Electronic Supplementary Information

Terephthalonitrile-derived nitrogen-rich networks for high performance supercapacitors

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Experimental details:

Materials Terephthalonitrile and anhydrous zinc chloride were purchased from Alfa Aesar and used as received.

Synthesis of TNNs Terephthalonitrile (500 mg, 3.9 mmol) and anhydrous zinc chloride (2.66 g, 19.5 mmol) were mixed in a glove box (argon with 0.1 ppm oxygen and 0.1 ppm water) and transferred into a quartz ampoule (Φ17 mm×180 mm). The ampoule was evacuated by vacuum, sealed and heated at the designated temperatures (400, 450, 500, 550, 600, 650, and 700℃) for 40 h. Then the ampule was cooled to the room temperature and opened. The black complex inside was washed thoroughly with 5% HCl solution, de-ionized water and tetrahydrofuran, and then dried under vacuum at 120°C for 24 h to get the TNNs.

Characterization The powder X-ray diffraction (XRD) measurements were executed on Rigaku D/max-2500B2 + /PCX system with Cu K α radiation. Field-emission scanning electron microscopy (FE-SEM) images were got from Hitachi S4800. Field-emission transmission electron microscopy (FE-TEM), scanning transmission electron microscopy (STEM) and elemental mapping images were got from a Tecnai G2 F20 U-TWIN microscope with STEM-HAADF attachment. Elemental analyses were performed from a FLASH EA1112 analyzer. Nitrogen sorption/desorption isotherms were measured at 77 K with an ASAP 2020 physisorption analyzer. The Brunauer-Emmett-Teller (BET) method and density functional theory (DFT) pore model were utilized to calculate the specific surface area and pore size distribution, respectively. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB250Xi apparatus at base pressure of 1×10^{-9} mbar, and X-ray source of Al Kα.

Preparation of TNNs-based electrodes Electrode films were prepared by grinding TNNs (85 wt %, about 50 mg), carbon black (10 wt%, Super P conductive, Alfa Aesar), and polytetrafluoroethylene (5 wt% PTFE, 60% in water, Aldrich Co. diluted to 6 % before use) in a mortar. The thin film was dried under vacuum at 120 °C for 24 h, and then cut to a circular shape with diameter of 12 mm and mass of about 2 mg. The circular film was pressed to a stainless steel mesh (400 mesh, 15 mm $\times$ 30 mm $\times$ 0.03 mm) as the working electrode.

Electrochemical measurements Electrochemical measurements were performed in a three-electrode system and a two-electrode system at the same time (1) three-electrode system: a TNNs film pressed on a stainless steel mesh as the working electrode, a platinum sheet (10mm×10mm) as the counter electrode, and an aqueous Ag/AgCl as the reference electrode. The three electrodes were immersed into a beaker containing 1M H_2SO_4 solution to form the three-electrode testing system; (2) two electrode system: two TNNs film with exactly the same weight were pressed on stainless steel mesh as two symmetry working electrodes. Then the two electrodes (with the distance of 15mm between the centers) were immersed into a beaker containing 1M H_2SO_4 solution to form the two-electrode testing system.

Cyclic voltammograms (CV), galvanostatic charge-discharge curves, and Nyquist plots were collected on a CHI660D electrochemical workstation.

The specific capacitance (C, F/g) was calculated from the slop of discharge curve using: (1) $C = \frac{I}{m} \times \frac{t}{V}$ (three-electrode system); (2) $C = 2 \times \frac{I}{m} \times \frac{t}{V}$ (two-electrode system), where I (unit: A) is the discharge current, m (unit: g) is the mass of TNNs in the working electrodes (three-electrode system) or in one single electrode (two-electrode system), t (unit: s) is the discharge time, and V (unit: V) is the discharge voltage.

