Electronic Supplementary Information (ESI†)

Hollow nitrogen-doped carbon spheres as an efficient and durable electrocatalyst for oxygen reduction

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Synthesis of Hollow nitrogen-doped carbon spheres (HNCS)

Iron (III) diethylene triaminepentaacetate (Fe-DTPA) is used as a solid precursor for carbon, nitrogen and iron, was carried out by using Swagelok union cells. Fe-DTPA (0. 6g) was filled into the cell at room temperature. The cell was closed and then placed at the center of the muffle furnace. The temperature was raised at a heating rate of 10 ^{0}C per minute up to a required temperature (700 ^{0}C and 900 ^{0}C), and held for 1 h. The reaction took place under the autogenic pressure of the precursor. The closed cell was gradually cooled down to room temperature. The yield of products obtained at 700 ^{0}C and 900 ^{0}C are found to be 35 and 30 wt%, respect to the weight of initial precursor. As-synthesized product (100 mg), oxide/metal filled carbon was stirred in 5 mL of concentrated HCl for 24 h to remove the oxide/metal core. The HNCS were recovered by centrifuging the contents at 10,000 rpm for 7 min for several times using water and ethanol. The black compound was washed with copious waters, and ethanol at last, and stored under vacuum overnight.

Characterization:

The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800Ⅱ) with an accelerating voltage of 3 kV. Before the SEM observation, the samples were coated with osmium. The microstructures and lattice fringe of samples were determined by field-emission transmission electron microscope (FE-TEM, Hitachi, HF-3300) with an acceleration voltage of 300 kV. For TEM analysis, samples were ultrasonically dispersed in ethanol, and then a drop of dispersion was deposited on copper grid and dry under UV lamp. The crystal structure of samples was investigated by powder X-ray diffraction (XRD, Panalytical Empyrean) using Cu Kα radiation at a generator voltage of 40 kV and a tube current of 30 mA. Elemental analysis was performed by X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, ESCALAB250 XPS system, Theta Probe XPS system) using monochromated Al K-alpha source at 15 kV and 150 W. Binding energy values at x-axis were calibrated by using C 1s from a carbon value taken as 284.6 eV. The amount of nitrogen and carbon in samples were accurately determined by elemental analyzer (C, H, N analysis).

Electrochemical oxygen reduction:

Electrochemical tests were carried out by rotating-disc-electrode (RDE) and rotating ring-disk electrode (RRDE) (Biologic, VSP). A 3-electrode system cell consisting of the glassy carbon, Pt wire and standard caramel electrode (SCE) act as working electrode, counter and reference electrodes, respectively. The catalyst ink for electrochemical measurements was fabricated by dispersing 5 mg of the catalyst in 250 μL isopropyl alcohol and 5 μL of Nafion (5%) by ultrasonication for 30 min to obtained homogenous ink. From this, the catalyst ink was coated on clean glassy carbon electrode surface with catalyst loading 0.5 mg cm^{-2} and 0.4 mg cm^{-2} for RDE and RRDE experiment, respectively. Then the solvent was naturally evaporated at room temperature. The oxygen reduction activities were measured by hydrodynamic voltammetry in an O_2-saturated 0.1 M KOH at room temperature. For RDE and RRDE, GC electrodes using 3 and 4 mm-diameter glassy carbon disks, respectively. The electrolyte solution was purged with nitrogen gas for 30 min before the electrochemical measurement. A flow of O_2 was maintained over the electrolyte during the measurement to ensure O_2 atmosphere inside the cell. The electron transfer number from Koutecky-Levich plots were determined by follow equation.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$

$$B = 0.62\, n\, F\, C_0\, D_0^{\frac{2}{3}}\, v^{-\frac{1}{6}}$$

Where, J is the experimentally measured current, J_L is the diffusion-limiting current, J_K is the kinetic current, ω is the angular velocity, F is the Faraday constant, C_0 is the saturated concentration of O_2 in 0.1M KOH (1.2 x 10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 0.1M KOH (1.9 x 10^{-5} cm^2 s^{-1}), and ν is the kinematic viscosity of the electrolyte. The “n” can calculate from slop by under plot of J^{-1} vs $\omega^{-1/2}$ and J_k is calculated from inverse of intercept.

