Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Transitional Metal (Fe, Co, Ni) Encapsulated in Nitrogen-Doped Carbon Nanotubes as Bifunctional Catalysts for Oxygen Electrode Reactions

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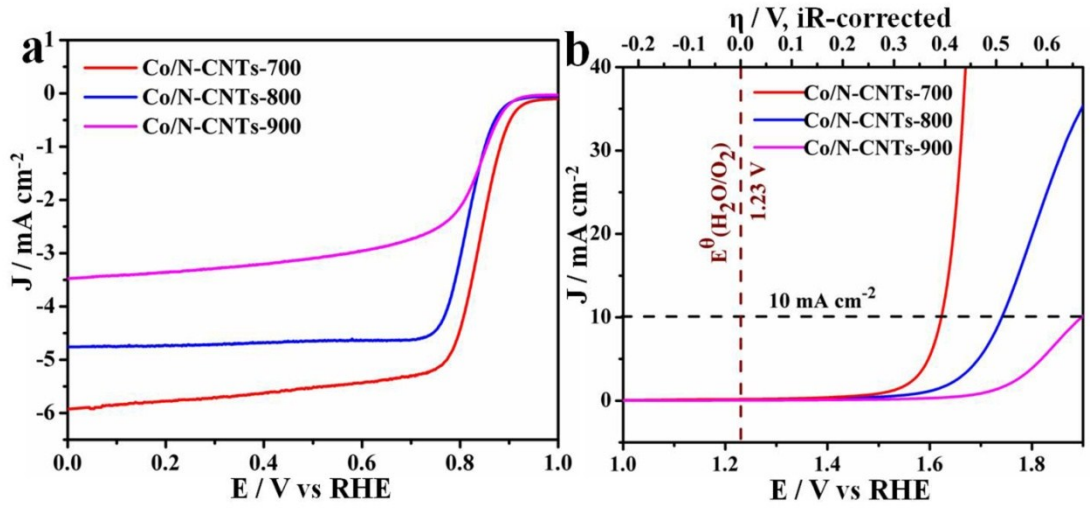

Fig. S1 Polarization curves of Co/N-CNTs catalysts in RDE tests (rotation rate:1500 rpm; pH 13; loading: 0.2 mg cm^{-2}).

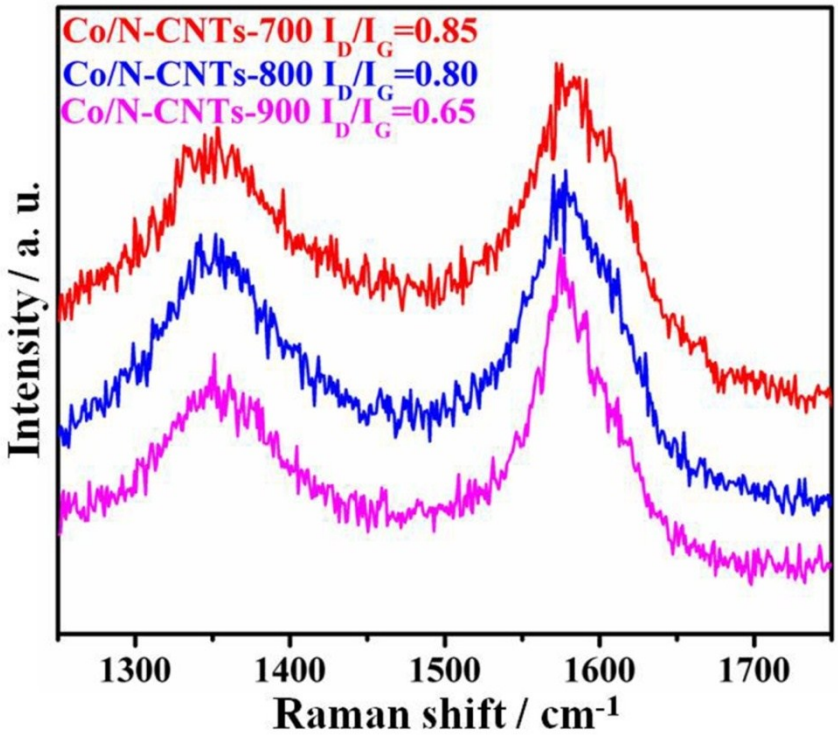

Fig. S2 Raman spectra for Co/N-CNTs samples carbonized under different temperatures.