Figure S1-S11:

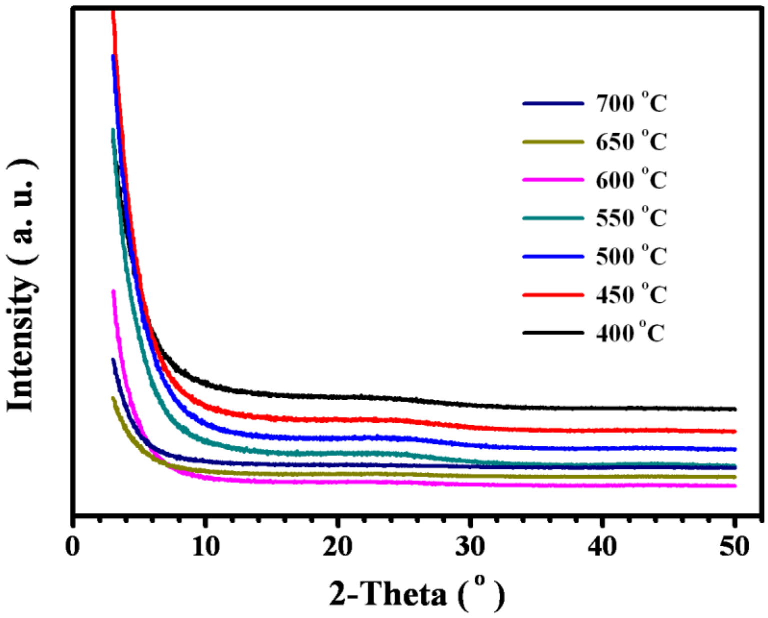

Fig. S1 XRD patterns of TNNs

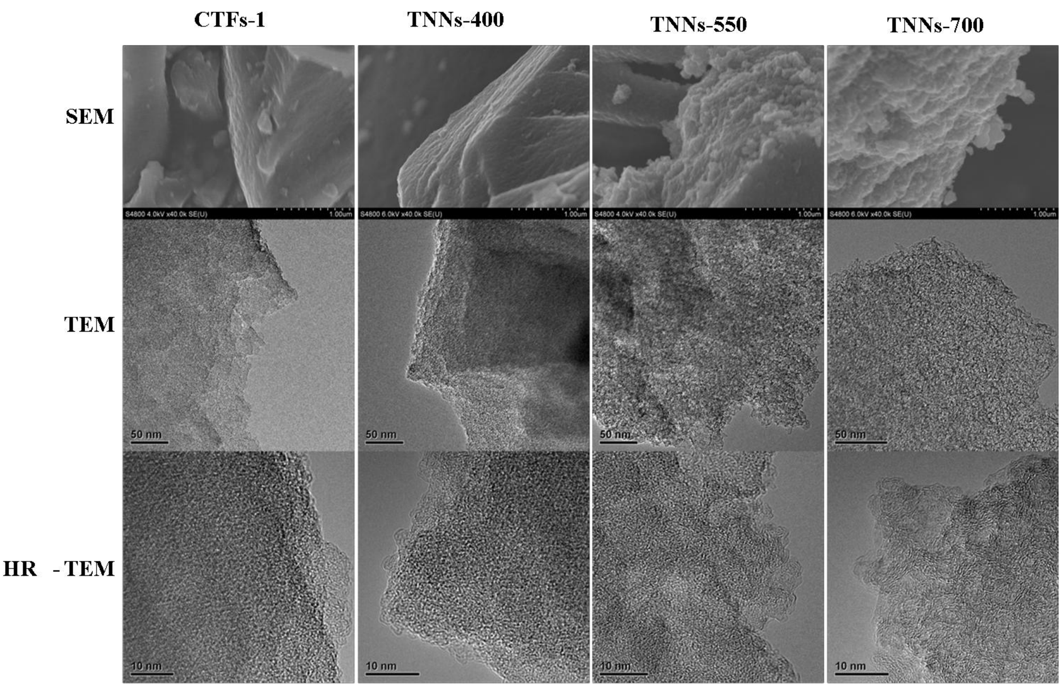

Fig. S2 FE-SEM, FE-TEM, and high-resolution TEM images of CTFs-1, TNNs-400, TNNs-550, and TNNs-700.

