Electronic Supplementary Information

Cobalt Hydroxide Nanosheet-Mediated Synthesis of Core-Shell Type $Mn_{0.005}Co_{2.995}O_4$ Spinel Nanocubes for Efficient Oxygen Electrocatalyst

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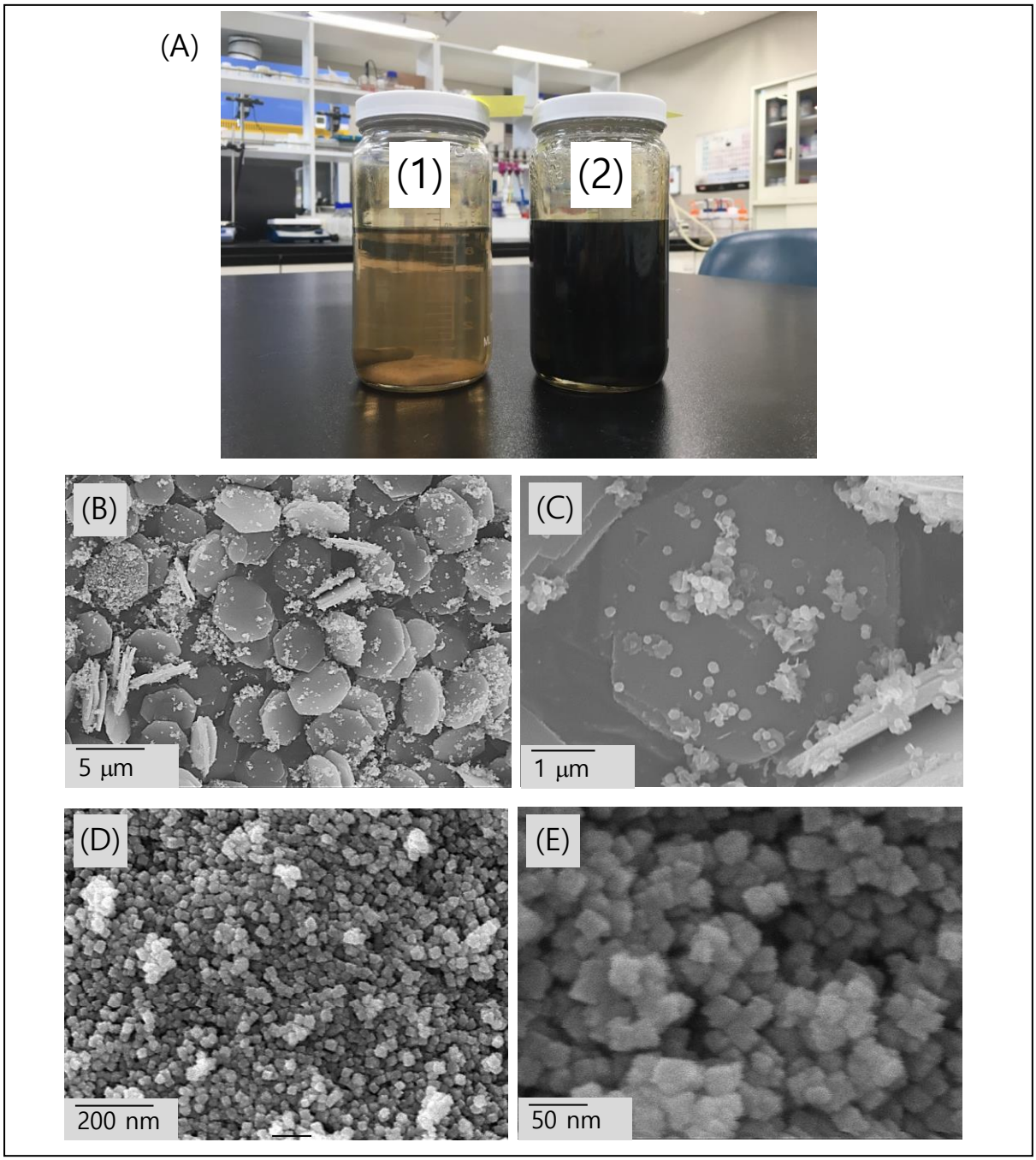

Figure S1. Photo of reaction products (A) synthesized at 90 °C in the absence (solution 1) and in the presence (solution 2) of exfoliated $Co(OH)_2$ nanosheet. Typical SEM images of solid products corresponding to the solution 1 (B and C) and to solution 2 (D and E). Initial composition of metal cations is Mn=0.005 and Co=2.995.