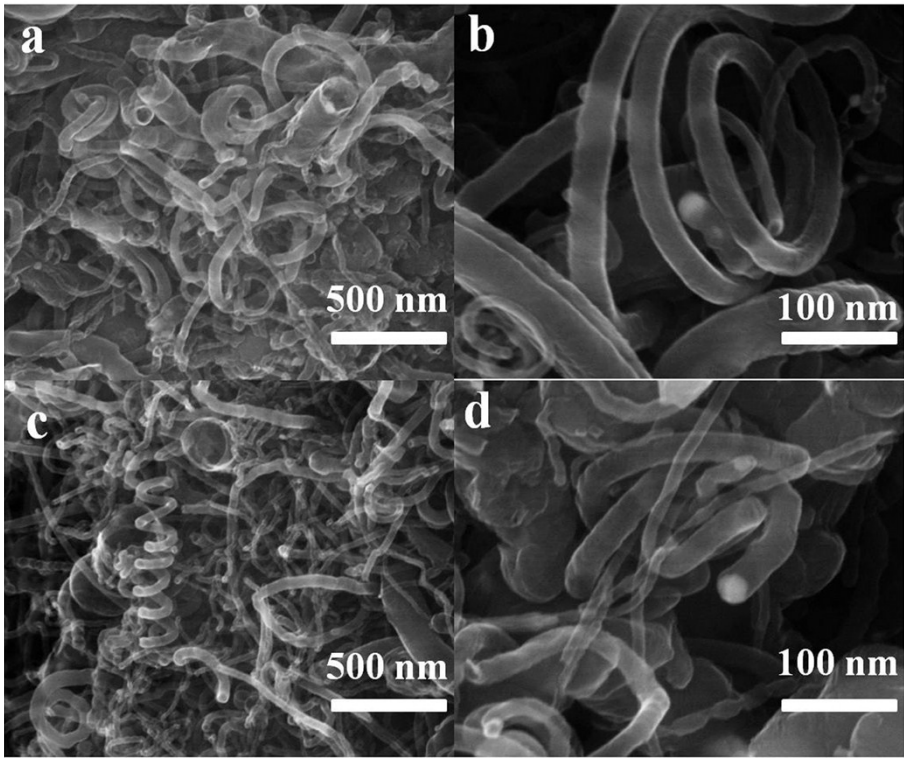

Fig. S3 SEM images of (a.b) Co/N-CNTs-800, (c.d) Co/N-CNTs-900.

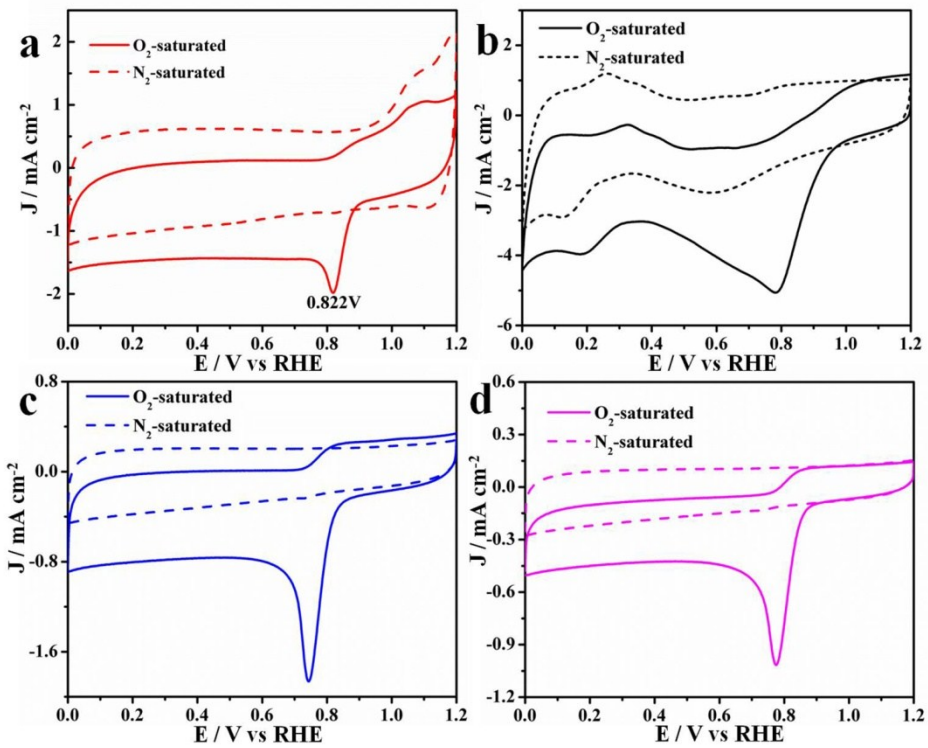

Fig. S4 Cyclic voltammograms of(a) Co/N-CNTs-700, (b) Pt/C, (c) Co/N-CNTs-800 and (d) Co/N-CNTs-900 at a scan rate of 50 mV s^{-1}.

