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Electronic Supplementary Information (ESI) for

Self-sponsored doping approach for controllable synthesis of S, N co-doped trimodal-porous structured graphitic carbon electrocatalyst

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Table S1 Atomic percentage of various N chemical states in SN/C-X samples.

Samples	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic-N (%)
SN/C-400	58.0±0.9	42.0±1.2	0.0
SN/C-500	57.5±0.8	42.5±0.7	0.0
SN/C-600	50.3±2.3	22.4±1.8	26.1±3.7
SN/C-700	48.0±1.4	22.1±2.3	30.0±2.5
SN/C-800	39.3±2.4	21.6±3.8	39.0±3.3
SN/C-900	35.5±2.5	21.6±1.8	42.6±0.9
SN/C-1000	23.2±1.8	19.1±2.1	57.7±2.7

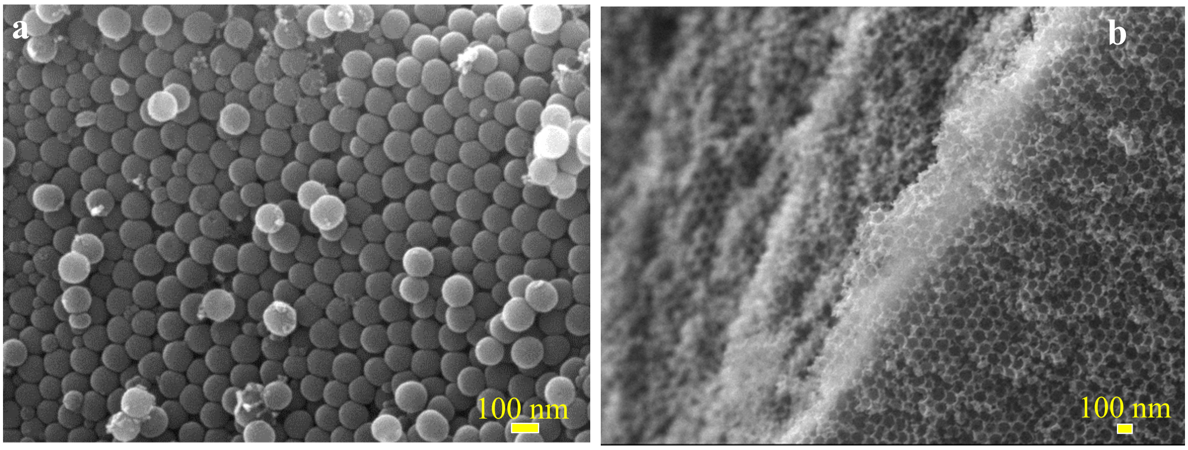


Fig. S1 (a) SEM of SN/C-900 after calcination. (b) SEM of SN/C-900 after removal of the silica template by HF.

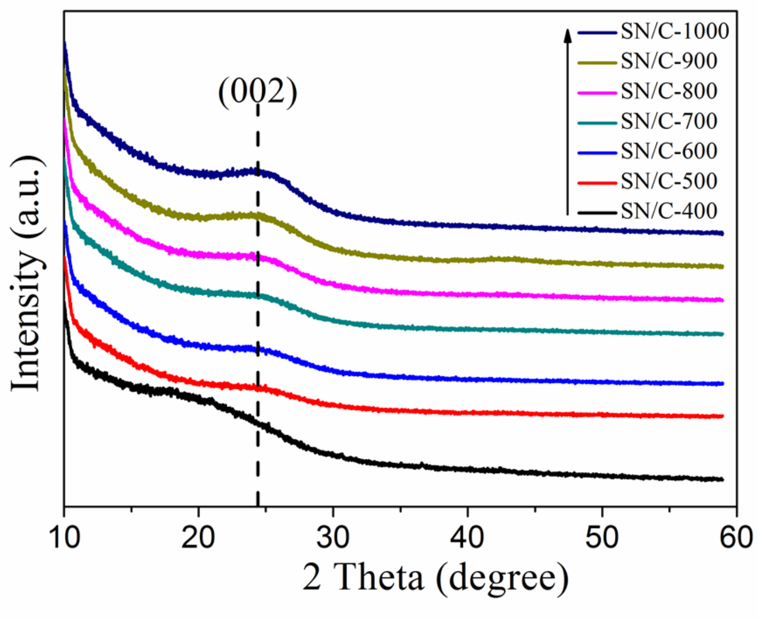


Fig. S2 Wide-angle XRD patterns of the SN/C-X samples.