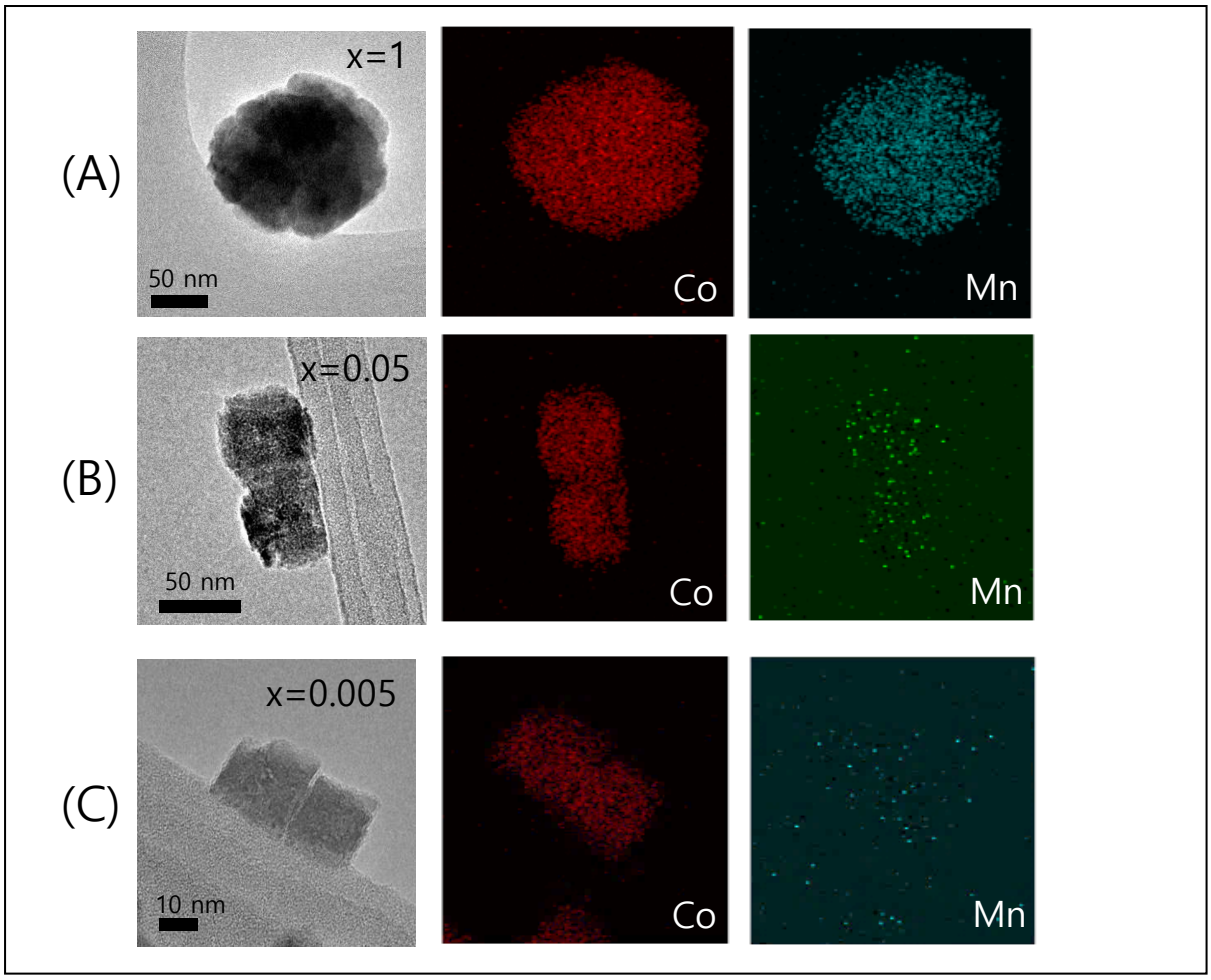

Figure S2. Elemental maps of Co and Mn with x=1.0 (A), x=0.05, and x=0.005, respectively.