The formation of HO_2^- and the electron transfer number from RRDE experiment were determined by follow equation;

$$H_2O_2(\%) = 200 \times \frac{I_R / N}{I_D + (I_R/N)}$$

$$n = 4 \times \frac{I_D}{I_D + (I_R/N)}$$

where, I_D is the disk current, I_R is the ring current, and N is the ring correction coefficient in RRDE experiment was determine to be 0.37 from the reduction of $Fe(CN)_6^{4-/3-}$ redox couple. The ring potential was held at 1.3 vs. RHE. For comparison of electrocatalyst, reference Pt/C (10 wt%, Johnson-Matthey) was used.

Calibration of SCE and conversion to RHE

The calibration of saturated Calomel electrode (SCE) reference electrode is performed in a standard three-electrode system. Pt wires were used as the working and counter electrodes, and the SCE as the reference electrode. Electrolytes are pre-purged and saturated with high purity H_2. Linear scanning voltammetry (LSV) is then run at a scan rate of 10 mV/s, and the potential at which the current crossed zero is taken to be the thermodynamic potential (vs. SCE) for the hydrogen electrode reactions (Figure S1). All potential in the RHE scale were converted from the SCE scale using E (RHE) = E (SCE) + 0.991 V in 0.1 M KOH.

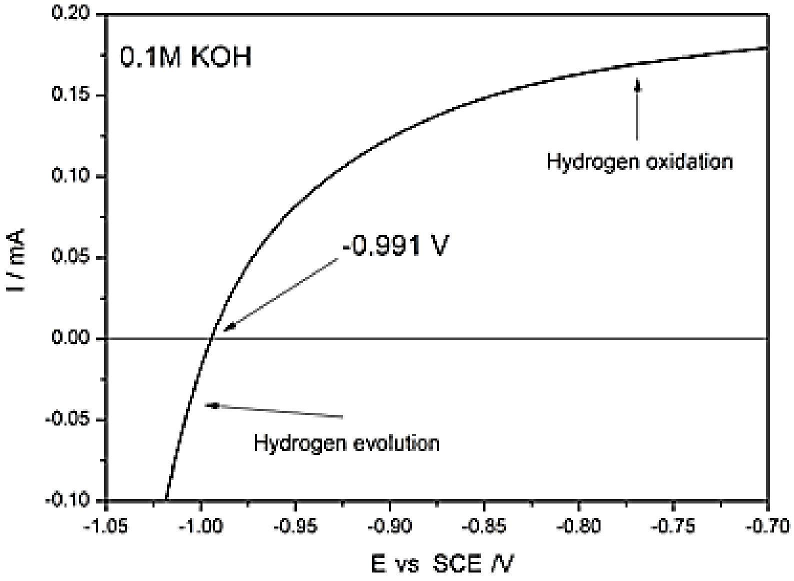

Fig. S1. Calibration of SCE to RHE

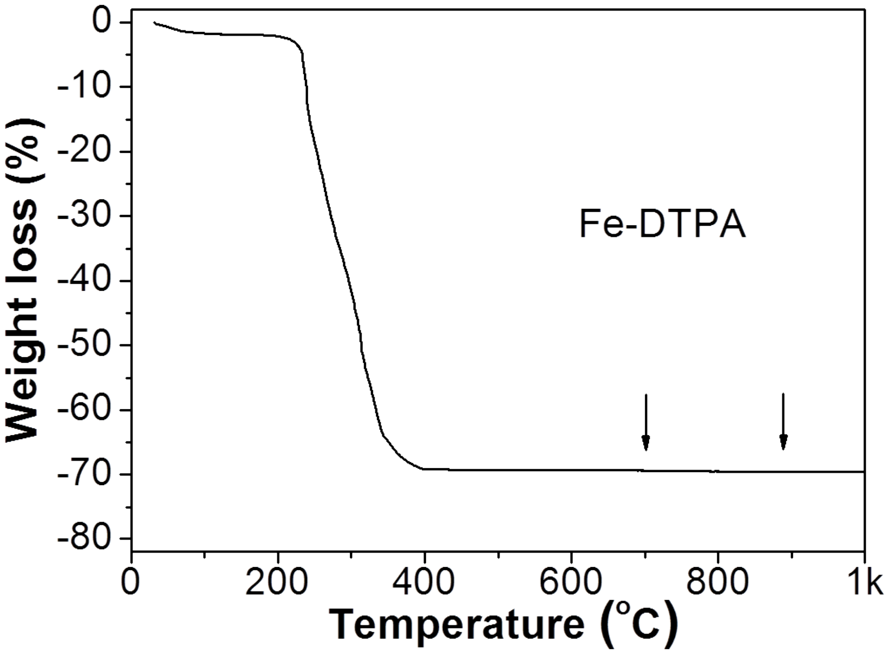

Fig. S2. Thermogram of Fe-DTPA precursor carried out in an air atmosphere with a heating rate of 10 °C min^{-1}

