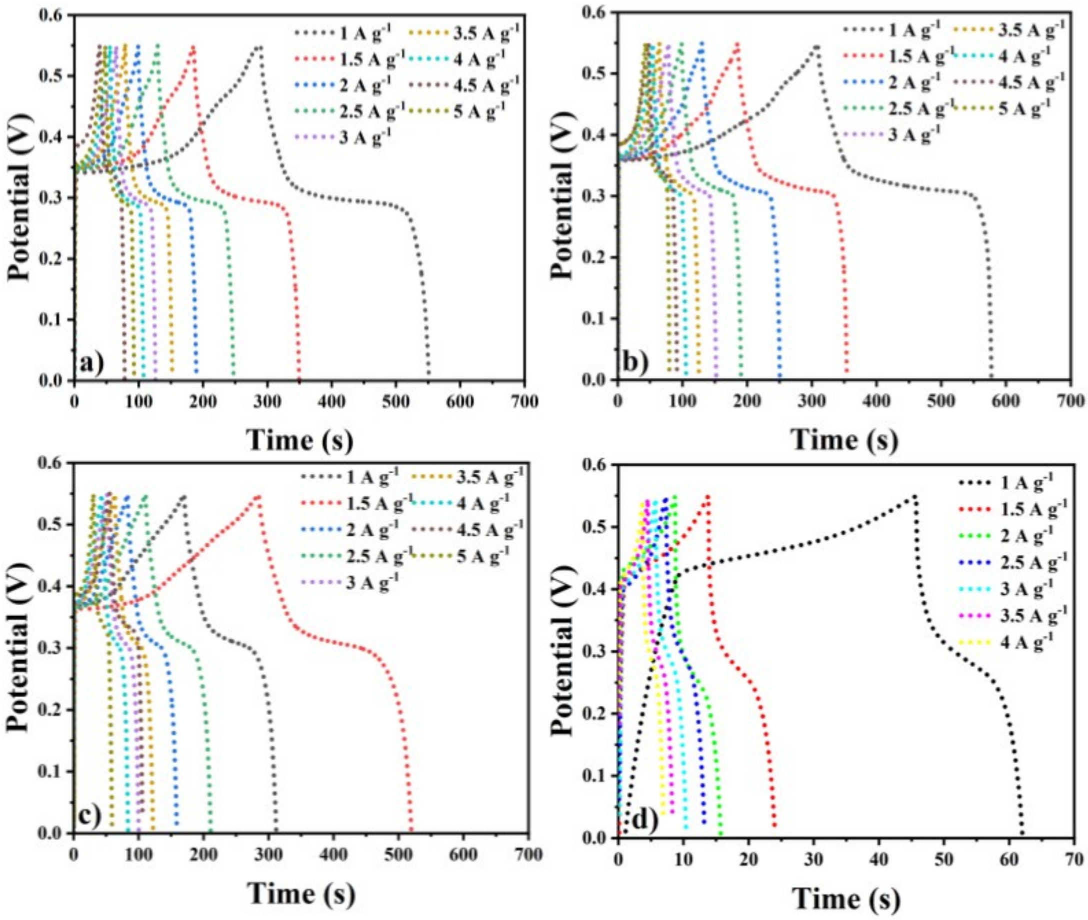


Figure S6 CP curves of a) Ni-TATB, b) Ni-TATB-300, c) Ni-TATB-375 and d) Ni-TATB-400 at different current densities.