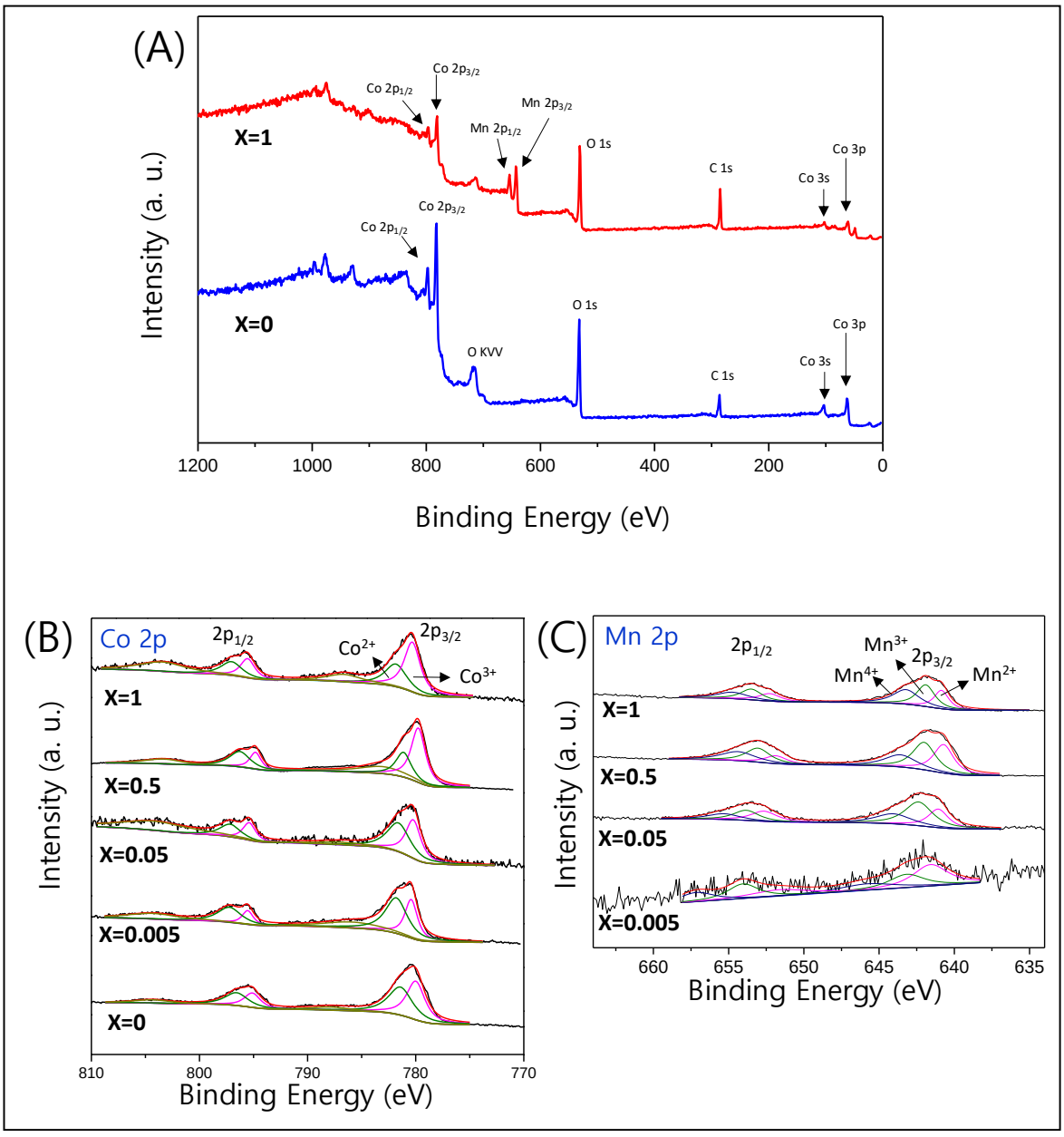

Figure S3. Wide XPS spectra (A), and high resolution XPS spectra of Co 2p (B) and Mn 2p (C) for $Mn_xCo_{3-x}O_4$ nanocubes with various x values.

