Supporting Information

Copolymer-Templated Nitrogen-Enriched Nanocarbons as Low Charge-Transfer Resistance and Highly Stable Alternative to Platinum Cathodes in Dye-Sensitized Solar Cells

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Fabrication of the counter electrode on FTO

0.1 wt% **CTNC**-series materials was dispersed in 2-propanol solution by ultrasonication for 30 min and the solution was left for 2 h to separate larger particles by sedimentation. The resulting solution was deposited directly on FTO (TEC-8, Pilkington) using an e-spray technique. First, the **CTNC** solution was loaded into a plastic syringe equipped with a 30-gauge stainless steel hypodermic needle. The needle was connected to a high voltage power supply (ESN-HV30). A voltage of ~ 4.6 kV was applied between a metal orifice and the conducting substrate at a distance of 5 cm, and substrate temperature of 60 °C. The feed rate was controlled by the syringe pump at a constant flow rate of 70 μL min^{-1}. For effective comparison, a conventional Pt CE was also prepared by deposition of *ca.* 20 μL/cm^2 of H$_2$PtCl$_6$ solution (2 mg of H$_2$PtCl$_6$ in 1 mL of ethanol), and then it was sintered at 400 °C for 15 min. To evaluate the electrocatalytic activity of sample materials, a symmetrical sandwich dummy cell was fabricated from two identical **CTNC**-FTO or Pt-FTO sheets, which were separated by 60 μm thick Surlyn (Solaronix, Switzerland) tape as a seal and spacer leaving 0.6 × 0.6 cm^2 active area. The cell was filled with an electrolyte solution through a hole in one FTO support which was finally closed by a Surlyn seal. The FTO sheet edges were coated by ultrasonic soldering (USS-9200, MBR Electronics) to improve electrical contacts.

Assembly of dye-sensitized solar cells

FTO plates were cleaned in detergent solution, water, and ethanol using an ultrasonic bath. The FTO substrates were immersed in 40 mM aqueous TiCl$_4$ solution at 70 °C for 30 min and washed with water and ethanol. A TiO$_2$ colloidal paste (Dyesol, 18NR-T) was screen-printed onto FTO/glass and sintered at 500 °C for 30 min in air. The thickness of the transparent layer was measured by using an Alpha-step 250 surface stylus-type profilometer (Tencor Instruments, San Jose, CA), and a paste for the scattering layer containing 400 nm sized

anatase particles (CCIC, PST-400C) was deposited by screen-printing and then dried for 1 h at 120 °C. The TiO$_2$ electrodes were sintered at 500 °C for 30 min. The resulting TiO$_2$ electrodes were immersed in a THF/ethanol (v/v, 1/2) solution containing 0.3 mM of **JK-306** sensitizer[S1] and 0.3 mM of a multi-functional coadsorbent HC-A (**SGT-301**)[S2-S5] (or 0.3 mM of N719 sensitizer only) and kept at room temperature for 12 h. The dye adsorbed TiO$_2$ photoanodes were assembled with **CTNCs**-FTO or Pt CEs using a thermal adhesive film (25 μm thick Surlyn, Du-Pont) as a spacer to produce a sandwich-type cell. The electrolyte solution was 0.22 M Co(bpy)$_3$(BCN$_4$)$_2$, 0.05 M Co(bpy)$_3$(BCN$_4$)$_3$, 0.1 M LiClO$_4$, and 0.8 M 4-*tert*-butylpyridine in acetonitrile. Another iodine electrolyte solution composed of 0.6 M DMPII, 0.1 M LiI, 0.05 M I$_2$, and 0.5 M TBP in acetonitrile was also used for the performance test of N719-based DSSCs. Electrolyte solution was introduced through a drilled hole on the CE *via* vacuum backfilling. The hole was sealed with cover glass using a Surlyn seal.