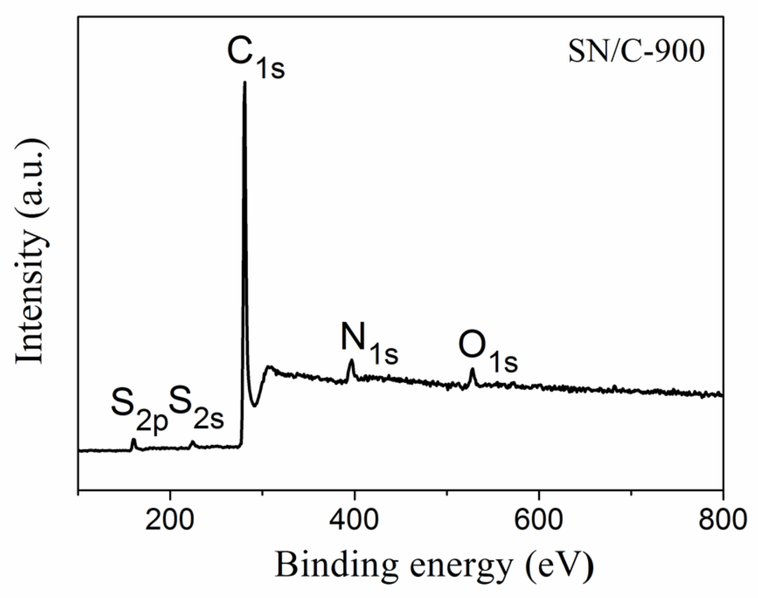


Fig. S3 X-ray photoelectron spectroscopy (XPS) survey spectrum of SN/C-900.

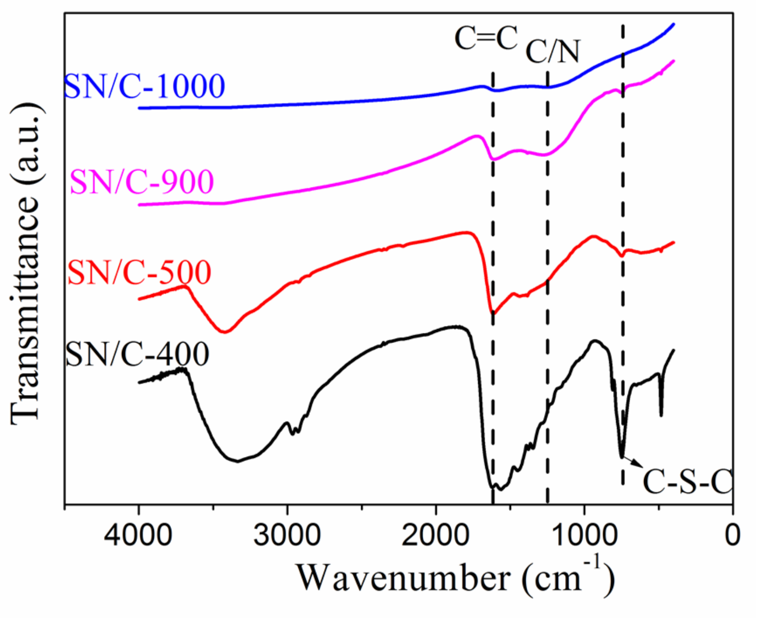


Fig. S4 FT-IR spectra of SN/C-X samples. Some characteristic bonds were observed and assigned to the stretching of carbonyl aromatic C=C bonds (1624 cm^{-1}), 753 cm^{-1}, which is assigned to the stretching of C-S-C bonds. The broadened band in the range of 1200-1400 cm^{-1} is attributed to the stretching mode of C-N heterocycles. The broad bands in the range of the 3000-3700 cm^{-1} region can be attributed to the adsorbed H_2O molecules or N-H vibration possibly due to uncondensed amine groups.