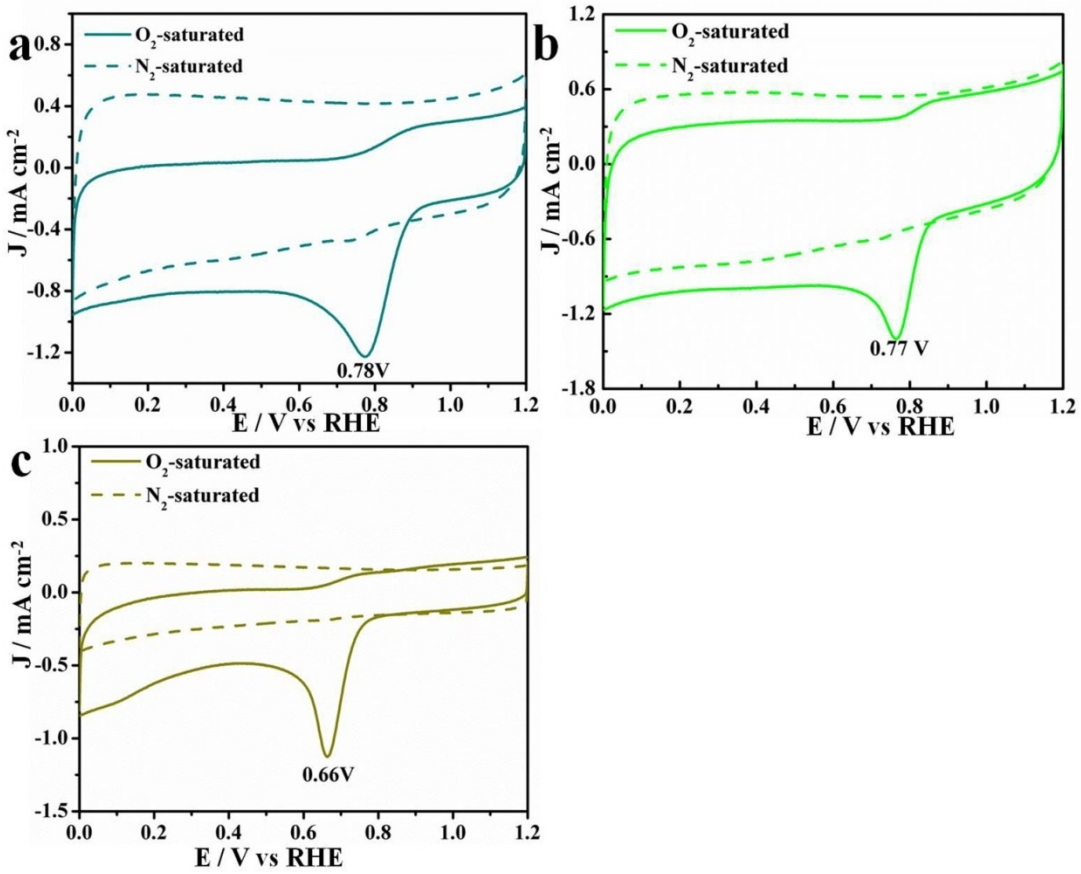

Fig. S5 Cyclic voltammograms of (a) Fe/N-CNTs, (b) Ni/N-CNTs and (c) MWCNTs at a scan rate of 50 mV s^{-1}.