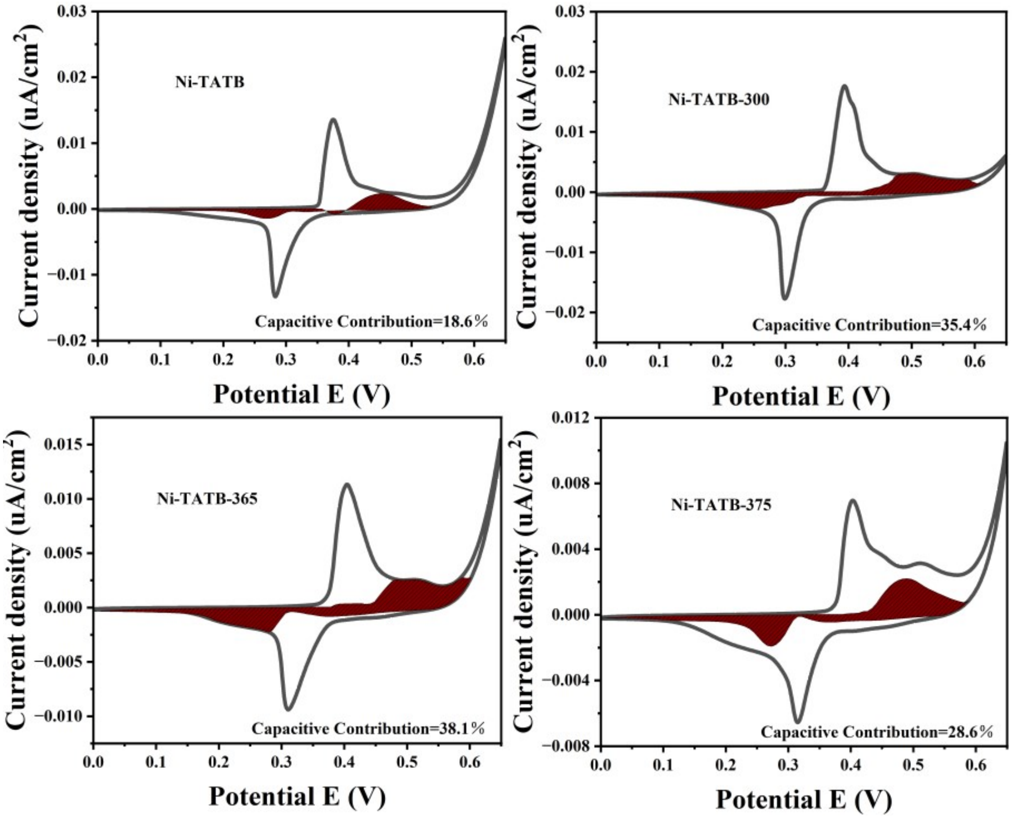


Figure S7 Voltammetric response for the as-prepared Ni-TATB, Ni-TATB-300, Ni-TATB-365, Ni-TATB-375 electrodes at a sweep rate of 2 mV s^{-1}

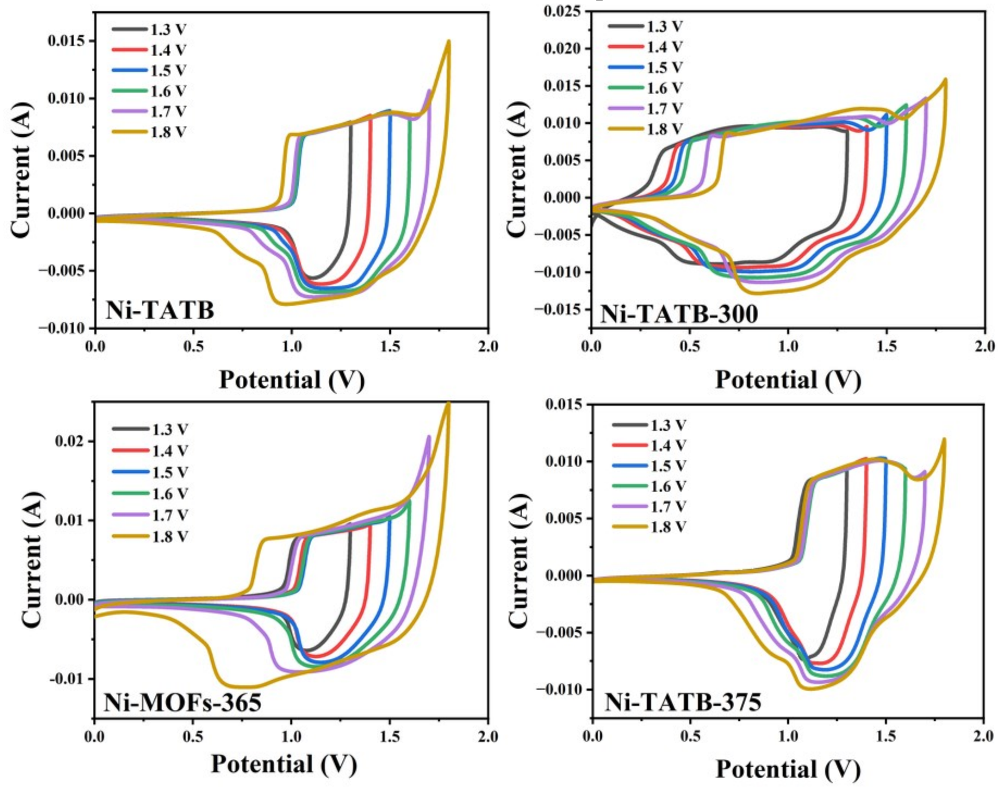


Figure S8 Polarization curve of Ni-TATB//AC, Ni-TATB-300//AC, Ni-TATB-365//AC, Ni-TATB-375//AC.