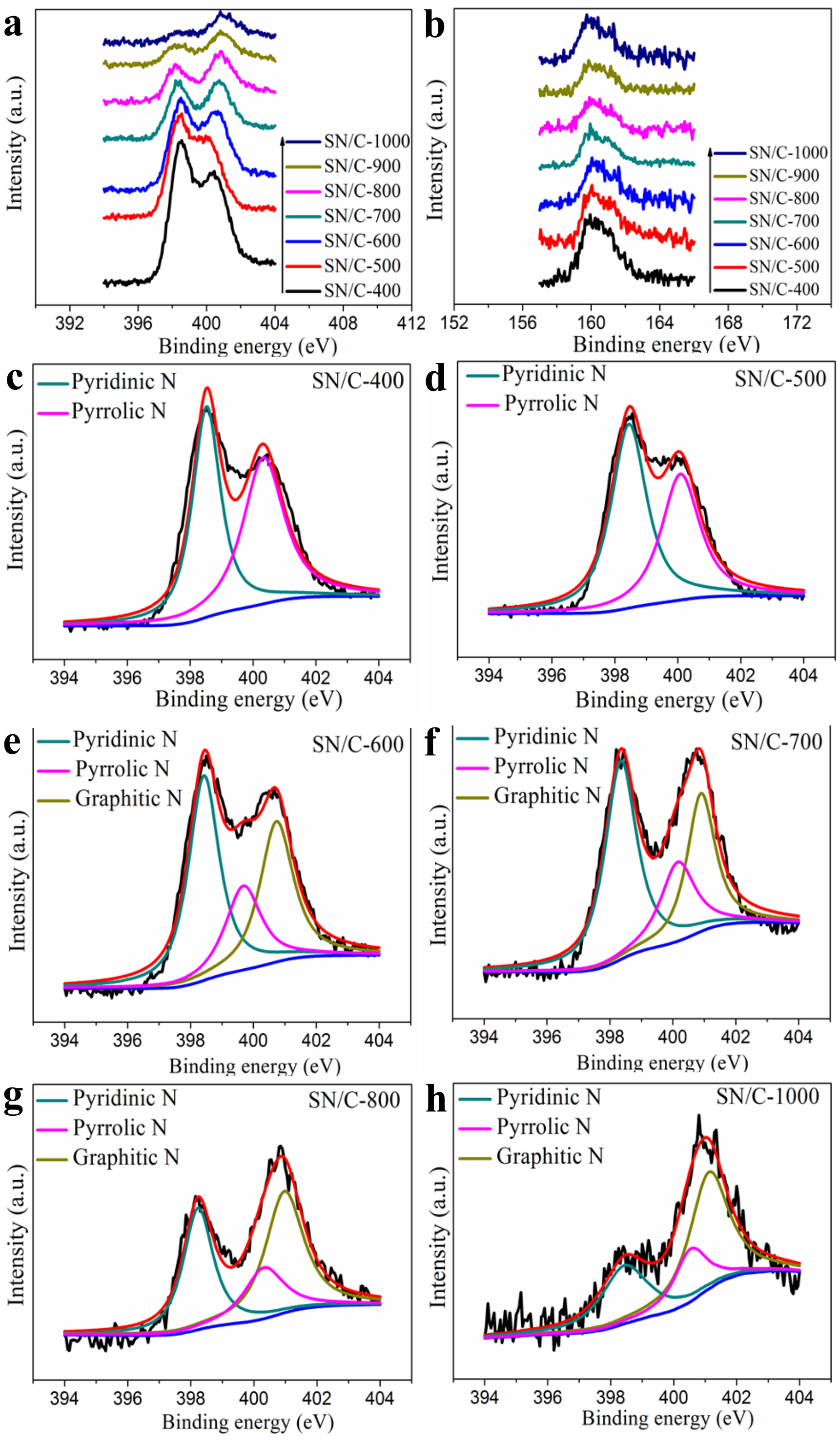


Fig. S5 (a) High resolution N and (b) S XPS spectra of SN/C-X. (c)-(h) High resolution N XPS spectrum of SN/C-X samples and the corresponding different peaks.

As seen from Fig. S5, the N1s spectra can be fitted into three peaks at 398.3±0.2 eV, 400.1±0.3 eV and 401.1±0.4 eV. The peaks with lower binding energy located at about 398.3 and 400.1 eV, respectively, corresponding to pyridinic-like and pyrrolic-like N, which can contribute to the π-conjugated system with a pair of *p*-electrons in the graphitic carbon layers. The higher binding energy located at about 401.1 eV corresponding to “graphitic” nitrogen, that is, the carbon atoms within the graphitic layers are substituted by nitrogen atoms. It can be seen at lower pyrolysis temperatures, only pyridinic- and pyrrolic-N were formed. After 600 ºC, graphitic-N was formed. Pyridinic-N was the dominated peak below 800 ºC until then it was overtaken by the graphitic-N. However, in higher pyrolysis temperatures, pyridinic- and graphitic-N was the dominate defects forms whereas pyrrolic defects type are less abundant. This is in accordance with expectations due to the higher diffusion rate of carbon at high temperatures leading to the formation of the more stable graphitic-N defect and agrees well with the study by Maldonado et al and Sharifi et al.[1, 2] This means that the chemical state of N in doped graphitic carbon layers can be easily modulated by changing the pyrolysis temperature. In comparison, all the high resolution S2p peaks of the SN/C prepared at different temperatures has one main peak at the binding energies of ∼164.0 eV, in agreement with the reported positions of -C-S-C- bond owing to their spin-orbit coupling.