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 100 mW cm^{-2}, which is the equivalent of one sun at Air Mass (AM) 1.5G at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was doubled-checked with an NREL calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current-voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software. The measurement-settling time between applying a voltage and measuring a current for the current-voltage characterization of DSSCs was fixed to 80 ms.
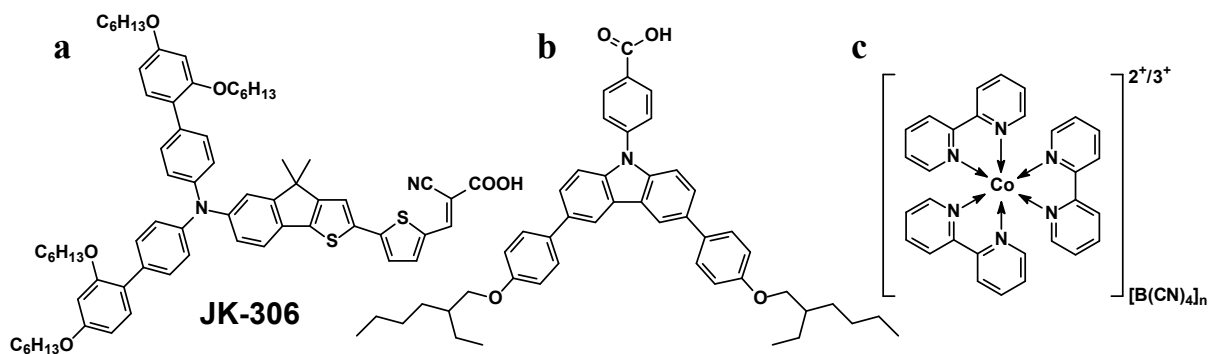
Chemical formulas: (a) **JK-306** sensitizer; (b) **HC-A** coadsorbent (**SGT-301**); (c) Co(bpy)$_3^{2+/}$ $^{3+}$redox couple.
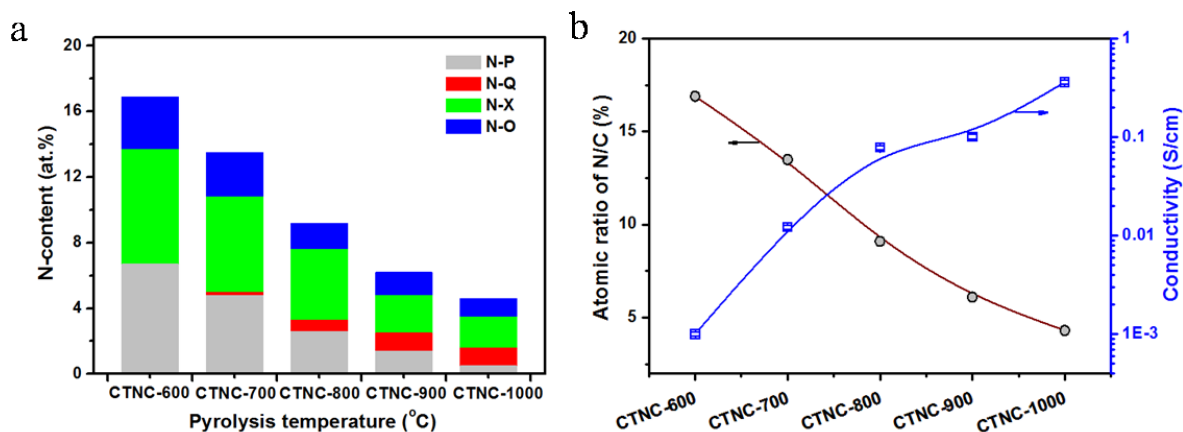

Fig. S1 (a) Nitrogen-bonding distributions in carbon framework. N-P; pyridinic N, N-Q; quaternary N, N-X; pyrollic N (or pyridonic N); N-O; pyridinic N-oxide. (b) Atomic ratio of N/C in carbon framework and their conductivity as a function of pyrolysis temperature.