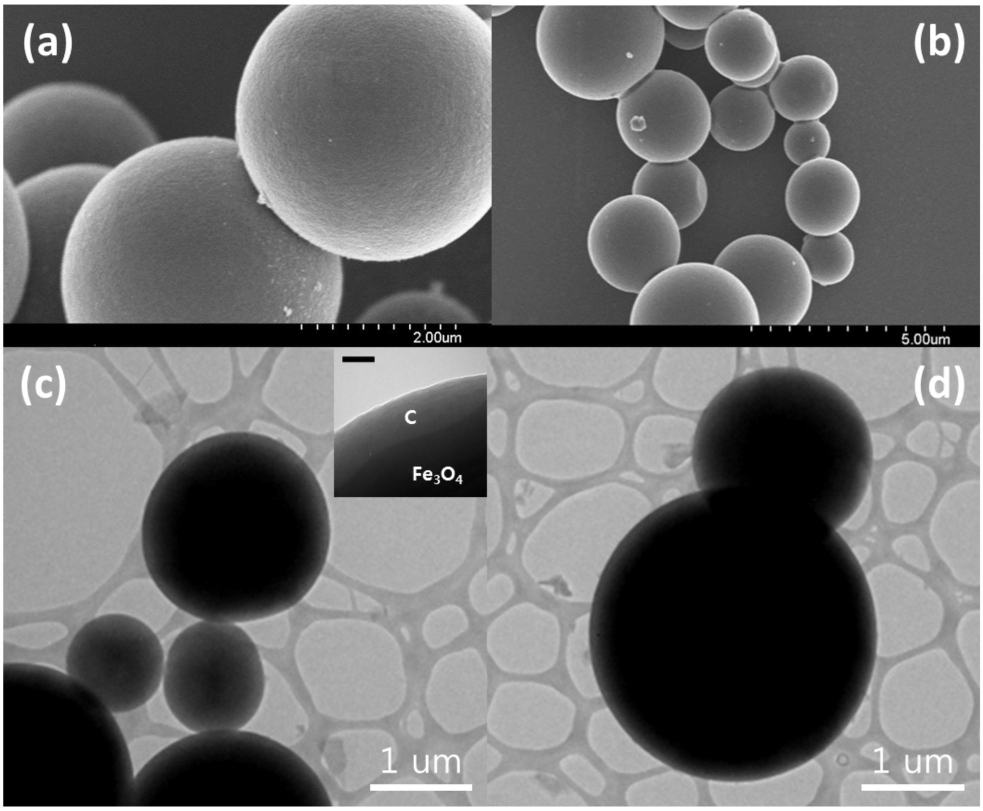

Fig. S3. Typical FESEM images of product obtained at (a) 700 ˚C (b) 900 ˚C and TEM images of (c) 700⁰C (d) 900⁰C.; inset in (c) shows TEM image of a sphere clearly depicts a thick carbon coating on Fe_3O_4 core (scale bar : 50nm).

