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Supporting Information for

Pseudocapacitive Titanium Oxynitride Mesoporous Nanowires with Iso-Oriented Nanocrystals for Ultrahigh-Rate Sodium-Ion Hybrid Capacitors†

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Experiment

1. Synthesis and characterization of Ti(O,N)-MP-NWs

Ti(O,N)-MP-NWs were obtained by annealing hydrogen titanate nanowires ($H_2Ti_3O_7$ NWs) in ammonia flow at different temperature. $H_2Ti_3O_7$ NWs were firstly synthesized by hydrothermal method reported elsewhere.[1] Briefly, TiO_2 anatase (2 g) was added into NaOH solution (30 mL, 15 M) under magnetic stirring for 1 h. Then, the suspension was transferred to a Teflon-lined stainless steel autoclave and heated in an electric oven at 180 ^oC for 72 h. After cooling down at room temperature, the product was stirred in 0.1 M HCl solution for 24 h. The material was filtered, washed with deionized water and alcohol, and dried at 70 ^oC for 12 h. Finally, $H_2Ti_3O_7$ NWs were converted to Ti(O,N)-MP-NWs by annealing in NH_3 flow (80 sccm) at various temperatures (700 and 800 °C) for 2 h with a heating rate of 5 $^oC\ min^{-1}$. The TiO_2(B) NWs were synthesized by annealing at 600 °C for 2 h in ammonia flow. XRD pattern was collected by using a D8 Advance X-ray diffractometer with non-monochromated Cu Kα X-ray source at room temperature. Field-emission scanning electron microscopy (FESEM) images were collected with a JEOL-7100F STEM/EDS microscope. TEM and high-resolution TEM (HRTEM) images were recorded using Titan G2 60-300 with EDS image corrector. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a VG MultiLab 2000 instrument. Brunauer–Emmett–Teller (BET) surface areas were measured using a Tristar II 3020 instrument. The probe station and semiconductor device analyzer (B1500A) were used to measure the electrical conductivity of Ti(O,N)-700 nanowires.

2. Preparation of electrode and electrochemical tests

The electrochemical properties were investigated by assembly of 2016 coin cells in a glove box filled with pure argon gas. The working electrode materials were prepared with 90% active material and 10% carboxyl methyl cellulose (CMC). Then the mixed slurry was cast onto Cu foil and dried in a vacuum oven at 70 ^oC for 12 h. The mass loading of active materials was 1 – 1.5 mg cm^{-2}. Sodium blocks (China Energy Lithium Co., Ltd.) were cut into small pieces and used as the counter electrode. Glass fiber was used as separator. The electrolyte was composed of 1 M $NaClO_4$ dissolved in dimethyl carbonate (DMC) and ethylene carbon

(EC) (DMC : EC = 1 : 1, in volume) with 5% fluoroethylene carbonate (FEC). Galvanostatic charge/discharge cycling was studied with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested with an electrochemical workstation (Autolab PGSTAT302N). All of the measurements were carried out at room temperature.

3. Calculations of specific capacity, energy density and power density

The specific capacity (C g^{-1}) is calculated by Equation 1.[2]

$$Q = i \times t \tag{1}$$

Q (C g^{-1}) is the specific charge; i (A g^{-1}) is the specific current; t (s) is the charge or discharge time.

The energy density (E) and power density (P) are calculated based on Equations 2 and 3.[2]

$$E = \int V dQ \tag{2}$$

$$P = \frac{E}{t} \tag{3}$$

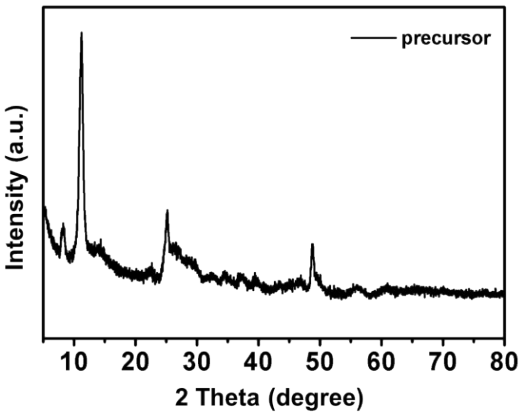

Fig. S1. XRD pattern of $H_2Ti_3O_7$ precursor.