In previous work,[S6] high-resolution N1s XPS spectra were used to determine the nitrogen states in the **CTNC** samples. By deconvoluting N1s spectra, four kinds of N species can be identified by the bonding states of the N atom, including pyridinic N (398.5 eV), pyrrolic or pyridonic N (indistinguishable) (400.5 eV), quaternary N (401.3 eV), and pyridinic N-oxide (403.2 eV). The composition atomic ratios of four types of N species in the five CTNC

samples are summarized in **Table S2** and **Fig. S1a**. This data shows an obvious difference in the content of N species between the samples. For **CTNC-600**, the pyridinic and pyrrolic/pyridonic configurations are dominant, and quaternary N sites are almost not present. Upon increasing the pyrolysis temperature to 1000 °C, the content of pyridinic and pyrrolic/pyridonic N sharply decreases to 0.5 wt% or 1.9 wt%, respectively, accompanied by the increase of quaternary N. An according drop in sheet resistance (**Fig. S1b**) with pyrolysis temperature suggests the formation of larger graphitic domains through fusion of smaller ones with a concurrent denitrogenation processes.
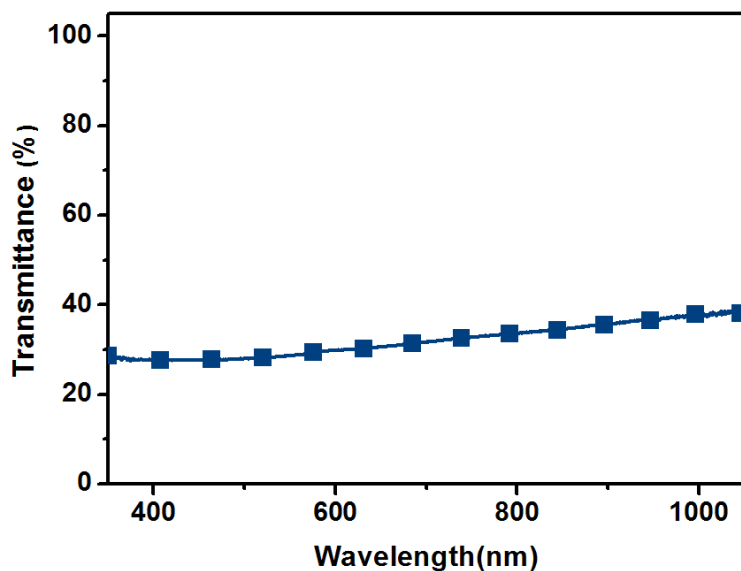

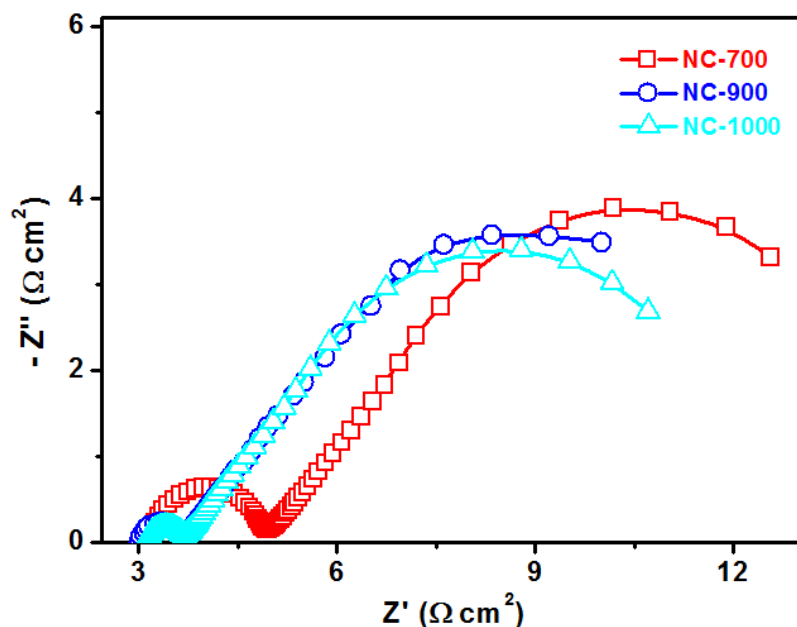**Fig. S2** Optical transmittance of CTNC film on FTO.