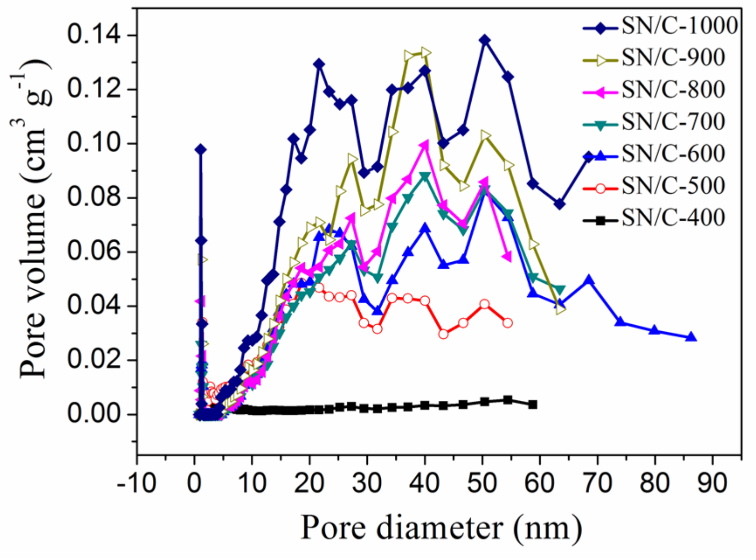


Fig. S6 Pore size distribution curves of SN/C-X samples.

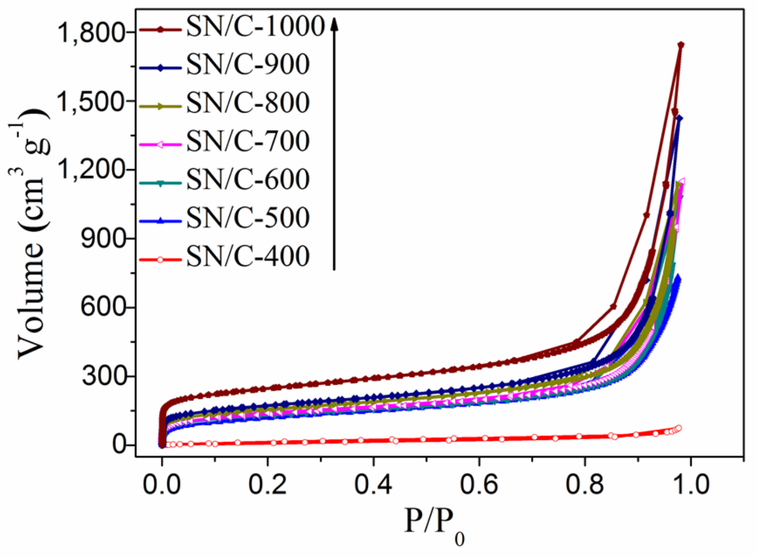


Fig. S7 The N_2 adsorption/desorption isotherm of SN/C-X.

