2D Layered Non-precious Metal Mesoporous Electrocatalysts for Enhanced Oxygen Reduction Reaction

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Table S1. N_2 adsorption/desorption data of meso-M–N–C/N–G nanocomposites.

Nanocomposites	S_{BET} ($m^2 \cdot g^{-1}$)	V_p[a] ($cm^3 \cdot g^{-1}$)	D_p[b] (nm)
Meso-Fe–N–C/N–G	776	1.31	3.9/6.4
Meso-Co–N–C/N–G	468	0.83	3.6
Meso-Ni–N–C/N–G	436	0.81	3.6

[a] BJH desorption cumulative volume of pores between 1.70 nm and 300.0 nm diameter.

[b] Calculated by the BJH method from the desorption isotherm linear plot.

Table S2. Summary of N and Fe contents in N–G, meso-Fe–N–C, and meso-Fe–N–C/N–G nanocomposites obtained by calcining at 700, 800, 900, and 1000 ºC.

N and Fe contents (at.%)	N–G	Meso-Fe–N–C	Meso-Fe–N–C/N–G (700 ºC)	Meso-Fe–N–C/N–G (800 ºC)	Meso-Fe–N–C/N–G (900 ºC)	Meso-Fe–N–C/N–G (1000 ºC)
Ammonia N	0.29	—	—	—	—	—
Pyridinic N	2.60	1.52	1.61	1.08	0.74	0.68
Pyrrolic N	0.56	0.29	0.80	0.65	0.22	0.27
Graphitic N	0.60	1.32	1.75	1.32	1.50	1.34
Quaternary N^+–O^-	—	—	0.46	0.30	0.09	0.07
Total N	4.05	3.13	4.62	3.35	2.55	2.36
Fe	—	0.10	0.22	0.14	0.12	0.09

Table S3. Summary of Fe and N contents in meso-Co–N–C, meso-Ni–N–C/N–G, and meso-Fe–N–C/N–G nanocomposites synthesized with different Fe/N molar ratios.

N and Fe contents (at.%)	Meso-Co–N–C/N–G	Meso-Co–N–C/N–G	Meso-Fe–N–C/N–G Fe/N = 3:1	Meso-Fe–N–C/N–G Fe/N = 2:1	Meso-Fe–N–C/N–G Fe/N = 1:2
Pyridinic N	1.08	1.53	0.54	0.45	0.62
Pyrrolic N	0.51	0.47	0.20	0.47	0.53
Graphitic N	1.37	2.04	0.86	0.88	1.53
Quaternary N+–O-	0.21	0.49	0.16	0.27	0.24
Total N	3.17	4.53	1.76	2.07	2.92
Fe	—	—	4.15	1.12	0.04

Table S4. Summary of the ORR catalytic activity of meso-Fe–N–C/N–G nanocomposites and relevant leading transition metal/carbon-based ORR catalysts reported in recent literatures measured in 0.1 M KOH with the electrode rotating speed at 1600 rpm.

Catalysts	Onset potential (V. vs RHE)	Half-wave potential (V. vs RHE)	Diffusion-limiting current at 0.5 V ($mA\cdot cm^{-2}$)	Electron transfer number	Durability/Remarks	Reference
Meso-Fe–N–C/N–G	1.03	0.89	5.41	3.99-4.13	95.3% retention of j under 0.5 V for 2.8 h	This work
Meso-Co–N–C/N–-G	0.97	0.84	5.11	4.02-4.19	No available	This work
Fe-N/MC	0.99	0.86	4.80	3.7-3.8	90% retention of j under 0.7 V for 2.8 h	1
FePhen@MOF-ArNH3	1.02	0.86	5.2	-	9mV penalty of E1/2 after 1000 cycles	2
Fe@C-FeNC	1.03	0.899	5.3	4.0	No available	3
Fe-NG	1.025	0.837	6.5	3.8-4.0	90% retention of j under 0.7 V for 8.3 h	4
S–Fe/N/C	0.911	0.799	4.7	3.95	98.3% retention of j under 0.8V for 5.5 h	5
Fe/N/G	1.04	0.86	5.1	3.89-4.0	No available	6
Fe-N/C-900	1.02	0.85	5.43	4.02	95.3% retention of j under 0.5 V for 2.8 h	7
Fe-NMCSs	1.027	0.86	5.3	4.05	95.3% retention of j under 0.55 V for 6.9 h	8
Fe-N-C(f)	0.97	0.85	5.6	3.5-4.0	No available	9
Fe3C/Fe-N-C	0.98	0.82	5.0	-	No available	10
Fe/Fe3C/N/C	0.98	0.87	6.03	3.7-3.85	62% retention of j under 0.81 V for 5.6 h	11
Fe/Nx/C	1.05	0.87	6.15	3.9	No available	12
Fe/N/C	1.03	0.82	8.11	3.97	79% retention of j under 0.84 V for 11 h	13
Fe/N/C	092	0.81	4.68	3.96	30.4 mV penalty of E1/2 after 10000 cycles	14
Fe/Fe2.5C/N/C	0.90	0.72	4.92	3.85	42 mV penalty of E1/2 after 5000 cycles	15
Fe3C/N/CNT	0.96	0.83	5.21	3.92	Negligible degradation of Eonset and jL after 3000 cycles	16