Fig. S3 (a) Nyquist plots of symmetrical dummy cells consisting of different electrodes with frequency ranging from 10^6 to 0.1 Hz, and amplitude of the alternating current set to 10 mV using an $Co(bpy)_3^{2+/3+}$ based electrolyte.
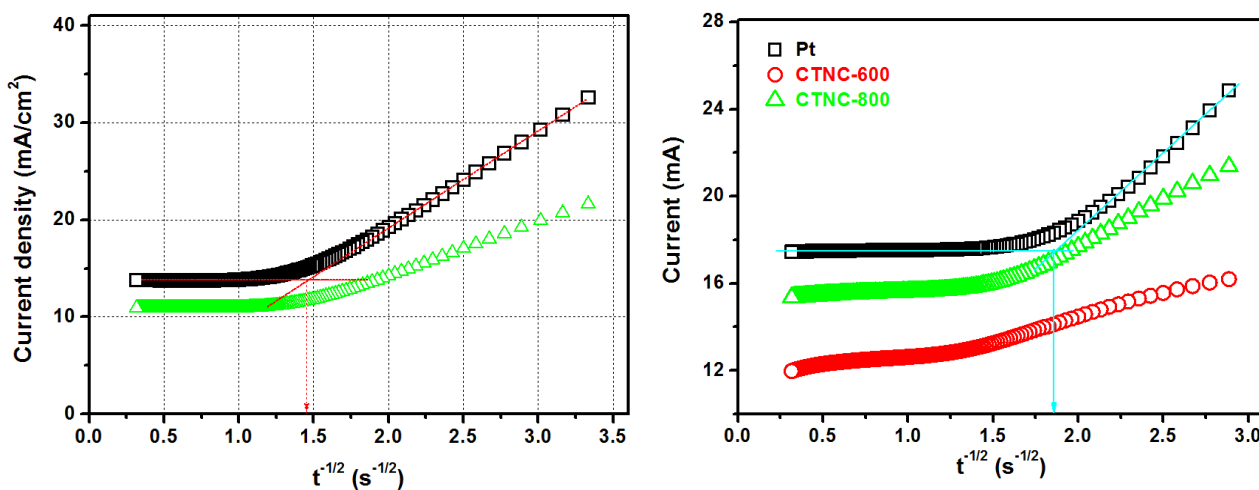

Fig. S4 Potential-step chronoamperometry (CA) plots on symmetrical dummy with the **CTNC-800** (black) and Pt (green) electrodes in $Co(bpy)_3^{2+/3+}$ electrolyte (left) and for **CTNC**-600, **CTNC**-800, and Pt electrodes in the I^-/I_3^- redox couple system (right). Potential was stepped from 0 to 0.8 V and held for 10 s. To examine the mass transport properties of $Co(bpy)_3^{3+}$, CA measurements were carried out at room temperature. Shortly after the

potential step, the current follows the semi-infinite Cottrell-like decay. The current drops linearly with $t^{-1/2}$ (t is time) as long as the concentration profiles in front of each electrode merge to form a single linear profile. At this stage, the current attains a steady state value, which is equal to the limiting current. Extrapolation of both linear components of the CA plots provides intersection at the so-called transition time (t), which provides the diffusion coefficient D according to the eq. (S2).[S7]

$$\frac{nFAC \cdot \sqrt{D}}{\sqrt{\pi t}} = \frac{2nFAC \cdot D}{\delta} \qquad \text{(S1)}$$

$$D = t^{-1}\left(\frac{\delta^2}{4\pi}\right) \qquad \text{(S2)}$$

From the data in **Fig. S4** and eq. (S2), we can calculate the values of $D = 6.94 \times 10^{-6}$ and 6.83×10^{-6} cm^2/s for **CTNC**-800 and Pt dummy cells, respectively.