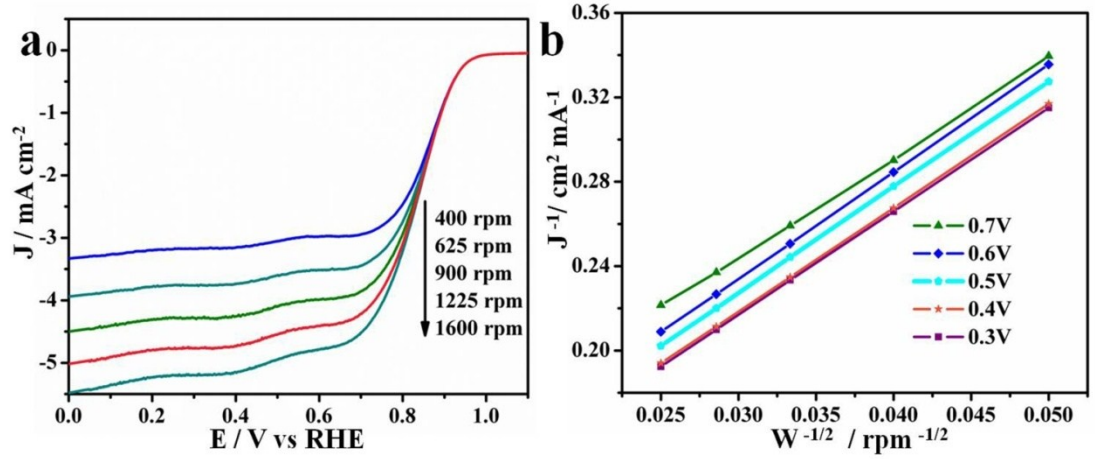

Fig. S6 (a) Linear sweep voltammograms and (b) K-L plots at different potentials for Fe/N-CNTs catalyst in O_2-saturated 0.1 M KOH solution.

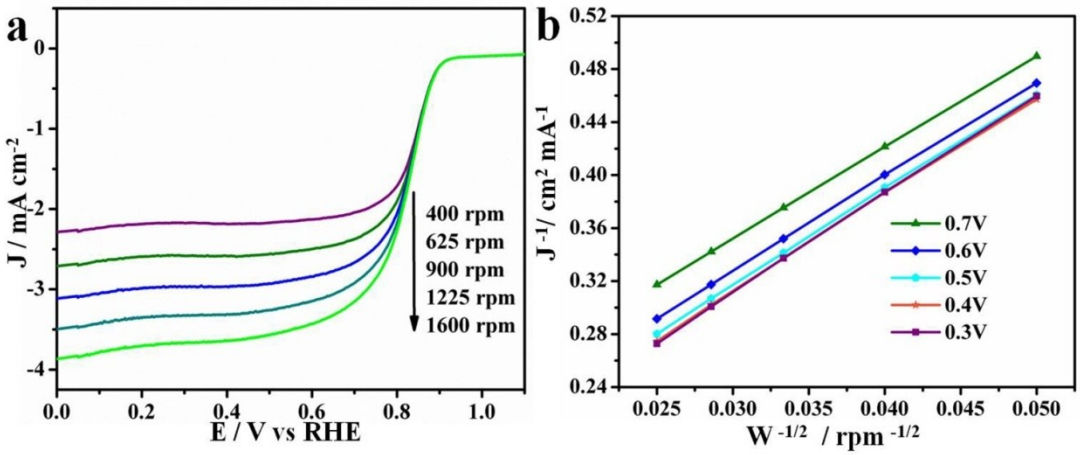

Fig. S7 (a) Linear sweep voltammograms and (b) K-L plots at different potentials for Ni/N-CNTs catalyst in O_2-saturated 0.1 M KOH solution.