FexC/NGR	0.98	0.86	3.74	3.87	30 mV penalty of E1/2 after2000 cycles	17
Fe-N/C	0.98	0.84	4.81	3.97	93.3% retention of j under 0.70 V for 2.8 h	18
N–Fe-co-doped carbonblack	0.94	0.82	5.12	3.9	12 mV penalty of E1/2 after 30 000 cycles	19
PDMC-800	0.94	0.78	3.5	3.78	No available	20
Fe3C/C-800	1.05	0.83	3.8	unknown	20 mV penalty of E1/2 after 4500 cycles	21
(Fe,Co)@NGC	0.91	0.85	5.6	3.8	91 % retention of j for under 0.50 V for5.6 h	22
CNTs@Fe–N–C	0.98	0.85	5.35	3.95-4	18 mV penalty of E1/2 after 1000 cycles	23
Fe–N–C	0.99	0.86	6.8	3.96	4 mV penalty of E1/2 after 5000 cycles	24
Fe–N–C/Vu	0.93	0.78	5.70	3.9	2.5% penalty of Jlim after 5000 cycles at 0.75V	25
Fe–N–C/KB	0.92	0.78	5.54	3.8	17.9% penalty of Jlim after 5000 cycles at 0.75V	25
PANI-4.5Fe-HT2(SBA–15)	0.95	0.84	4.5	3.4-4.0	2 % retention of j under 0.57 V for 5.0 h	26
Fe–N/C	0.91	0.81	4.3	3.7–3.9	4 % retention of j under 0.7V for 2.8 h	27
Co/N/C	0.90	0.77	4.5	3.95	9 mV penalty of E1/2 after10 000 cycles	28
Co/N/C	0.84	0.65		3.8	90% retention of j for 2.8 h	29
Co/N/rGO	0.83	0.75	3.16	3.97	80% retention of j under0.66 V for 6 h	30
GNC-Co	55 mV negative to Pt/C	15 mV negative to Pt/C	4.0	3.78	11 mV penalty of E1/2 after 2 000 cycles	20
CoO@Co/N–C	0.94	0.82	5.7	4	No available	31
Co–N–C	0.95	0.81	6.6	3.91	No available	24

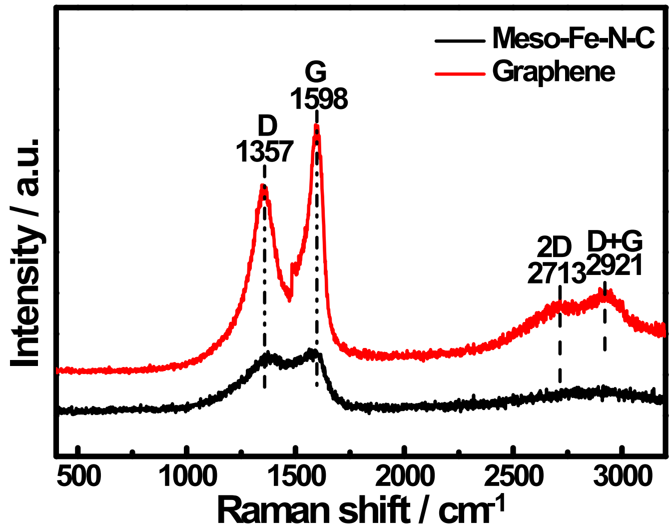

Figure S1. Raman spectra of graphene and meso-Fe–N–C nanocomposites.