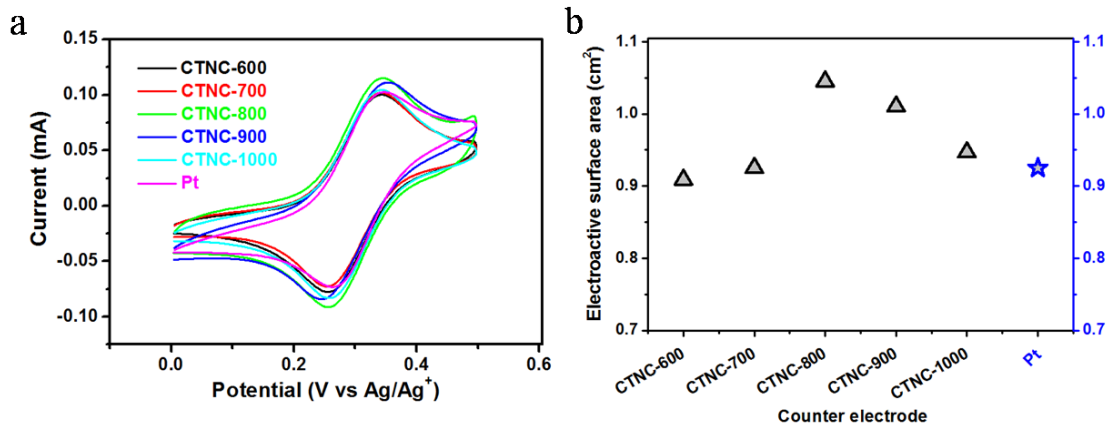**Fig. S5** (a) CV curves of Pt and **CTNC** electrodes in Co(bpy)$_3^{2+/3+}$ solution. The electrolyte concentration was 100 times lower than that used in a typical DSSC performance test along with 0.1 M LiClO$_4$ as supporting electrolyte. (b) The calculated electroactive surface area of different counter electrodes. The test area is 0.43 cm^2 (πr^2).

The electro-active surface area was caculated according to the Randles-Sevcik equation,

$$A = \frac{I_{pc}}{2.69 \times 10^5 \times n^{3/2} \times D^{1/2} \times V^{1/2} \times C} \qquad (S3)$$

where, A is the electro-active surface area (cm²), I_{pc} is the peak current (A), and $n = 1$, $D = 6.94 \times 10^{-6}$ (**CTNC**-electrodes) and 6.83×10^{-6} cm²/s (Pt-electrode) obtained from chronoamperometry (**Fig. S4**), V is the scan rate (10 mV/s), C is the concentration (mol/ml).

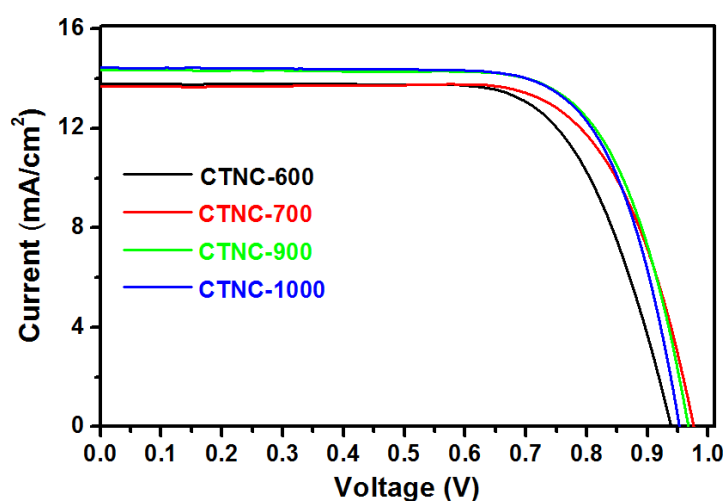| CE	CTNC-600	CTNC-700	CTNC-800	CTNC-900	CTNC-1000	Pt
Electro-active surface area (cm²)	0.909	0.925	1.045	1.011	0.947	0.925

Fig. S6 Current-voltage curves of the Co(bpy)$_3^{2+/3+}$-based DSSCs with CTNC-600, **CTNC**-700, **CTNC**-900, and **CTNC**-1000 CEs under one sun illumination (AM 1.5 G). The TiO$_2$ film thickness is 8.5 (5.5 + 3) μm. All cells were tested with a metal shadow mask having an aperture area of 0.16 cm², but without consideration of masking the sides of the DSSCs.