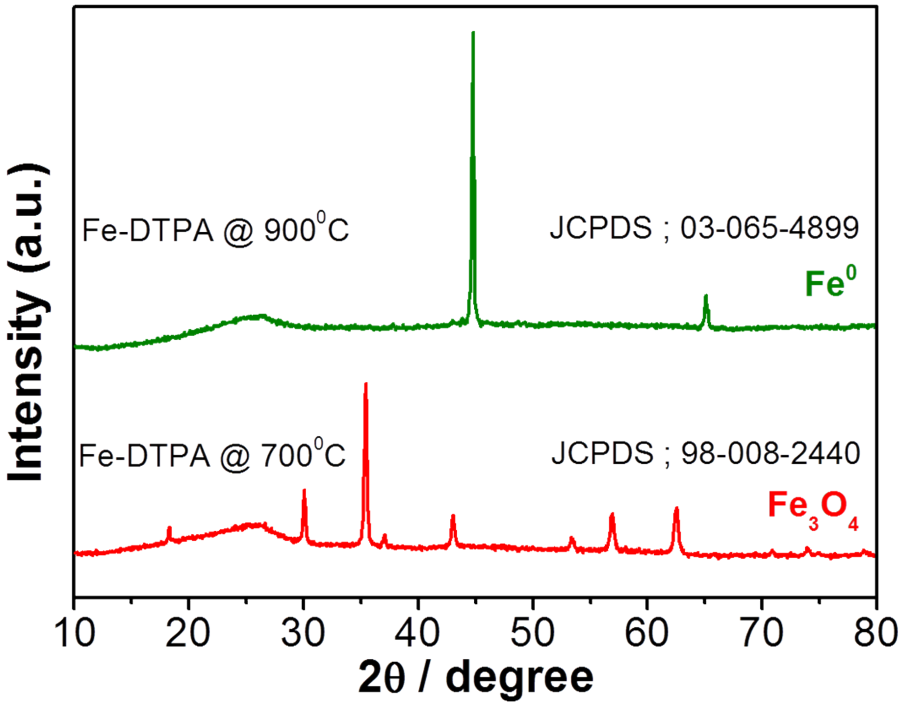

Fig. S4. XRD patterns of as-synthesized products prepared at 700 ˚C and 900 ˚C for 1h (before acid treatment)

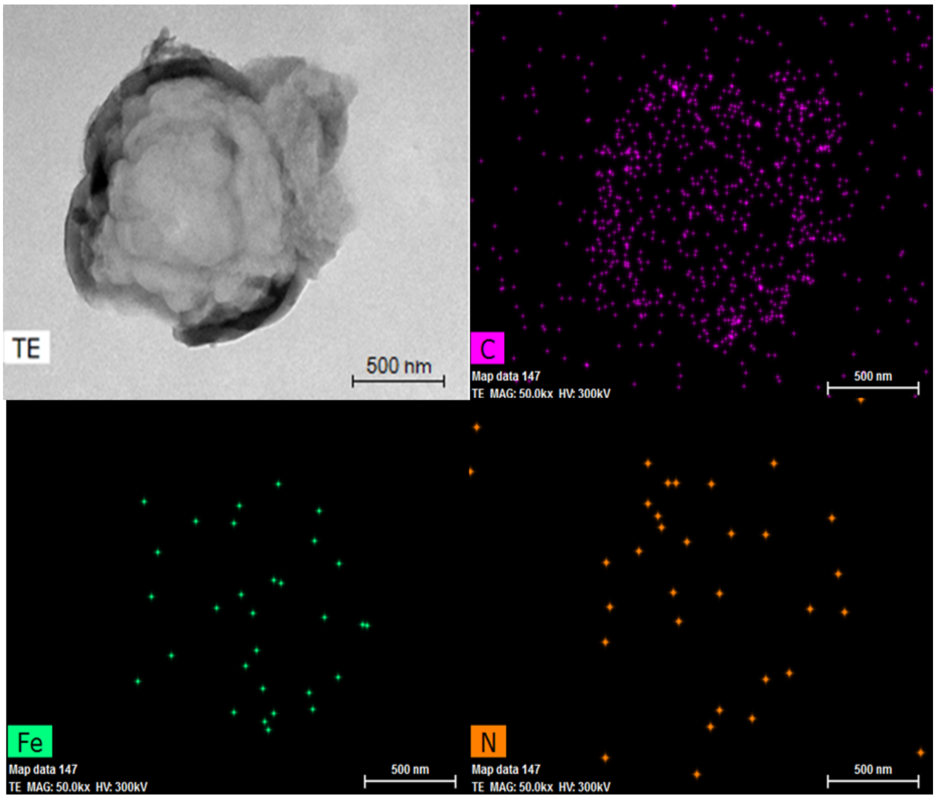

Fig. S5. The TEM image of HNCS71 and corresponding EDX mapping results for the elements $C_{k\alpha}$, $Fe_{k\alpha}$,and $N_{k\alpha}$