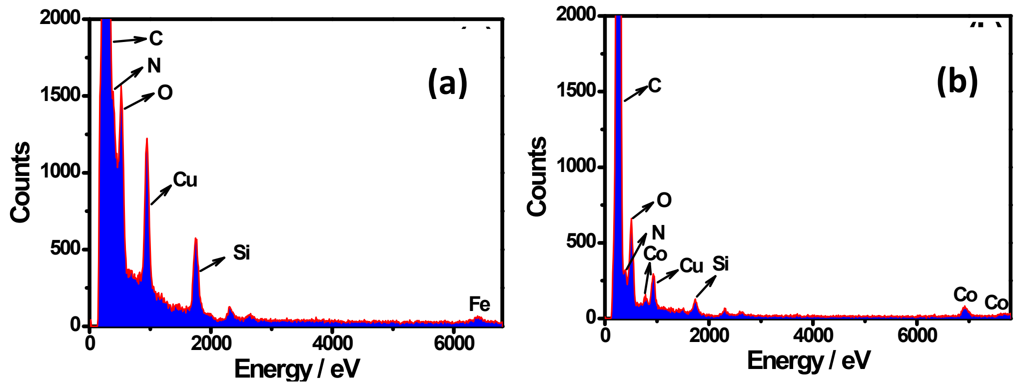

Figure S2. EDX spectra of (a) meso-Fe–N–C/N–G and (b) meso-Co–N–C/N–G.