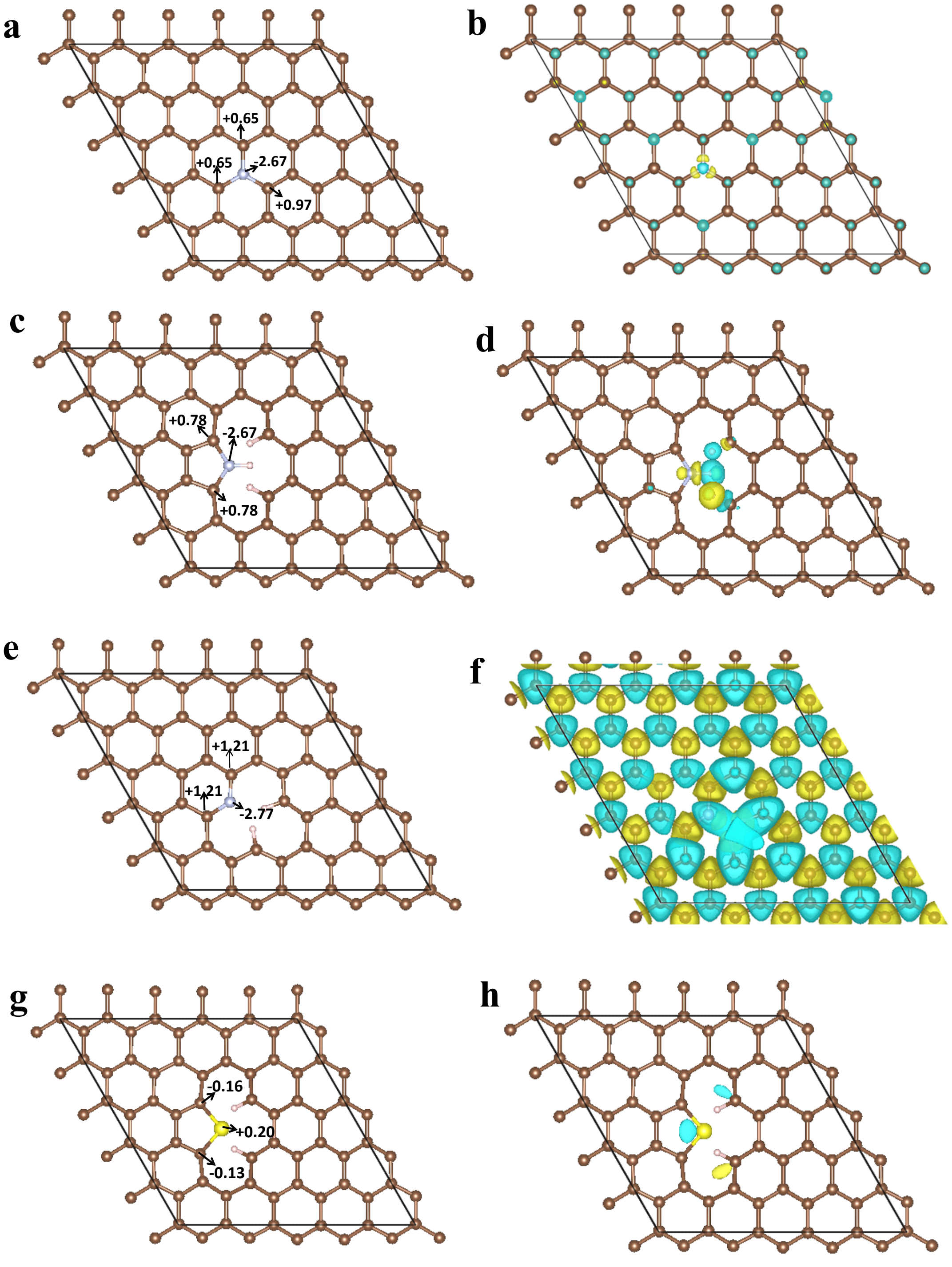


Fig. S8 Charge and spin density of graphitic-N (a, b), pyrrolic-N (c, d) and pyridinic-N (e, f) doped graphitic carbon sheets, respectively. (g, h) charge and spin density of only S doped graphitic carbon sheet, respectively. Dark brown, gray, yellow and pink spheres represent C, N, S and H atoms in Fig. S8. (a), (c), (e) and (g), respectively. The blue and yellow contours indicate the spin densities of the samples with the spin density value of $\pm 2.0\times 10^{-7}$ electron Å^{-3}.