Table S1. Relative atomic ratio of Mn and Co in $Mn_xCo_{3-x}O_4$ nanocubes with various x values.

x ($Mn_xCo_{3-x}O_4$ nanocube)			
Expected	ICP-AES (bulk)	XPS (surface)	surface/bulk
1.0	0.9	1.4	1.5
0.5	0.45	0.72	1.6
0.05	0.06	0.15	2.5
0.005	0.008	0.014	1.75
0	Not detected	Not detected	Not detected

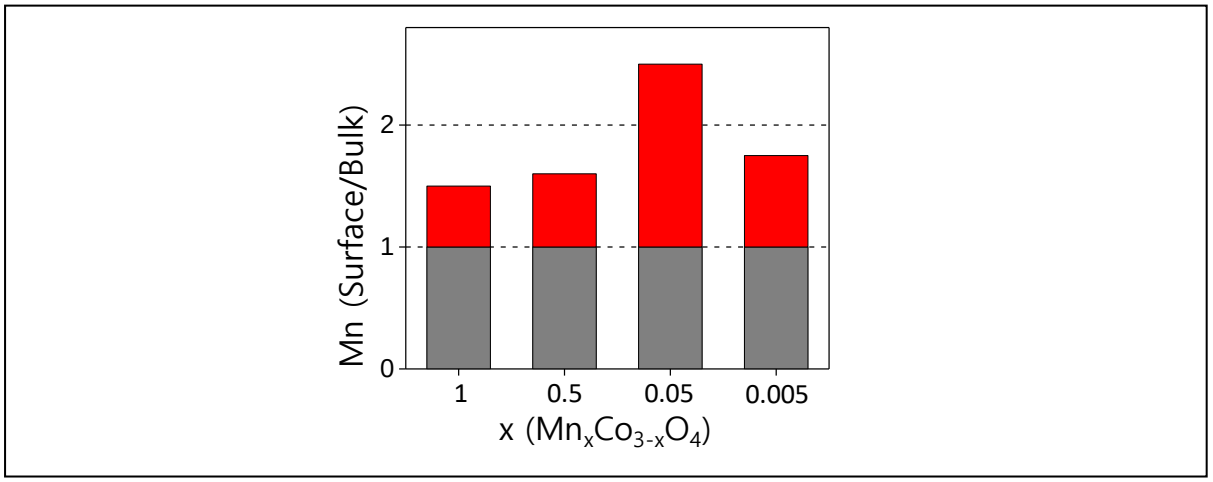

Figure S4. Surface to bulk ratios of Mn atom with various x values. The bulk values were measured by ICP-AES and the surface values were obtained by XPS, respectively.