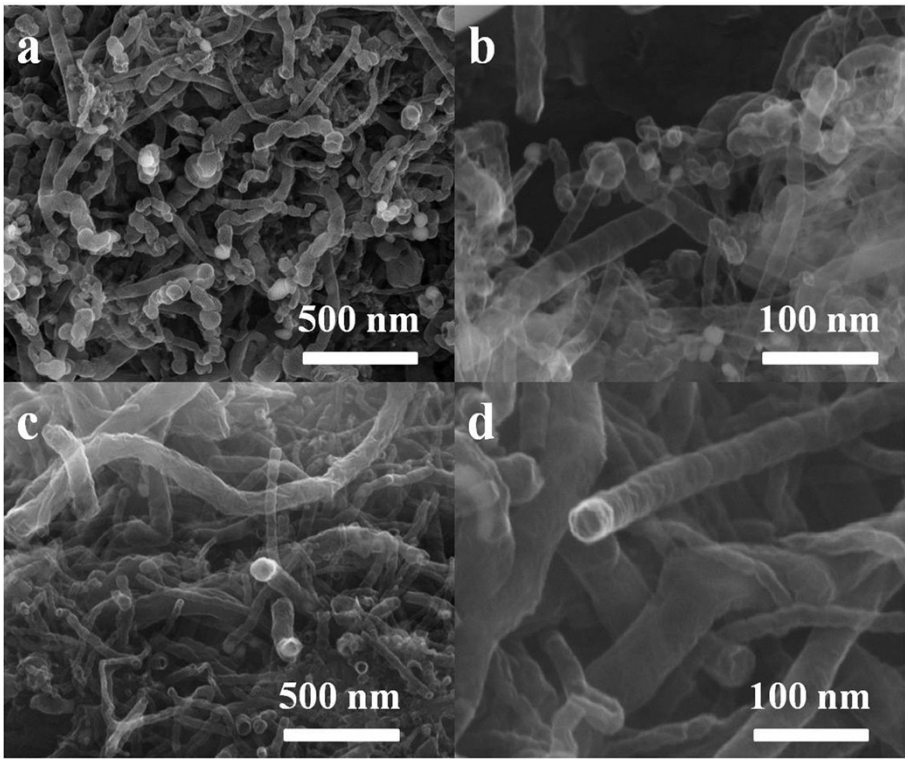

Fig. S8 SEM images of (a.b) Fe/N-CNTs, (c.d) Ni/N-CNTs.

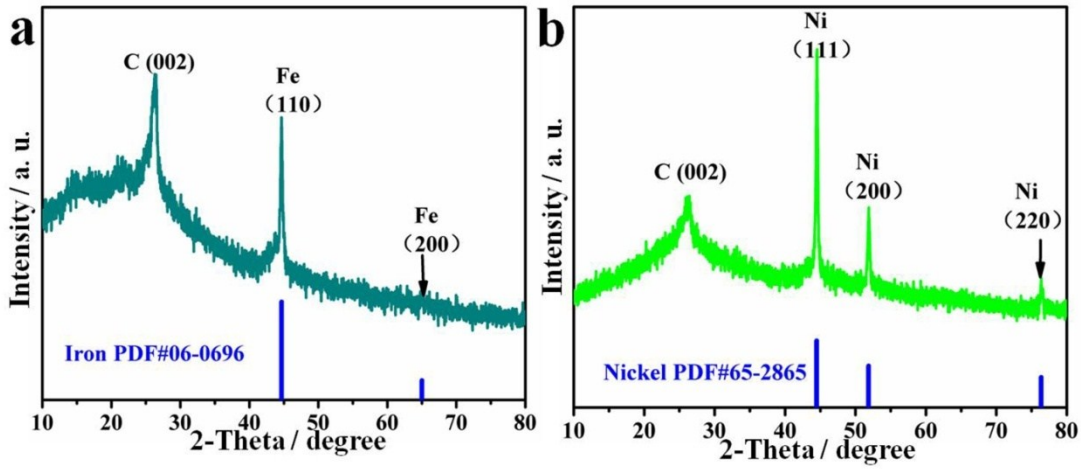

Fig. S9 (a) XRD pattern of Fe/N-CNTs and the JCPDS cards #06-0696 for the corresponding metallic iron. (b) XRD pattern of Ni/N-CNTs and the JCPDS cards #65-2865 for the corresponding metallic nickel.