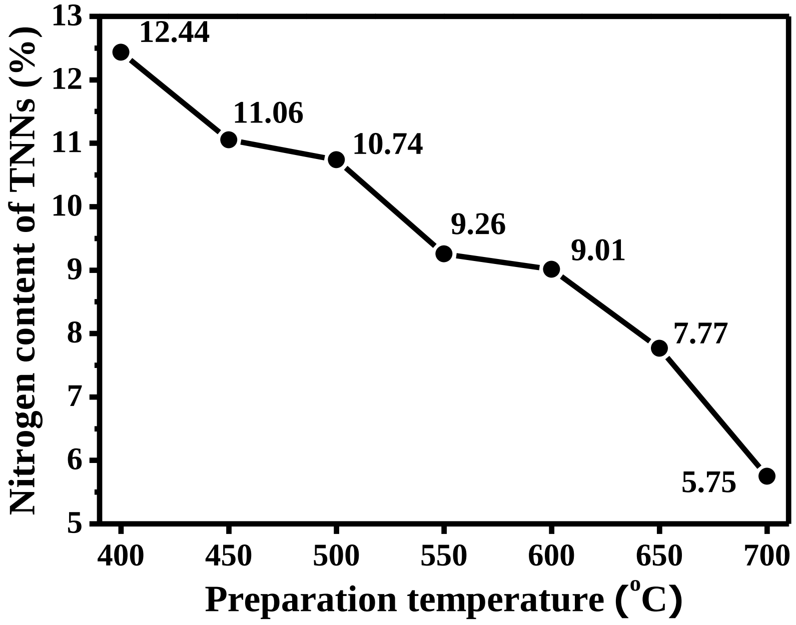

Fig. S3 Elemental analyses on nitrogen of TNNs synthesized at different temperatures.

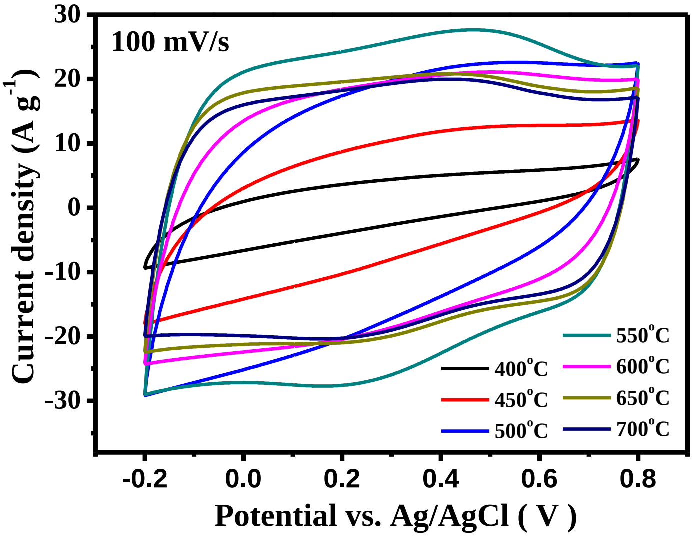

Fig. S4 CV curves at the scan speed of 100 mV/s (three-electrode system).