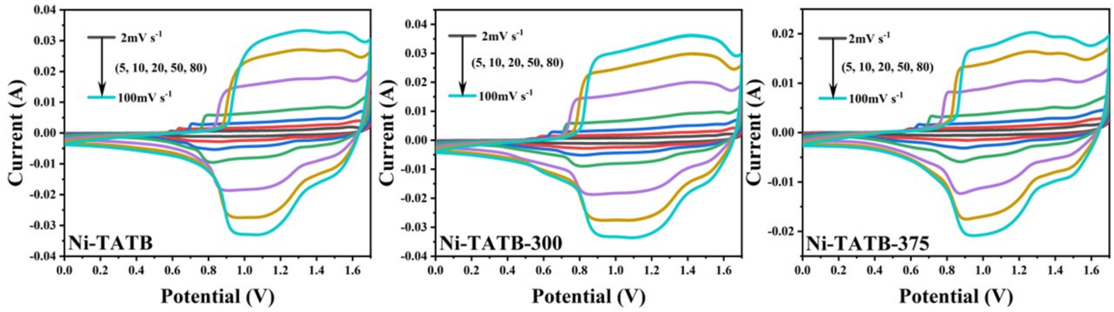


Figure S9 CV curve of Ni-TATB//AC, Ni-TATB-300//AC, Ni-TATB-375//AC devices.

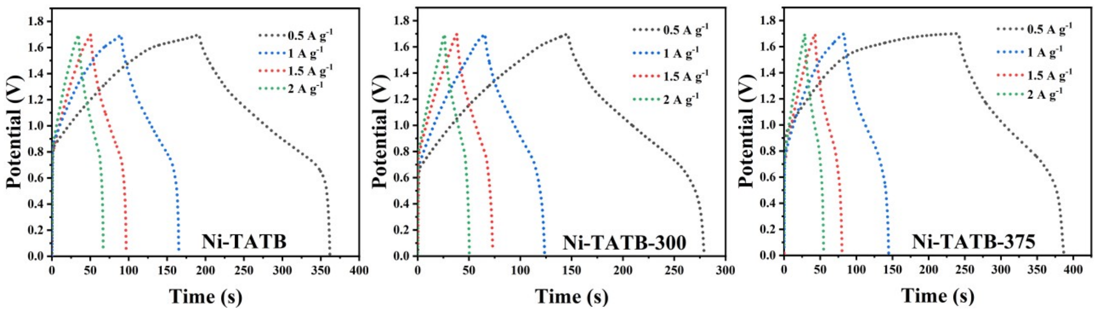


Figure S10 CP curve of Ni-TATB//AC, Ni-TATB-300//AC, Ni-TATB-375//AC devices.