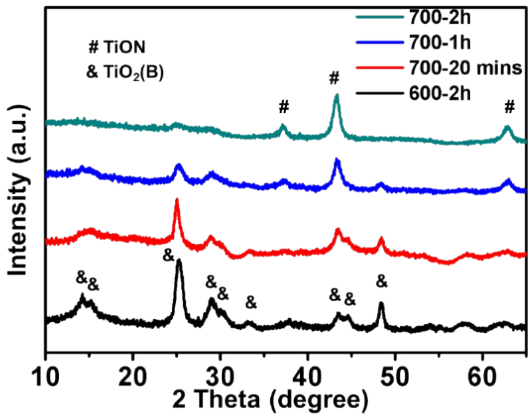

Fig. S2. XRD patterns of the representative products at different annealing temperatures and times.

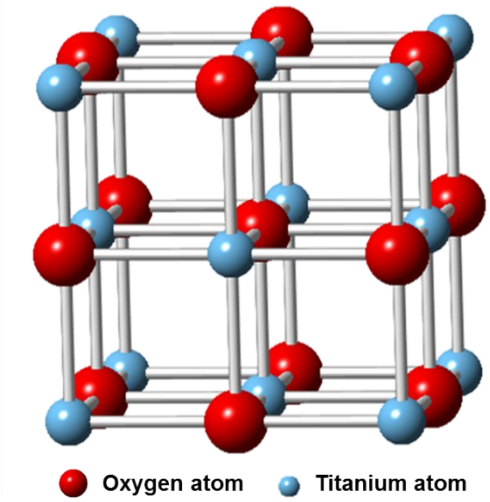

Fig. S3. Crystal structure model of TiO.

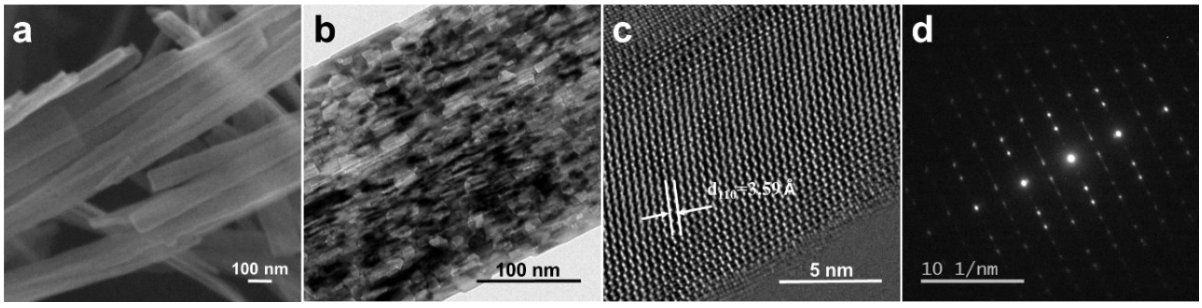

Fig. S4. Morphology characterization of TiO_2(B)-600: SEM image (a), TEM image (b), HRTEM image (c), and SAED pattern (d).

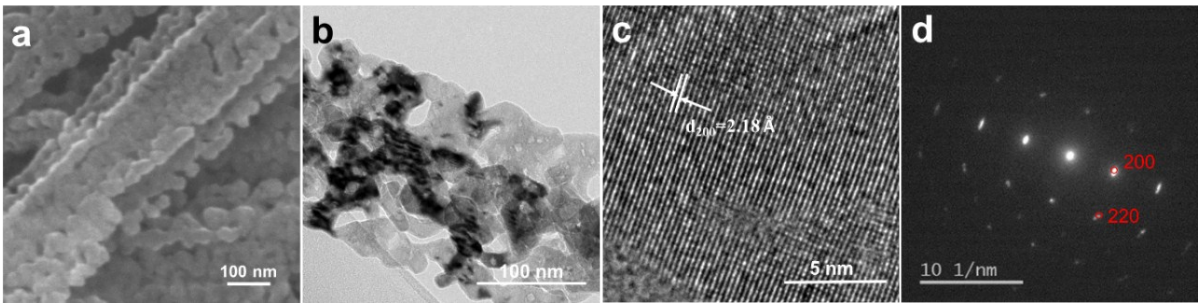

Fig. S5. Morphology characterization of Ti(O,N)-800: SEM image (a), TEM image (b), HRTEM image (c), and SAED pattern (d).

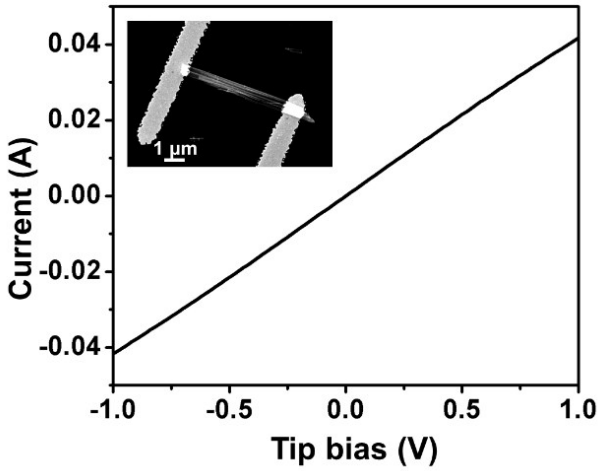

Fig. S6. *I-V* curve. Inset: single nanowire device for measuring the electric conducitvity.