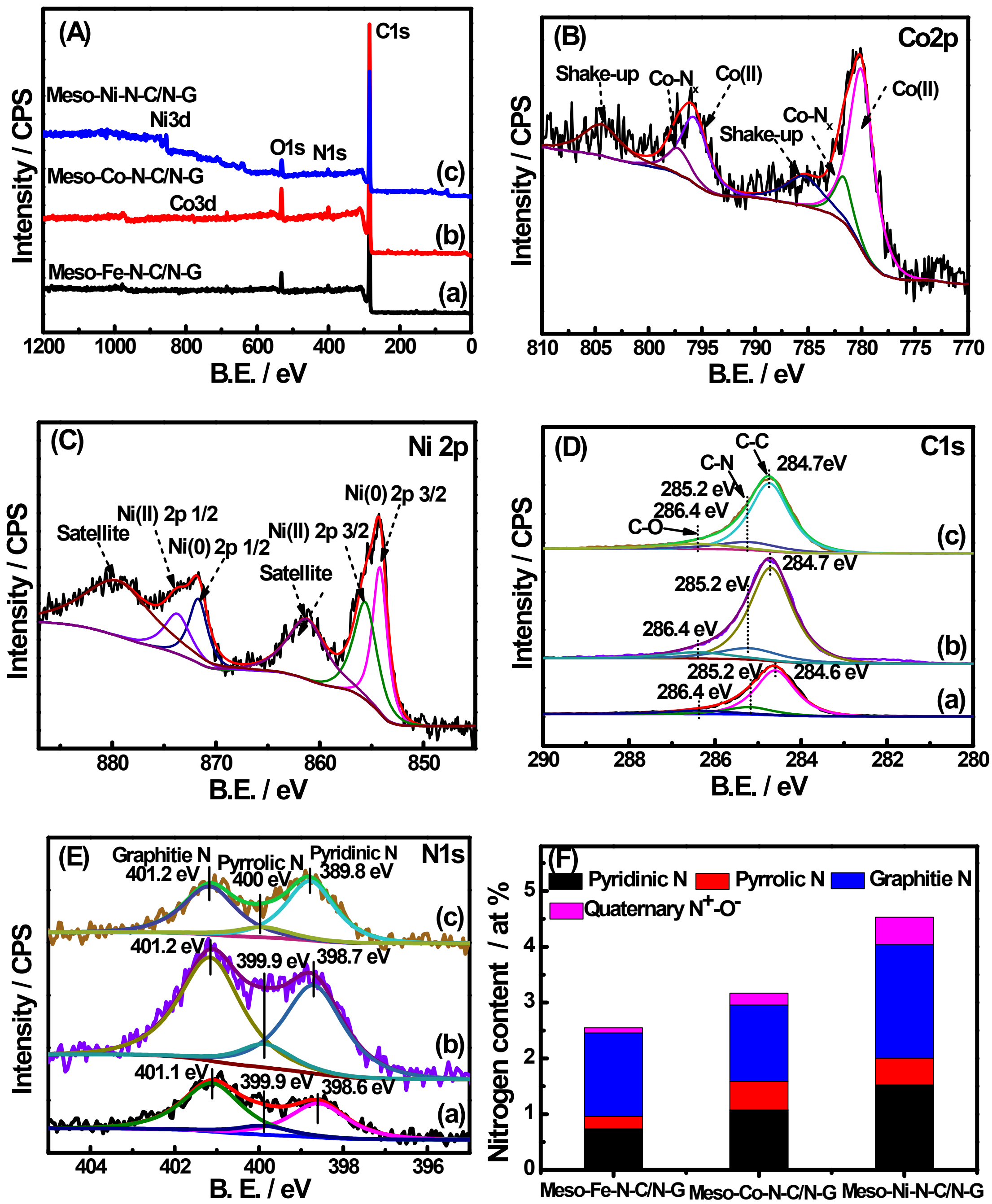

Figure S3. (A) XPS survey of meso-Fe–N–C/N–G, meso-Co–N–C/N–G and meso-Ni–N–C/N–G. High-resolution XPS spectra of (B) Co2p for meso-Co–N–C/N–G and (C) Ni2p for meso-Ni–N–C/N–G nanocomposites. High-resolution XPS spectra of (D) C1s and (E) N1s for (a) meso-Fe–N–C/N–G, (b) meso-Co–N–C/N–G, and (c) meso-Ni–N–C/N–G. (F) Concentration of N dopants in (a) meso-Fe–N–C/N–G, (b) meso-Co–N–C/N–G, and (c) meso-Ni–N–C/N–G nanocomposites.