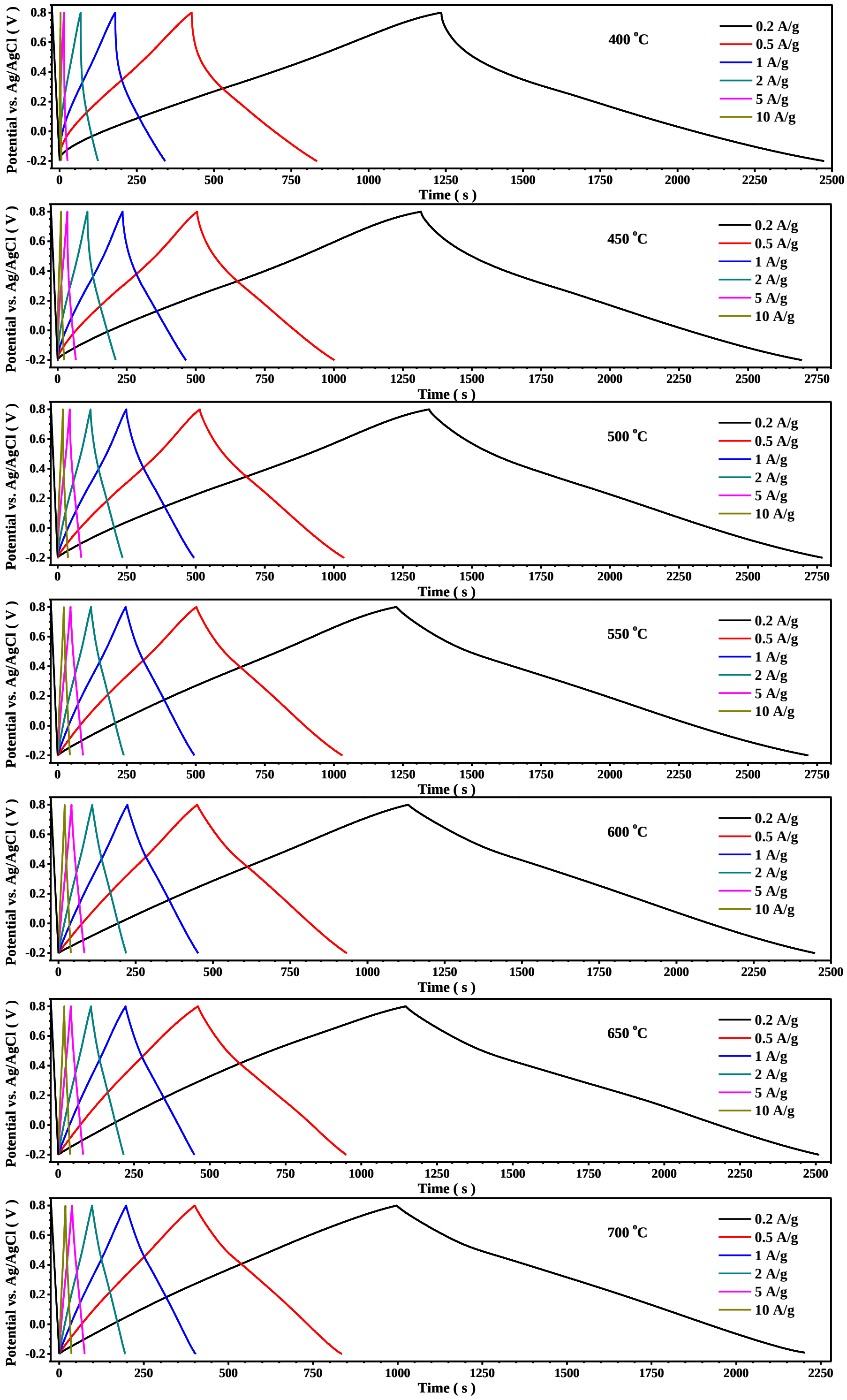

Fig. S5 Galvanostatic charge-discharge curves at different current densities (three-electrode system). When the synthesis temperature is 550℃ or higher and the current density is 0.5 A/g or higher, the charge-discharge curves are almost symmetric and linear, which suggest the excellent electrochemical performance of TNNs.