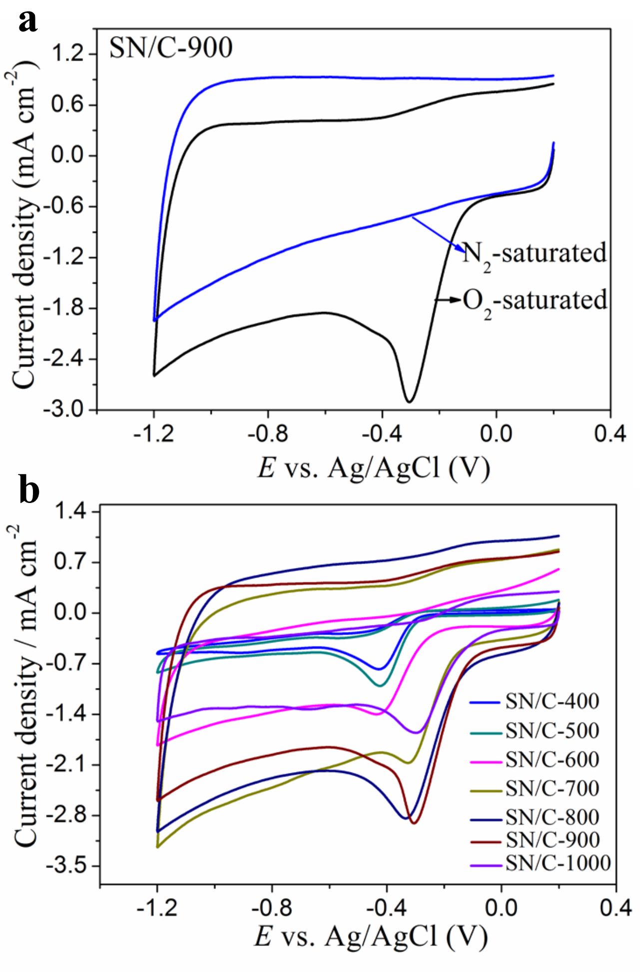
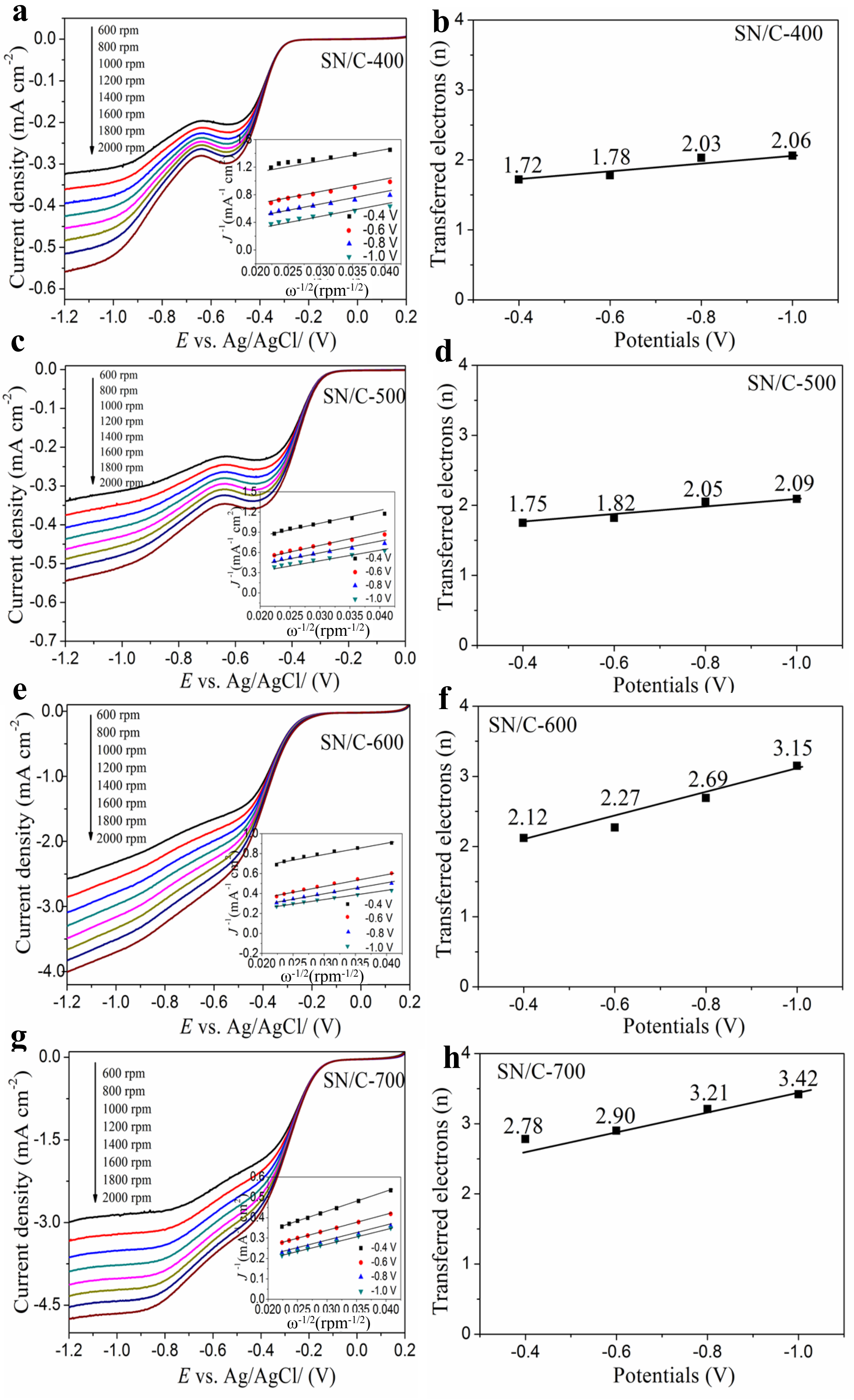


Fig. S9 (a) Cyclic voltammograms of the ORR at SN/C-900 electrode in N_2 or O_2 saturated KOH solution and (b) Cyclic voltammograms of SN/C-X samples obtained at different temperatures in O_2 with a scan rate of 100 mV s^{-1} in the potential range from -1.2 to +0.2 V at room temperature, respectively.

 a
b
c
d
e
f
g
h
600 rpm
800 rpm
1000 rpm
1200 rpm
1400 rpm
1600 rpm
1800 rpm
2000 rpm
SN/C-400
SN/C-500
SN/C-600
SN/C-700
Current density (mA cm^{-2})
E vs. Ag/AgCl/ (V)
J^{-1}(mA^{-1} cm^{2})
$\omega^{-1/2}$(rpm$^{-1/2}$)
-0.4 V
-0.6 V
-0.8 V
-1.0 V
Transferred electrons (n)
Potentials (V)
1.72
1.78
2.03
2.06
1.75
1.82
2.05
2.09
2.12
2.27
2.69
3.15
2.78
2.90
3.21
3.42