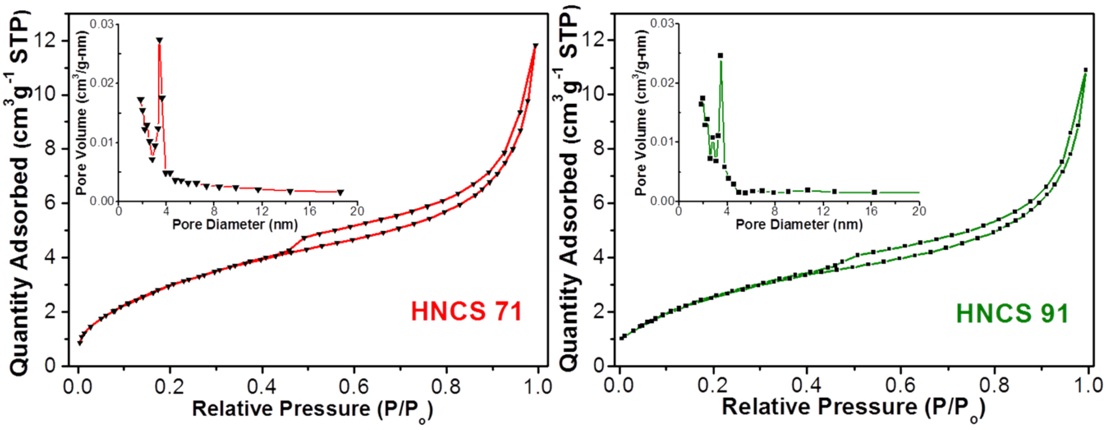

Fig. S6. BET surface area analysis of (**a**) HNCS71 (**b**) HNCS91 catalysts; insets show BJH pore-size distribution.