Fig. S7 Current-voltage curves of the I^-/I_3^--based DSSCs with CTNC-600, **CTNC**-700, **CTNC**-900, and **CTNC**-1000 CEs under one sun illumination (AM 1.5 G). The TiO$_2$ film thickness is 8.5 (5.5 + 3) μm. All cells were tested with a metal shadow mask having an aperture area of 0.16 cm^2, but without consideration of masking the sides of the DSSCs.
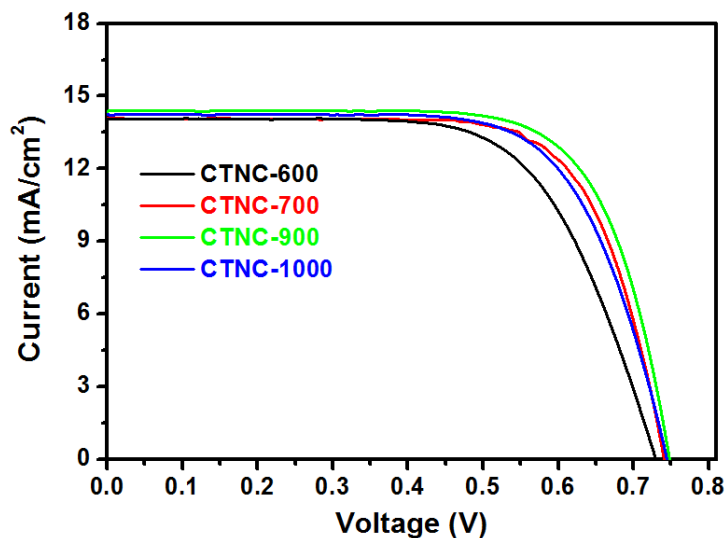
Table S1. Surface area and pore size analysis by N$_2$ isotherm

CTNC Sample	Surface area (m^2/g)			S_{mes}/S_{BET}	Pore volume (cm^3/g)
	S_{BET}	S_{mic}	S_{mes}		
CTNC-600	461	264	210	0.46	0.65
CTNC-700	498	277	223	0.45	0.67
CTNC-800	485	278	220	0.45	0.65
CTNC-900	509	256	254	0.50	0.71
CTNC-1000	564	227	328	0.58	0.76

Table S2. The composition atomic ratios of each type of N species in five CTNC samples

CTNC samples	O/C (±0.5) (at.%)	N/C (±0.8) (at.%)	Pyridinic N/C (at.%)	Quaternary N/C (at.%)	Pyrrolic N(or pyridonic N)/C (at.%)	Pyridinic N-oxide/C (at.%)
CTNC-600	7.1	16.9	6.7	-	7.0	3.2
CTNC-700	7.3	13.5	4.8	0.2	5.8	2.7
CTNC-800	7.3	9.1	2.6	0.7	4.3	1.6
CTNC-900	7.2	6.1	1.4	1.1	2.3	1.4
CTNC-1000	5.9	4.3	0.5	1.1	1.9	1.1

Table S3. EIS parameters for the studied N-enriched carbon cathodes (mean value of five dummy cells), with $Co(bpy)_3^{3+/2+}$ redox shuttle

CE	R_S (Ω cm^2)	R_{CT} (Ω cm^2)	C_{dl} (μF cm^2)	J_0 (mA cm^{-2})
CTNC-600	1.81±0.24	5.01±0.57	8.76±0.20	5.06±0.70
CTNC-700	1.56±0.04	0.71±0.17	7.42±0.54	37.80±9.20
CTNC-800	1.55±0.04	0.31±0.04	4.87±0.30	84.31±12.91
CTNC-900	1.52±0.08	0.38±0.03	11.32±0.77	68.50±6.10
CTNC-1000	1.53±0.03	0.34±0.03	17.51±0.55	76.09±6.59
Pt	1.62±0.27	1.35±0.36	20.94±2.90	19.98±5.20

Table S4. Photovoltaic performance of the DSSCs with different counter electrodes

Counter electrode	V_{OC} (mV)	FF (%)	J_{SC} (mA/cm^2)	PCE (%)
CTNC-600	945 (729)	67.4 (65.8)	14.16 (14.06)	9.02 (6.75)
CTNC-700	976 (740)	72.1 (71.9)	13.68 (14.07)	9.63 (7.50)
CTNC-900	967 (748)	73.0 (72.1)	14.35 (14.38)	10.13 (7.75)
CTNC-1000	953 (744)	73.4 (69.4)	14.44 (14.22)	10.09 (7.36)

( )Photovoltaic performance of the N719-based DSSCs with different CEs in I^-/I_3^- redox electrolyte.

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