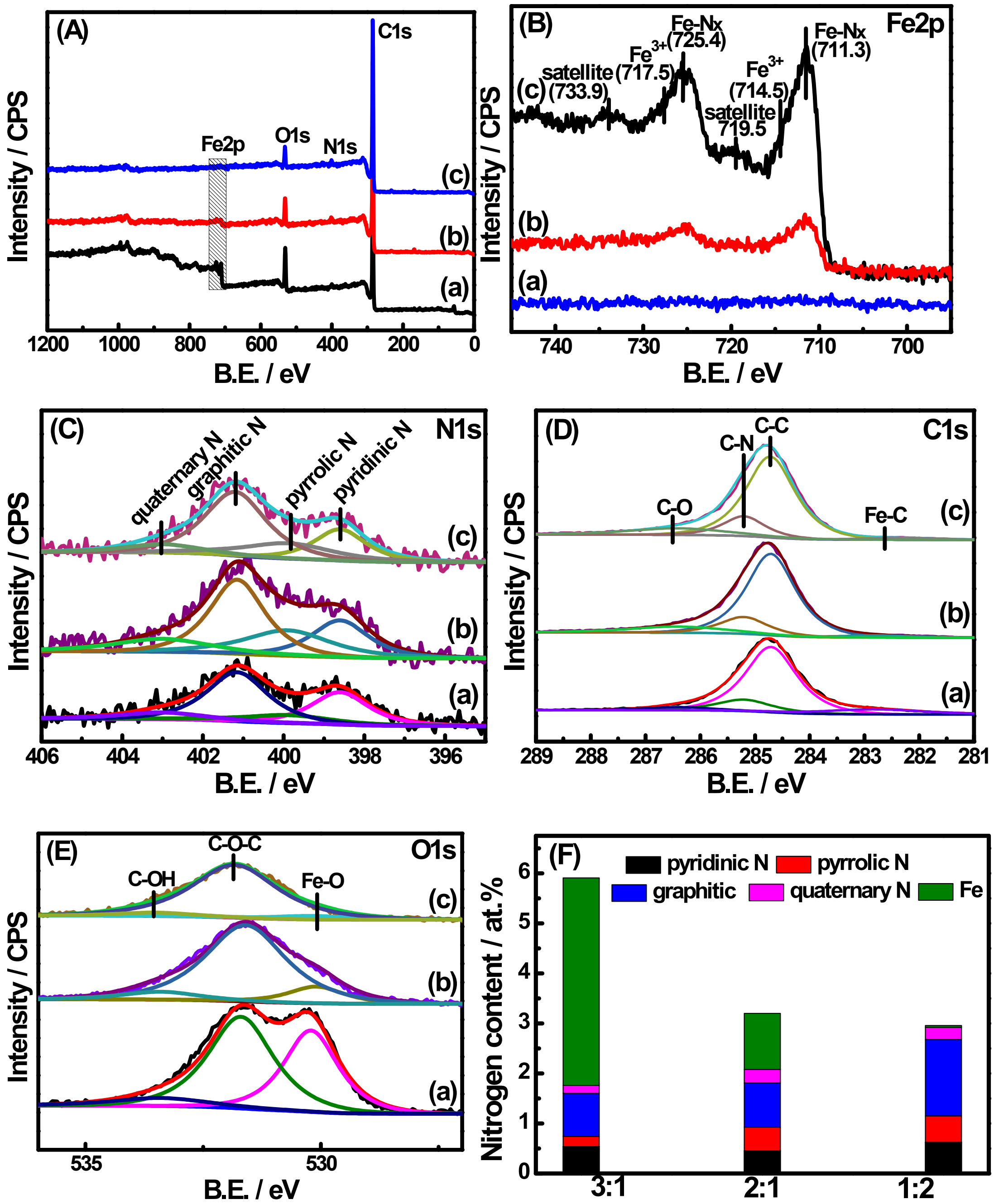

Figure S4. (A) XPS survey and high-resolution spectra of (B) Fe2p, (C) N1s, (D) C1s, and (E) O1s of (a) meso-Fe–N–C/N–G (Fe/N = 3:1), (b) meso-Fe–N–C/N–G (Fe/N = 2:1), and (c) meso-Fe–N–C/N–G (Fe/N = 1:2). (F) Concentration of N dopants in (a) meso-Fe–N–C/N–G (Fe/N = 3:1), (b) meso-Fe–N–C/N–G (Fe/N = 2:1), and (c) meso-Fe–N–C/N–G (Fe/N = 1:2).

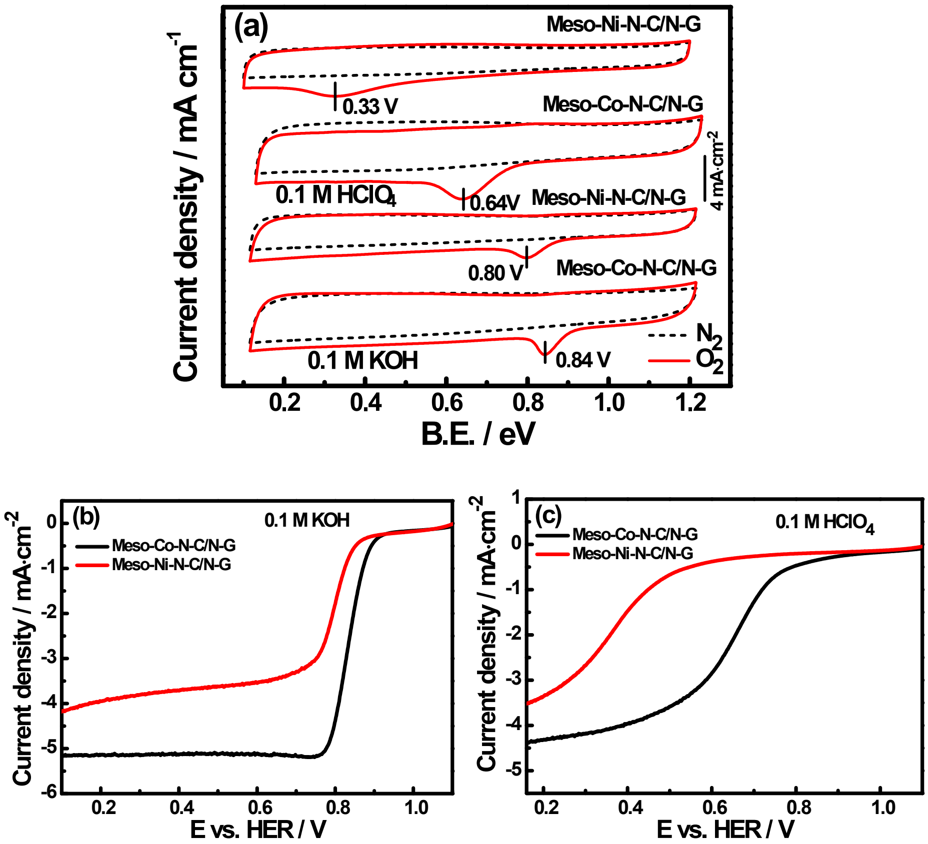

Figure S5. (a) Cyclic voltammograms of meso-Co–N–C/N–G and meso-Ni–N–C/N–G nanocomposites in N_2- and O_2-saturated 0.1 M KOH and 0.1 $HClO_4$ media at a scan rate of 50 mV·s^{-1}. (b) LSV curves of meso-Co–N–C/N–G and meso-Ni–N–C/N–G at a rotation rate of 1600 rpm in O_2-saturated 0.1 M KOH medium at a scan speed of 10 mV/s. (c) LSV curves of meso-Co–N–C/N–G and meso-Ni–N–C/N–G nanocomposites at a rotation rate of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ medium at a scan speed of 10 mV/s.