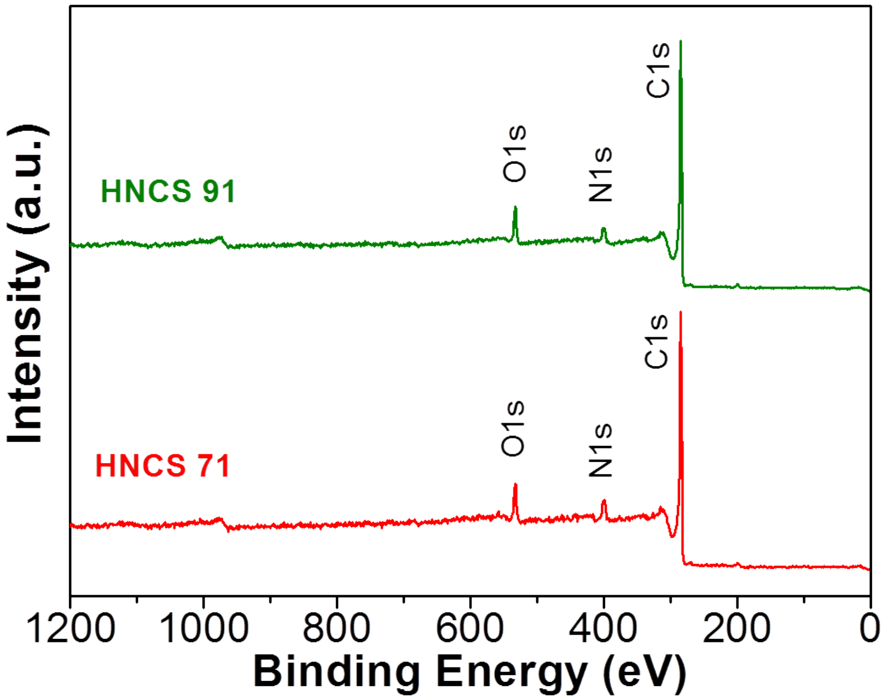

Fig. S7. XPS survey spectra of HNCSs

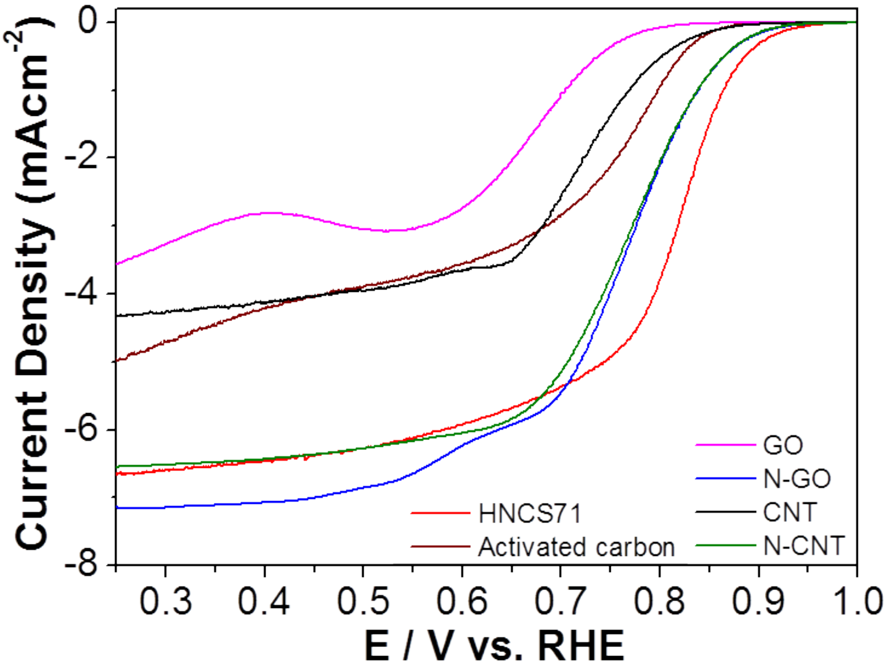

Fig. S8. RDE voltammograms of HNCS71, Activated carbon, GO, N-GO, CNT, and N-CNT catalysts obtained at 1600 rpm in O_2-saturated 0.1 M KOH

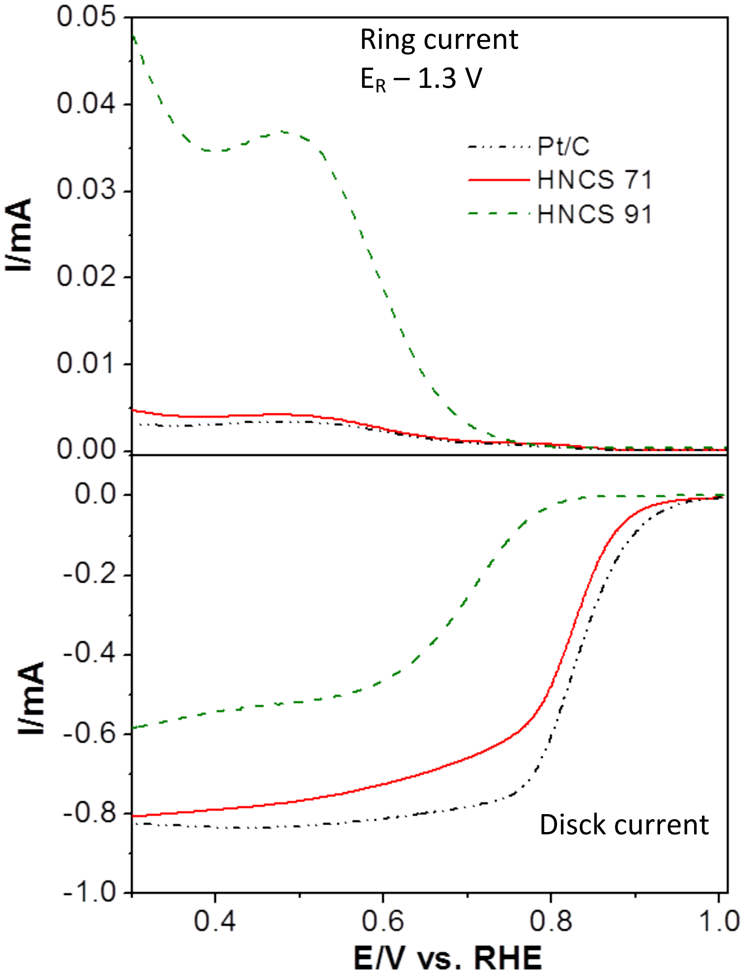

Fig. S9. RRDE response of HNCS71, HNCS91 and Pt/C catalysts obtained at 1600 rpm in O_2-saturated 0.1 M KOH. (HNCSs catalyst loading- 0.4 mg cm^{-2} ; Pt/C -30 µg cm^{-2})