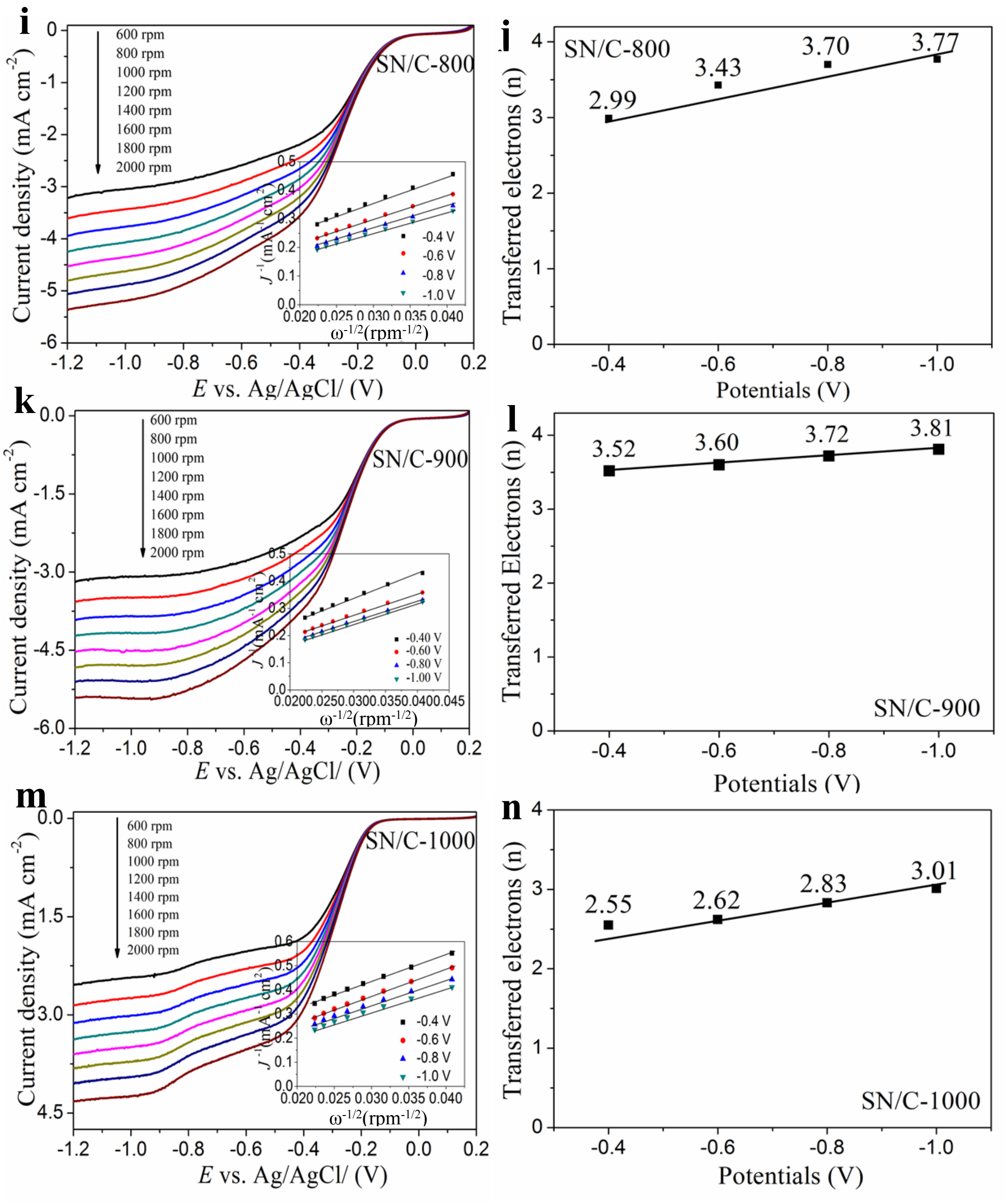


Fig. S10 Linear sweep voltammograms of (a)–(n) SN/C-X samples and the corresponding Koutecky–Levich plots (inset) and transferred electrons. All the tests were conducted from 0.2 V to -1.2 V with a scan rate of 10 mV s^{-1} in an O_2 saturated 0.1 M KOH aqueous electrolyte.