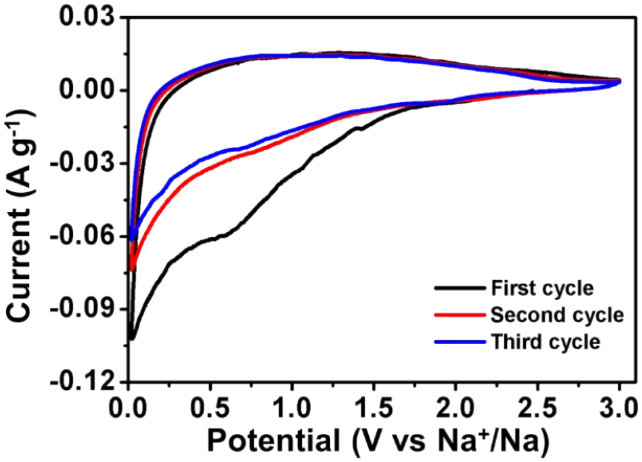

Fig. S7. The CV curves of TiO_2(B)-600 at 0.2 mV s^{-1}.

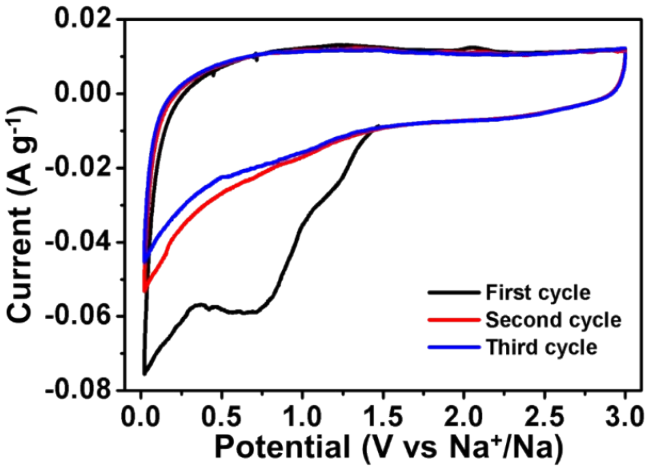

Fig. S8. The CV curves of Ti(O,N)-800 at 0.2 mV s^{-1}.

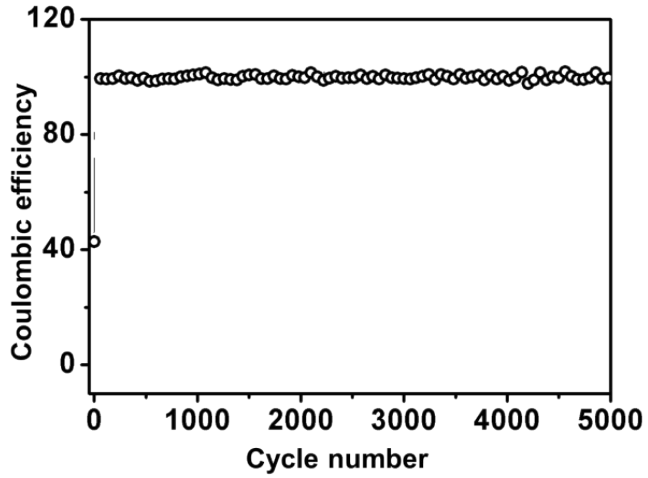

Fig. S9. Coulombic efficiency of Ti(O,N) at 1 A g^{-1}.

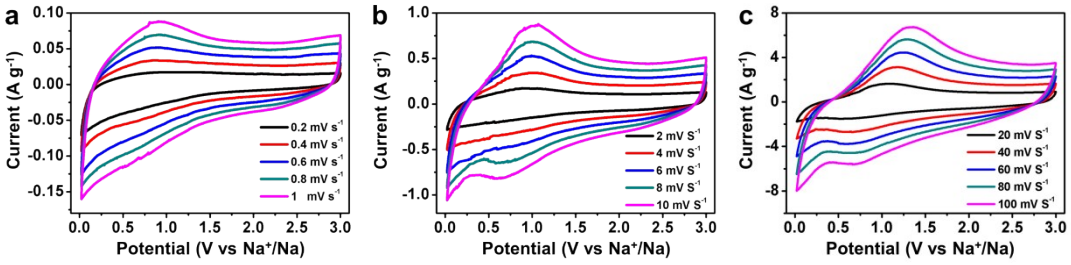

Fig. S10. CV curves of Ti(O,N)-700 electrode at 0.2-1 mV s^{-1} (a), 2-10 mV s^{-1} (b), 20-100 mV s^{-1} (c).