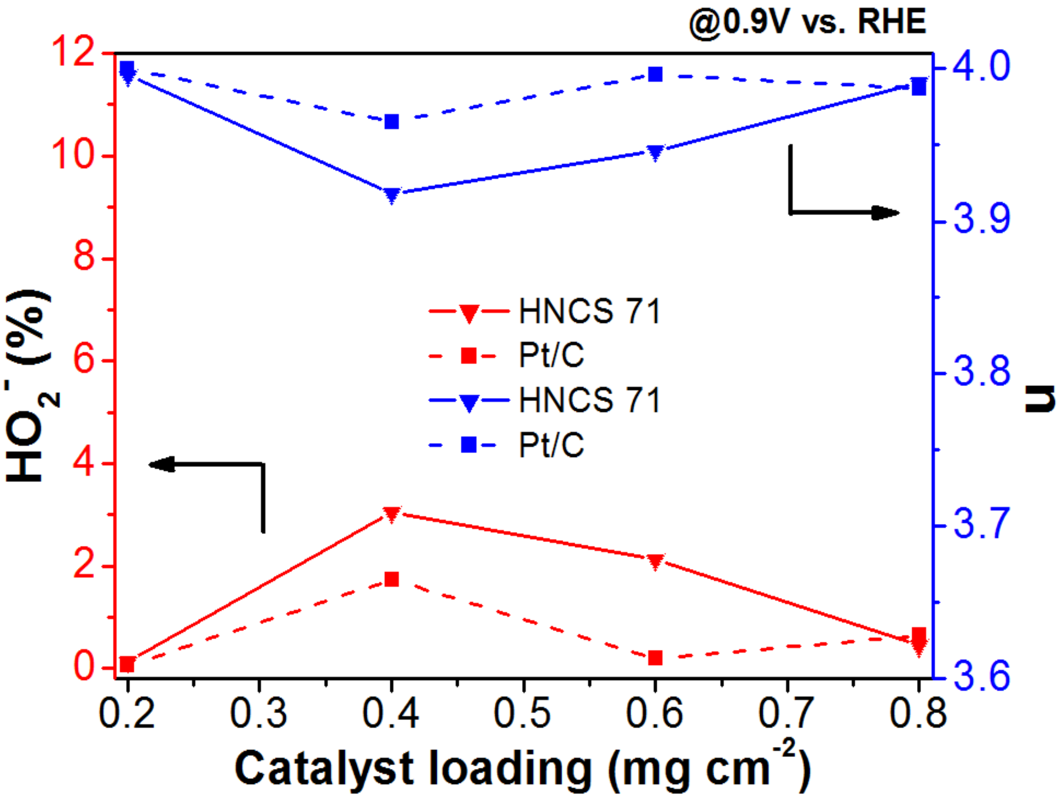

Fig. S10**.** The effect of catalyst loading on formation of peroxide and the electron transfer number of HNCS71 and Pt/C catalysts.

Table S1. The ORR data of the electrocatalysts derive from Fig. S8

Catalyst materials	Half-wave potential, $E_{1/2}$ (E/V vs. RHE)	Reference source
HNCS 71	0.820	**
Activated carbon	0.755	Sigma-Aldrich
Graphene Oxide (GO)	0.652	**
Carbon nanotube (CNT)	0.722	Sigma-Aldrich
N-GO	0.770	**
N-CNT	0.765	**

** Present study

Table S2. The physical and electrochemical properties of HNCS 71 and HNCS 91

Catalyst	**Surface area (m^2 g^{-1}) (a)**	**no. of Electron Transfer**	**Nitrogen distribution (%)**				**Total N Content (%) (b)**	**N/C ratio**
			N_1	**N_2**	**N_3**	**N_4**		
HNCS71	11.82	3.90	26.51	4.19	59.09	9.76	10.4	0.13
HNCS91	10.79	2.82	15.71	7.07	68.77	7.92	4.12	0.05
Pt/C (Johnson Mathew)	-	3.95	-	-	-	-	-	-

(a) Measured Brunauer-Emmett-Teller (BET)

(b) Measured by X-ray photoelectron spectroscopy (XPS)

Table S3. The CHN elemental analysis of HNCSs

Catalyst	**C**	**H**	**N**	**N/C ratio**
HNCS71	83.38	0.7	11.4	0.136
HNCS91	91.47	0.2	3.89	0.042