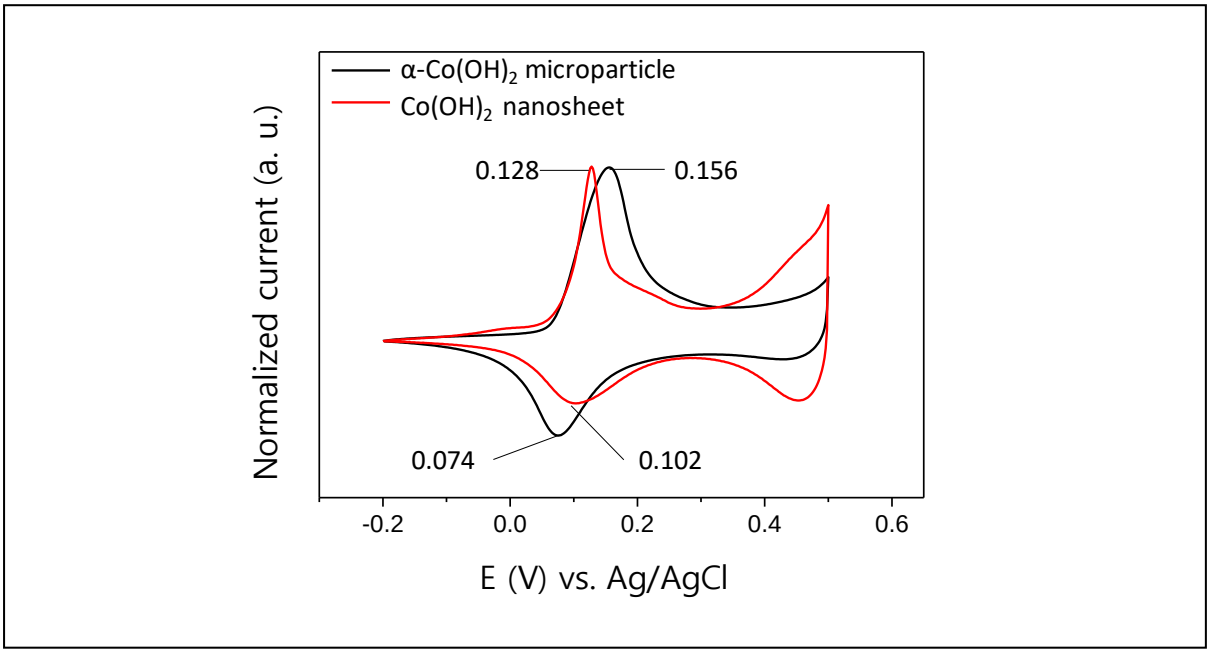

Figure S5. CV curves of GC electrodes modified with α-$Co(OH)_2$ microparticles (black line) and $Co(OH)_2$ nanosheet (red line).

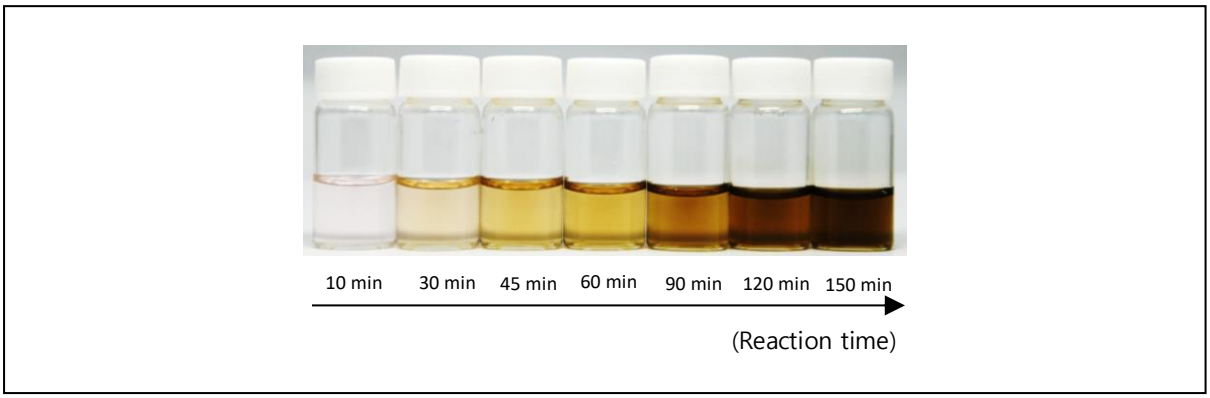

Figure S6. Solution color is dramatically changed as a reaction of time function. Asterisk in (A) indicates the peak for Co^{2+}(aq).