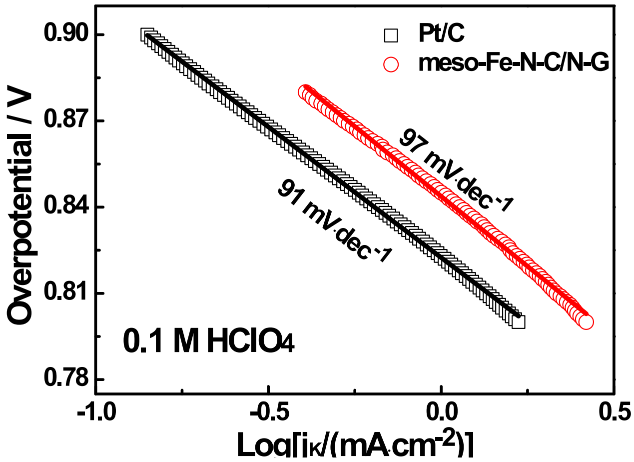

Figure S6. Tafel plots of Pt/C and Meso-Fe-N-C/N-C catalysts in O_2 saturated 0.1 M $HClO_4$ solution.

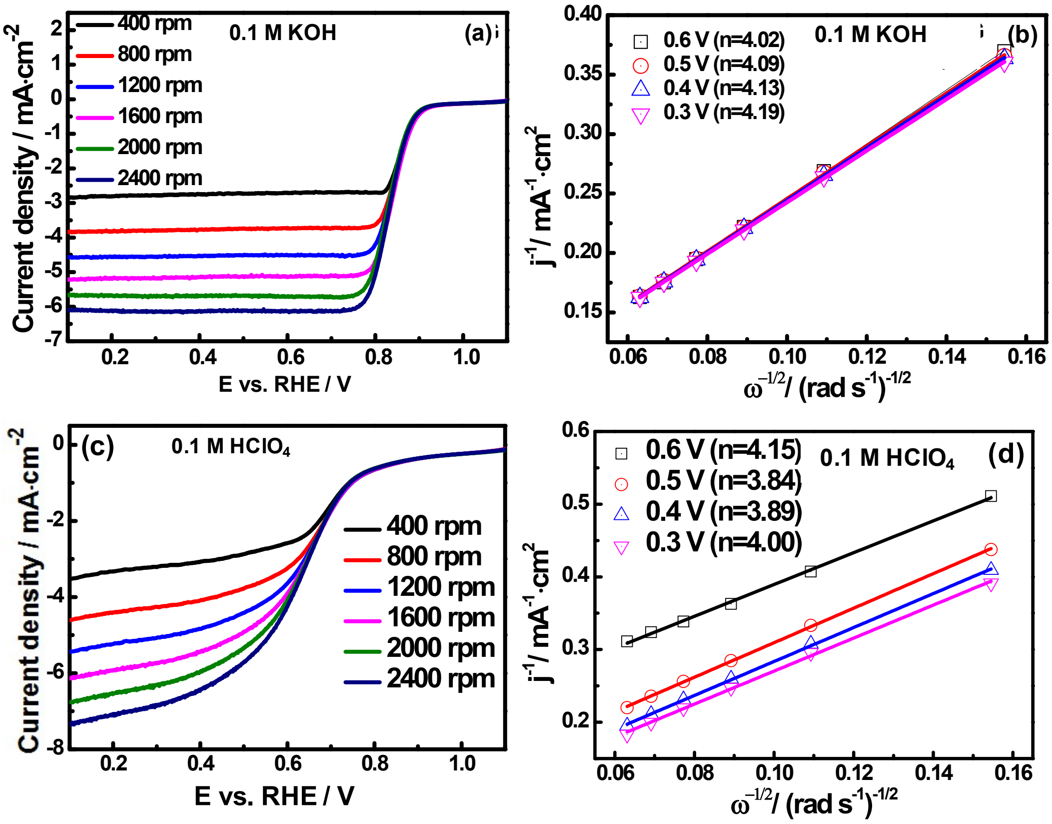

Figure S7. (a and c) LSV curves of meso-Co–N–C/N–G nanocomposites at the rotation rates of 400 to 2400 rpm in 0.1 M KOH and 0.1 M $HClO_4$ media. (b and d) The corresponding K–L plots at different potentials in 0.1 M KOH and 0.1 M $HClO_4$ media.

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