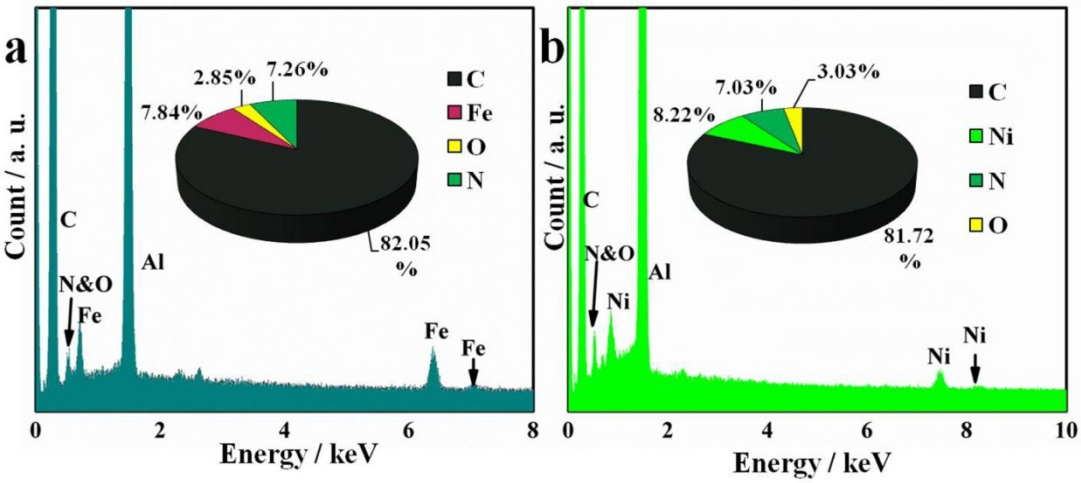

Fig. S10 EDX spectra and the content of C, N, Metal and O in (a) Fe/N-CNTs and (b) Ni/N-CNTs, the signal of Al is from the Al substrates.

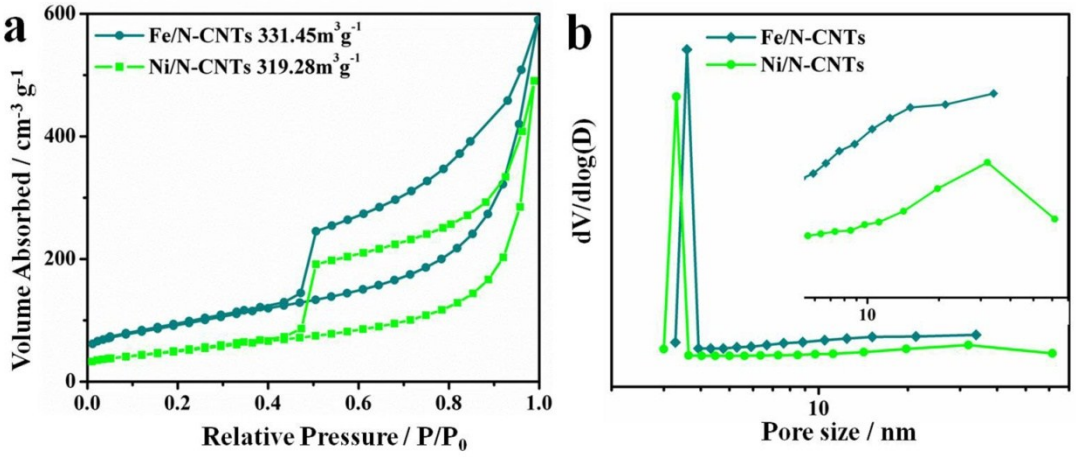

Fig. S11 (a) N_2 adsorption/desorption isotherm and (b) the corresponding pore size distribution of the Fe/N-CNTs and Ni/N-CNTs.

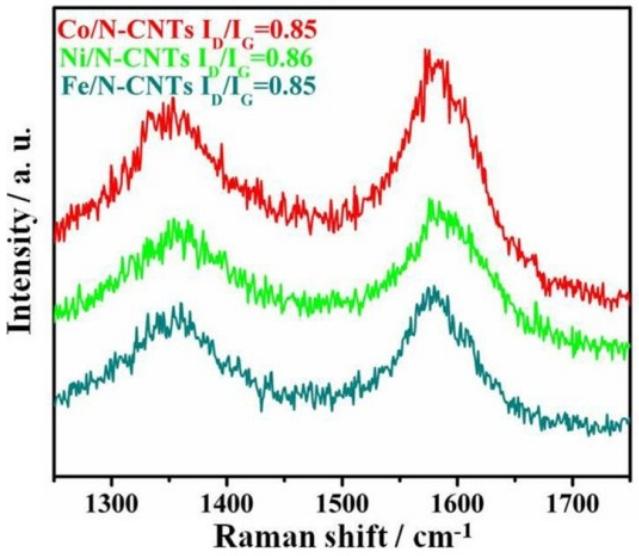

Fig. S12 Raman spectra for Co/N-CNTs, Ni/N-CNTs and Fe/N-CNTs samples.