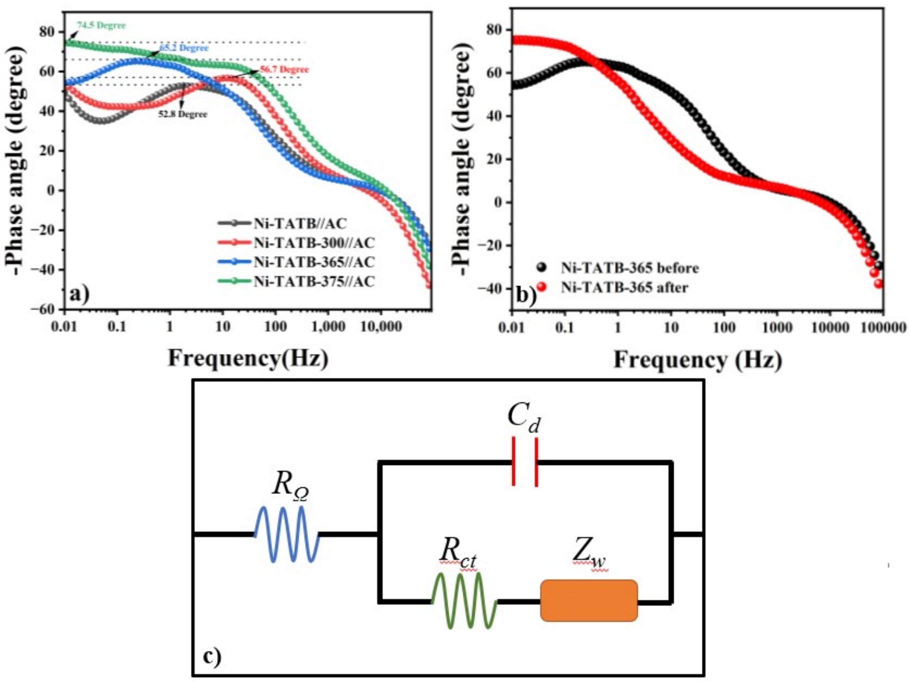


Figure S11 a) Bode phase angle for Ni-TATB//AC, Ni-TATB-300, Ni-TATB-365, Ni-TATB-375//AC devices; b) Bode phase angle for Ni-TATB-365 before and after the 5000 charge-discharge cycles; c) equivalent circuit diagram.

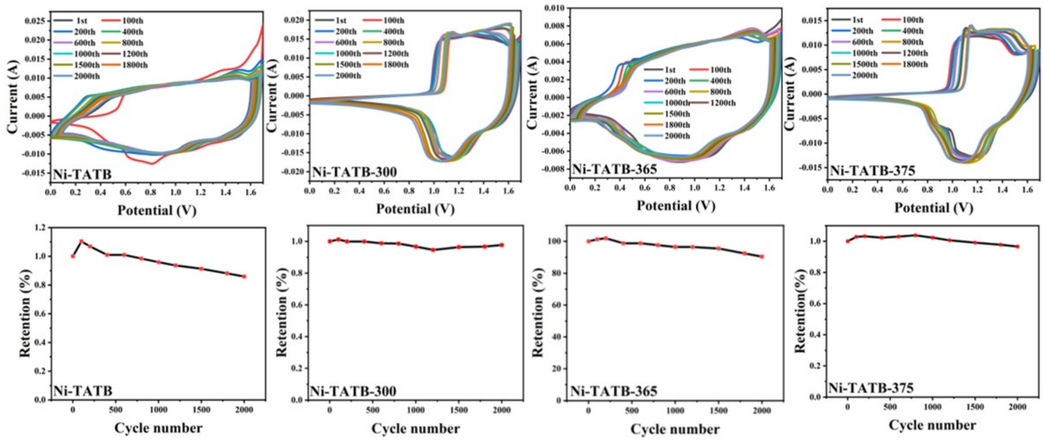


Figure S12 CV circle test for Ni-TATB//AC, Ni-TATB-300, Ni-TATB-365, Ni-TATB-375//AC devices at 30 mV s^{-1} for 2000 cycles.

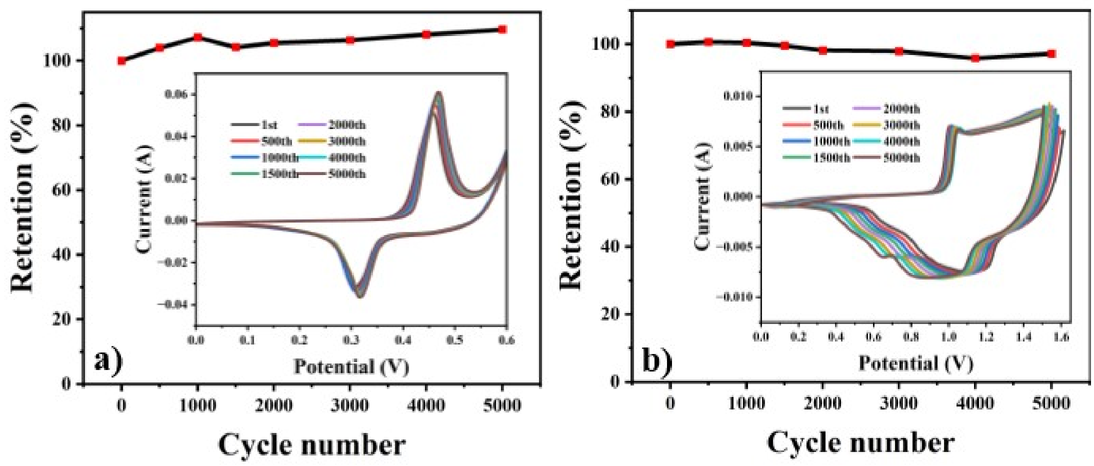


Figure S13 a) CV circle test for Ni-TATB-365 at 30 mV s^{-1} for 5000 cycles; b) CV circle test for Ni-TATB-365//AC device at 30 mV s^{-1} for 5000 charge-discharge cycles.

References:

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