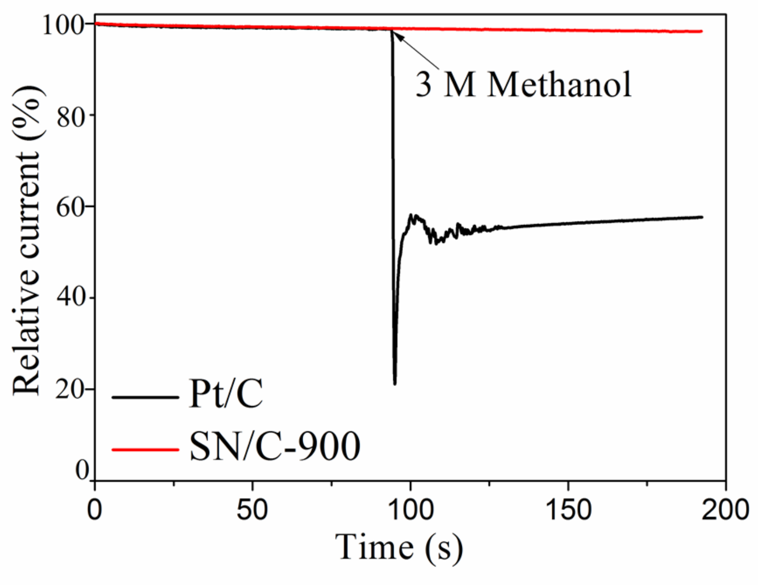


Fig. S11 Chronoamperometric response for ORR at SN/C-900 and Pt/C electrodes on addition of 3 M methanol after about 100 s.

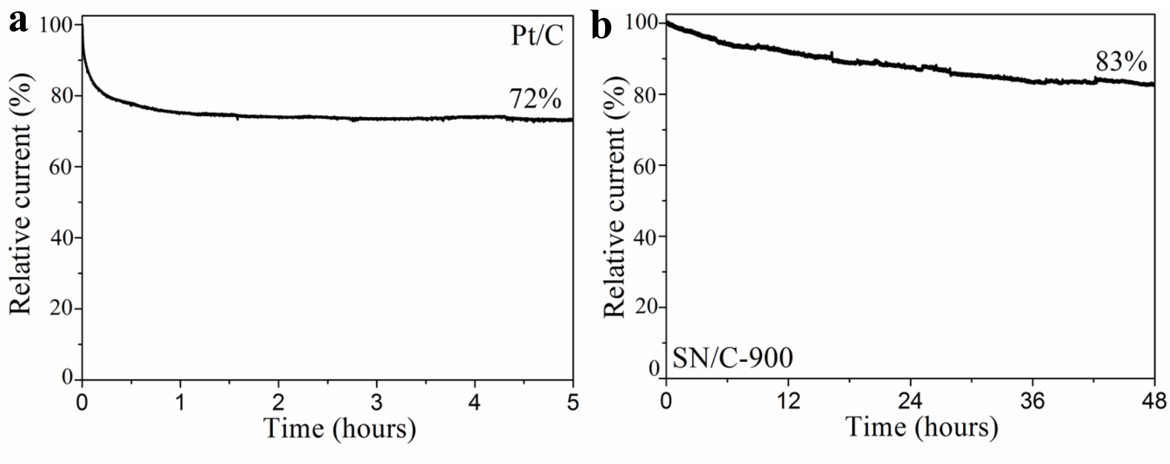


Fig. S12 Durability evaluation of (a) Pt/C and (b) SN/C-900 electrode for 2 days at -0.4 V and a rotation rate of 1000 rpm.

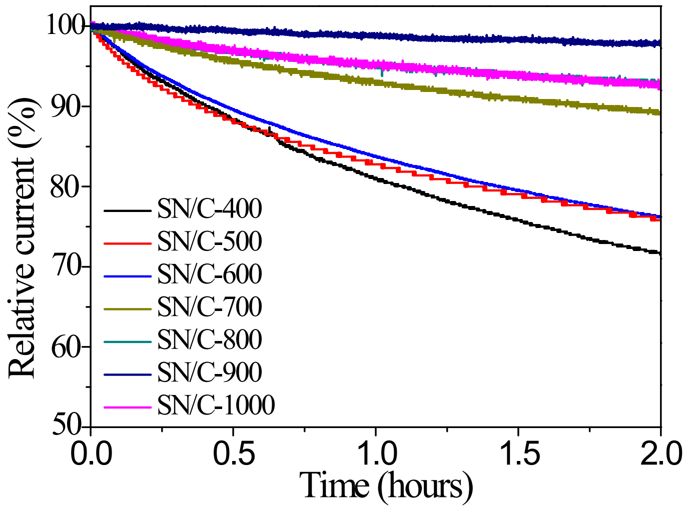


Fig. S13 Durability evaluation of SN/C-X catalysts for 2 hours at -0.4 V and a rotation rate of 1000 rpm in O_2-saturated 0.1 M KOH solution.

References

1. S. Maldonado,. S. Morin, K. J. Stevenson, *Carbon*, 2006, **44**, 1429.

2. T. Sharifi, F. Nitze, H. Barzegar, C. Tai, M. Mazurkiewicz, A. Malolepszy, L. Stobinski, T. Wågberg. *Carbon*, 2012, **50**, 3535.