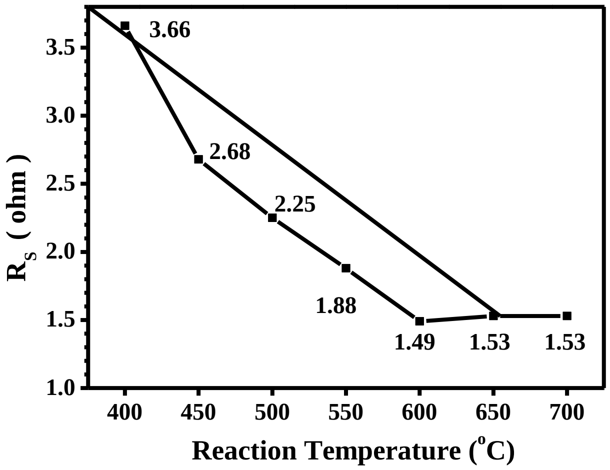

Fig. S6 Equivalent series resistances extracted at 10 Hz (three-electrode system).

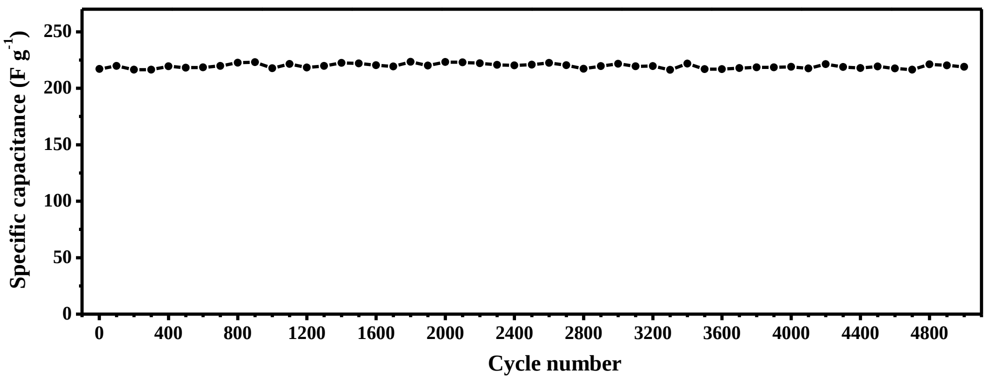

Fig. S7 Cycling performance of TNNs-550 electrodes at a current density of 10 A/g (three-electrode system).

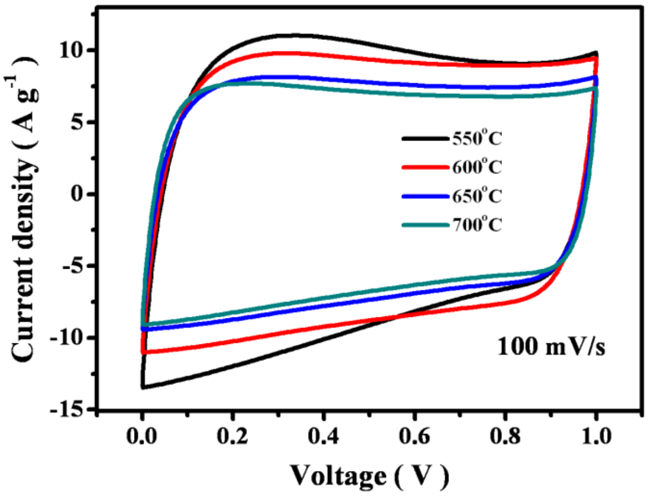

Fig. S8 CV curves at the scan speed of 100 mV/s (two-electrode system).