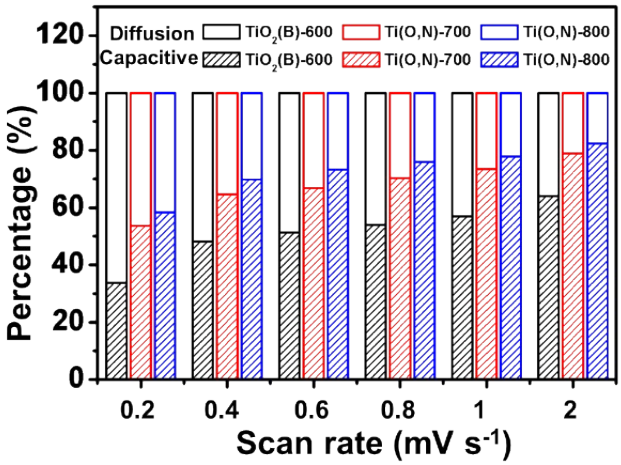

Fig. S11. Capacitive and diffusion-controlled capacity contribution about the three samples at different scan rate.

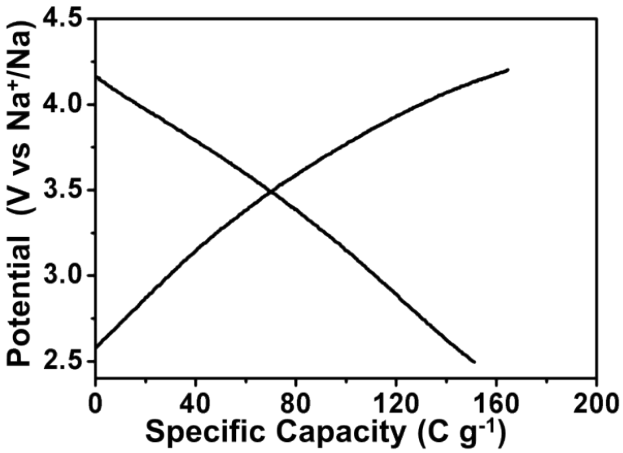

Fig. S12. Charge/discharge curves of AC at 0.1 A g^{-1}.

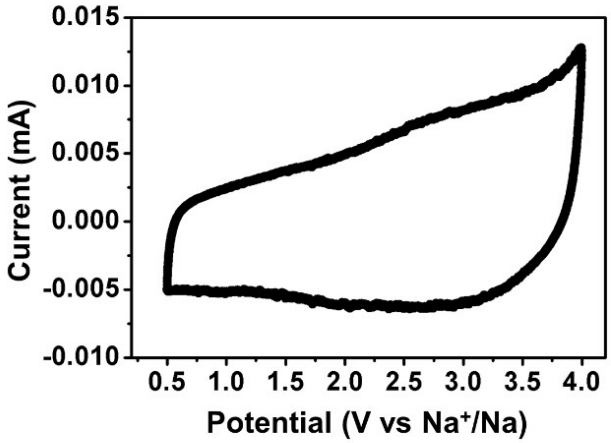

Fig. S13. The CV curve of Na-HEC at a scan rate of 0.2 mV s^{-1}.

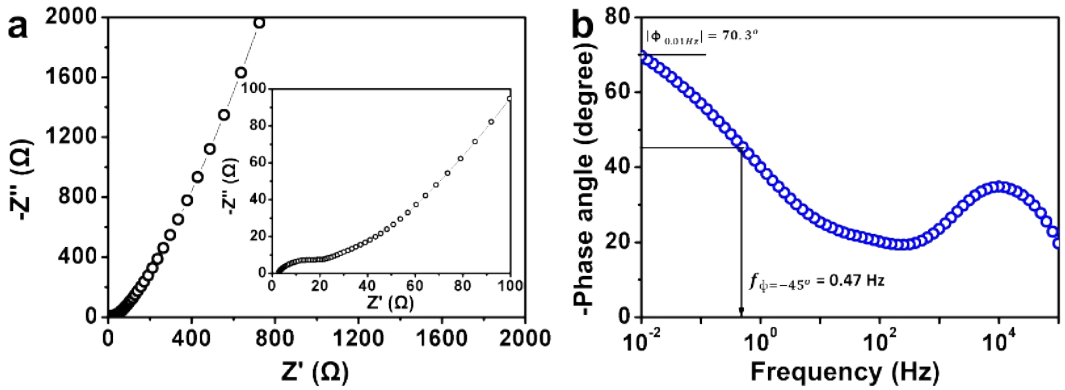

Fig. S14. (a) Nyquist plots (the inset shows the enlarged Nyquist plots at the high frequency region). (b) Bode plots of phase angle versus frequency.