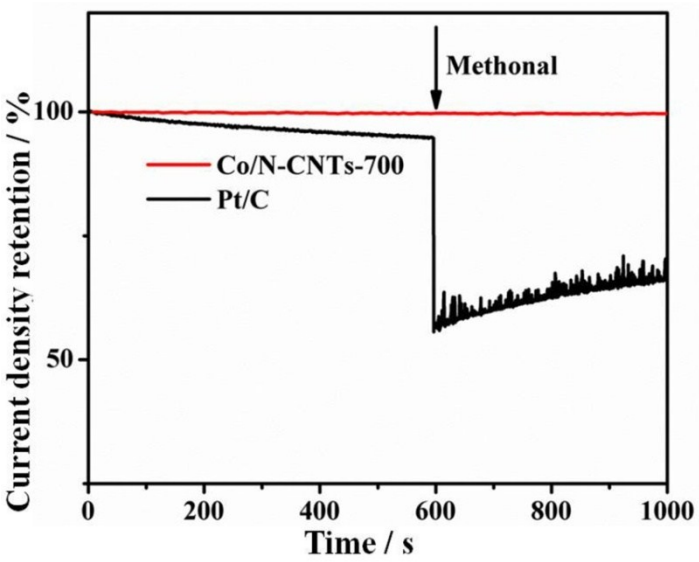

Fig. S13 I-t plots of Co/N-CNTs and Pt/C at 0.55 V (vs. RHE) with a rotation rate of 900 rpm in O_2-saturated 0.1 M KOH with the adding of methanol (1.0 M).

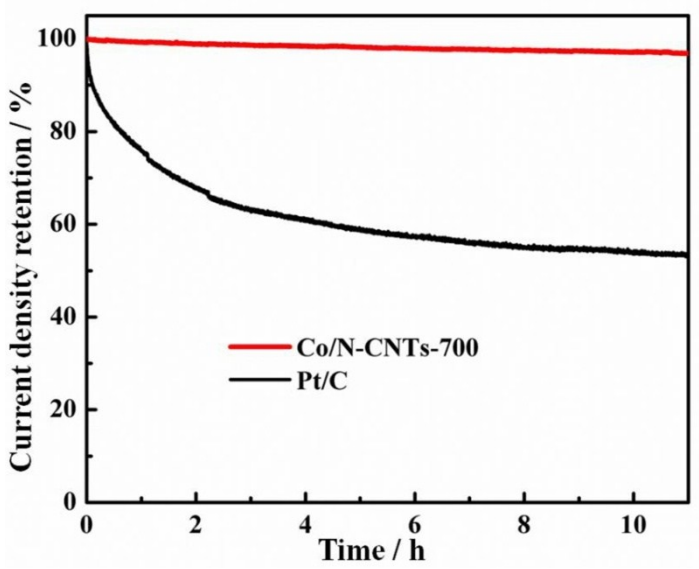

Fig. S14 I-t plots of Co/N-CNTs and Pt/C at 0.6 V.

Table S1 Elemental composition by XPS (at%)

Sample	C 1s	N 1s	O 1s	M 2p (M = Fe,Co,Ni)
Co/N-CNTs	87.78	8.36	2.21	1.63
Fe/N-CNTs	87.69	8.42	2.32	1.57
Ni/N-CNTs	87.52	8.49	2.26	1.73

Table S2. Comparison of bifunctional oxygen electrode activities of Co/N-CNTs-700 *vis-à-vis* some representative bifunctional oxygen catalysts recently reported. [a]

Catalysts	E_{ORR} (V) at J = -3 mA cm^{-2}	E_{OER} (V) at J = 10 mA cm^{-2}	Oxygen electrode ΔE (V) = E_{OER} --E_{ORR}	Refs.
$NiCo_2S_4$@N/S-rGO	0.76	1.70	0.94	S1
$NiCo_2O_4$	0.75	1.72	0.97	S2
20 wt% Ir/C	0.69	1.61	0.92	S3
$NiCo_2O_4$-A_1	0.78	1.62	0.84	19
N-graphene/CNT	0.69	1.65	0.96	27
Co/N-C-800	0.74	1.60	0.86	S4
Pt/C BSCF/C=4:1	0.81	1.61	0.80	S5
Fe_3C@NG800-0.2	0.81	1.59	0.78	13
$Ni_{0.4}Co_{2.56}O_4$	0.79	1.75	0.96	S6
CoS_2(400)/N,S-GO	0.79	1.61	0.82	S7
Co/N-CNTs-700	0.84	1.62	0.78	This work

[a]Here all the potential values were converted to vs. RHE for comparison.

References:

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