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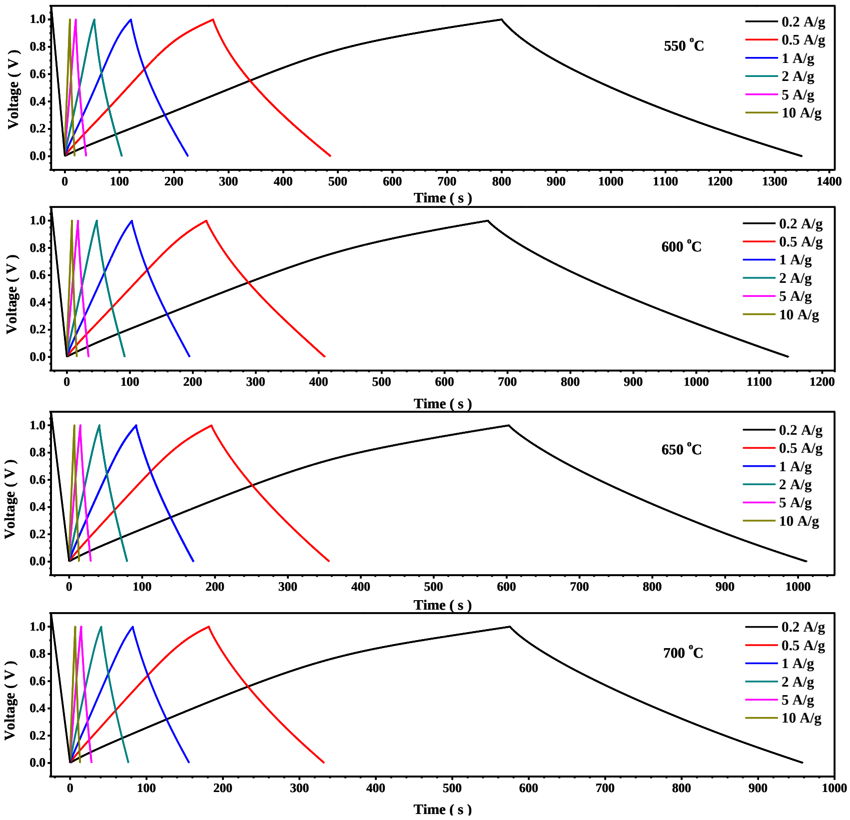

Fig. S9 Galvanostatic charge-discharge curves at different current densities (two-electrode system).