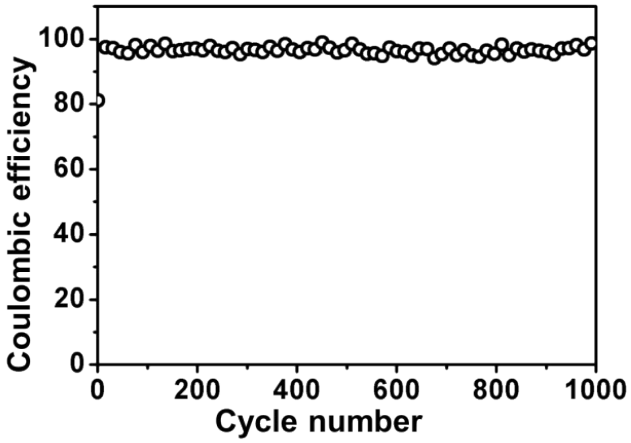

Fig. S15. Coulombic efficiency of AC//Ti(O,N) MP-NWs Na-HEC at 1 A g^{-1}.

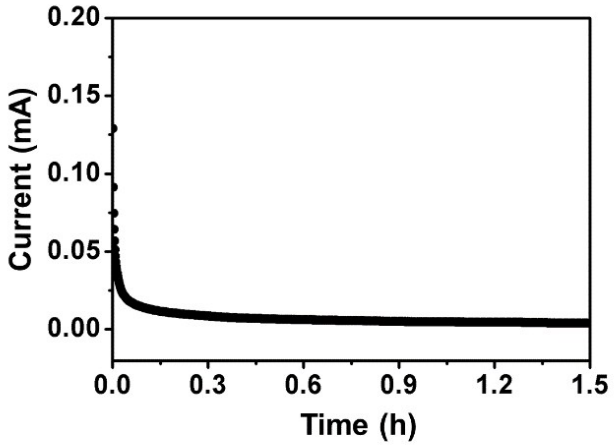

Fig. S16. Leakage current curve of Na-HEC charged at 100 mA g^{-1} to 4 V and kept at 4 V for 1.5 h.

Table S1. A summaries about mesoporous characteristics.

Sample	BET SSA [m^2 g^{-1}]	Pore Volume [cm^3 g^{-1}]	Average Pore Size [Å]
TiO_2(B)-600	29.02	0.06	98.50
Ti(O,N)-700	70.75	0.16	93.33
Ti(O,N)-800	49.25	0.13	118.23

Table S2. Values of the O/N, N/Ti ratios for all prepared titanium oxynitride samples. N, O, Ti at. % were extracted from the energy dispersive X-ray spectroscopy (EDS).

Sample	O/N ratio	N/Ti ratio	(N+O)/Ti ratio
Ti(O,N)-700	1.27	0.64	1.44
Ti(O,N)-800	0.51	1.10	1.65

Table S3. Comparisons of the detailed data about the similar EES devices**.**

Device (Cathode//Anode)	Electrolyte	Potential window	Energy density	Power density	Ref.
AC//Ti(O,N)	1 M $NaClO_4$ (DMC : EC = 1 : 1)	0.5 – 4 V	46 Wh kg^{-1} 27.2 Wh kg^{-1}	46 W kg^{-1} 3.3 kW kg^{-1}	Our work
TiN@GNS//Fe_2N@GNS	LiCl-PVA	0 - 1.6 V	10.9 Wh kg^{-1} 15.4 Wh kg^{-1}	11.5 kW kg^{-1} 6.4 kW kg^{-1}	3
TiN//TiN		0 – 3 V	12.3 Wh kg^{-1}	3 kW kg^{-1}	4
AC//TiO_2-RGO	1 M LiPF6 (EC : DEC = 1:1)	1 – 3 V	8.9 Wh kg^{-1}	8 kW kg^{-1}	5
AC//TiO_2 (anatase)		1 – 3 V	2.9 Wh kg^{-1}	8 kW kg^{-1}	5
AC//TiO_2 (B)	1 M LiPF6 (EC:DMC:DEC= 1:1:1)	0 – 2.8 V	10 Wh kg^{-1}	319 W kg^{-1}	6

References

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