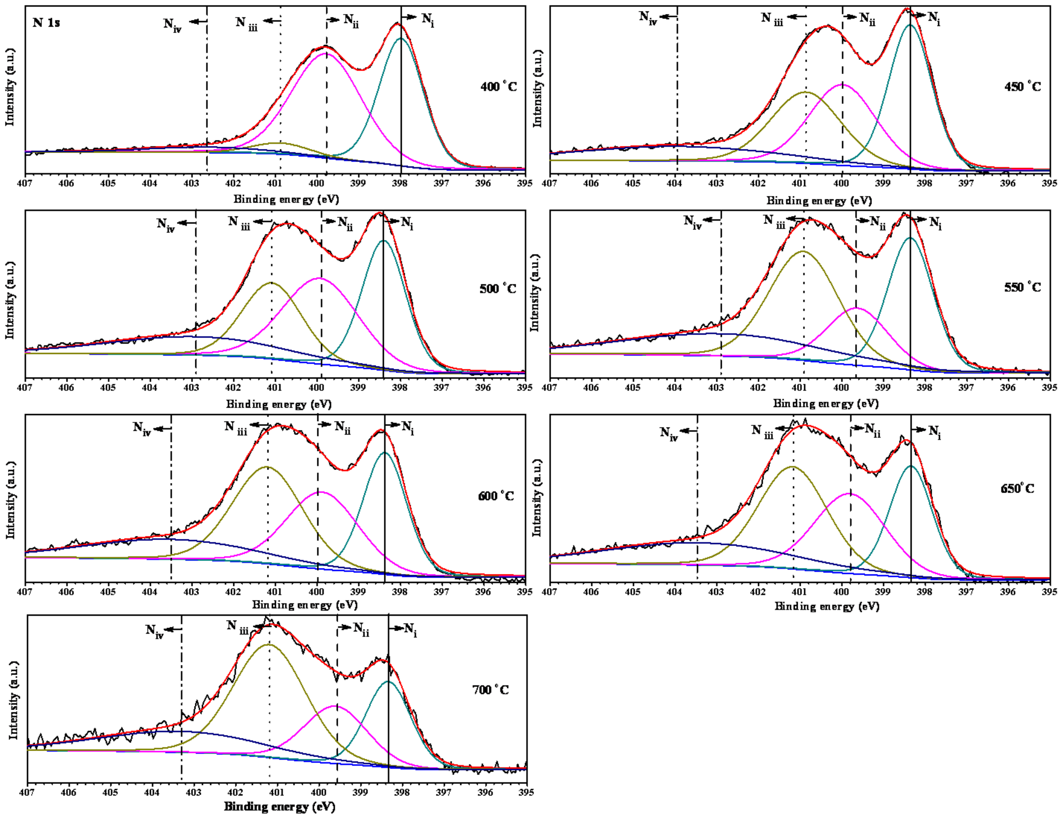

Fig. S10 N1s XPS spectra of TNNs, showing four N configurations as deconvoluted (N_i: pyridinic nitrogen, N_{ii}: pyrrolic nitrogen, N_{iii}: quaternary nitrogen, N_{iv}: oxidized nitrogen).

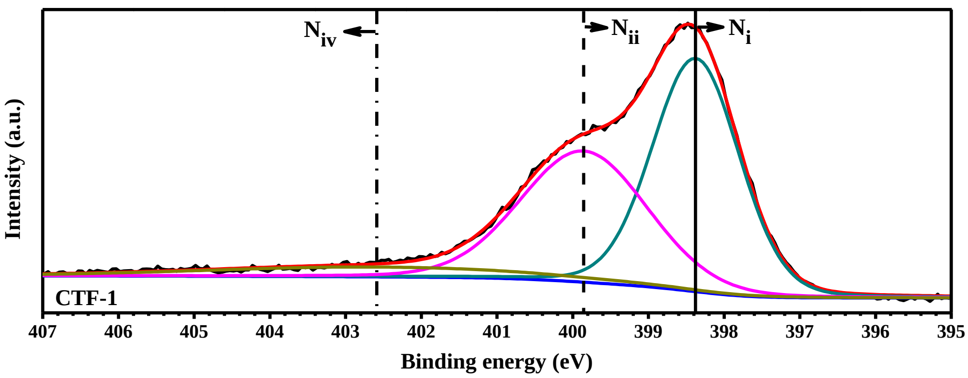

Fig. S11 N1s XPS spectrum of CTFs-1.

Sample	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore size (nm)
TNNs-400	1175	0.66	2.2
TNNs-450	1565	0.97	2.5
TNNs-500	1681	1.10	2.6
TNNs-550	1724	1.35	3.1
TNNs-600	2197	2.05	3.7
TNNs-650	2098	1.85	3.5
TNNs-700	2237	2.26	4.0

Table S1. Porosity measurement results of TNNs.

	N_i (397.98-398.40 eV)	N_{ii} (399.60-399.99 eV)	N_{iii} (400.86-401.19 eV)	N_{iv} (402.65-403.94 eV)
400 ℃	13370.94	17301.47	1541.951	1547.526
450 ℃	13212.8	11374.91	10599.2	6263.138
500 ℃	10329.55	11783.02	8244.573	5914.62
550 ℃	11215.08	6552.916	14178.38	8455.727
600 ℃	7101.51	7448.675	9167.55	4667.048
650 ℃	5063.55	6013.588	7483.738	4472.218
700 ℃	2308.671	2163.529	4914.843	2097.374

Table S2 Peak areas of four N-configurations (N_x) in TNNs. The atomic ratios of N_x (X stands for i, ii, iii, iv) of all samples are evaluated based on the equation

$$N_x = \frac{N_x}{N_i + N_{ii} + N_{iii} + N_{iv}} \times 100\%.$$