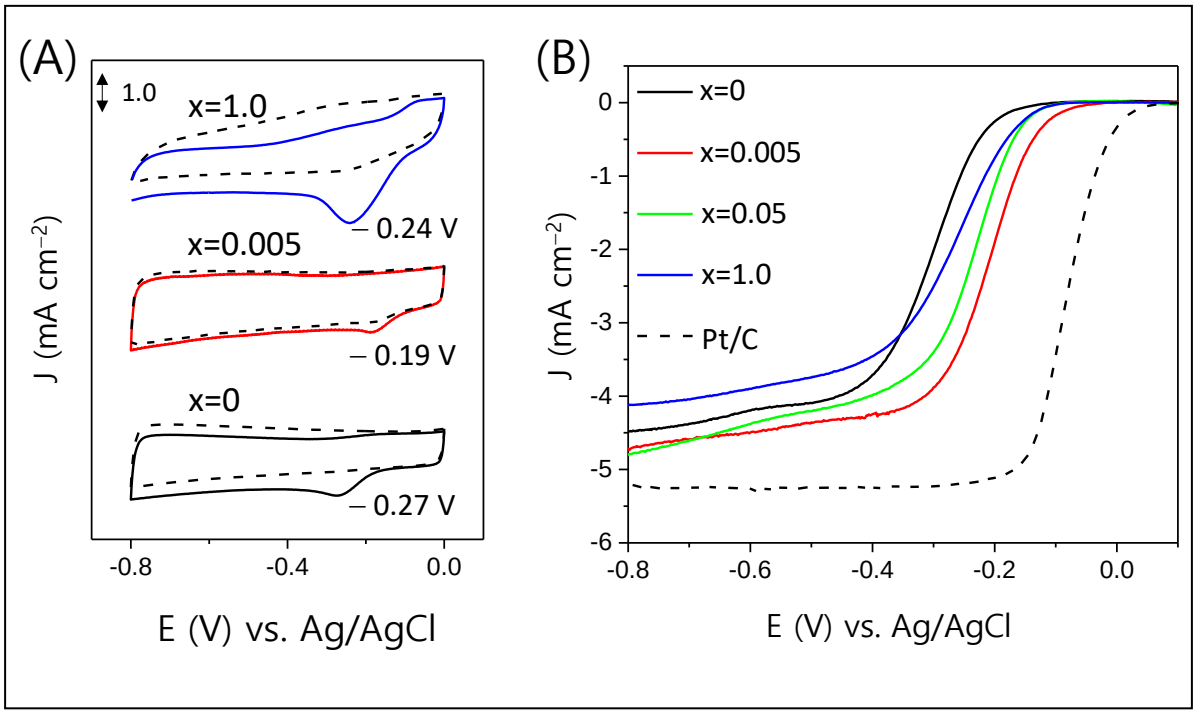

Figure S7. CV curves (A) and full ORR polarization curves (B) for GC electrode modified with spinel $Mn_xCo_{3-x}O_4$ nanocube on carbon black. Scan rate: 50 mVs^{-1} (A); 10 mVs^{-1} (B). CVs were performed in N_2-saturated (dashed line) and O_2-saturated (solid line) KOH (0.1 M) solution. ORR curves were performed in O_2-saturated KOH (0.1 M) solution at 1600 rpm.

Table S2. Summary of ORR activities of $Mn_xCo_{3-x}O_4$ nanocubes.

Catalysts	E_{onset} (V)	$E_{1/2}$ (V)	Current density ($mA \cdot cm^{-2}$) at -0.8V	Number of electrons
$Mn_xCo_{3-x}O_4$ (x=0)	-0.22	-0.30	4.55	3.6
$Mn_xCo_{3-x}O_4$ (x=0.005)	-0.12	-0.20	4.71	3.7
$Mn_xCo_{3-x}O_4$ (x=1)	-0.16	-0.26	4.12	3.2
$Mn_xCo_{3-x}O_4$ (x=0)[1]	-	-0.25	-	~ 4
$Mn_xCo_{3-x}O_4$ (x=0.4)[1]	-	-0.19	-	~ 4
c-CoMn[2]	-0.075	-0.25	-	3.80
c-Co_2Mn[2]	-0.11	-0.29	-	3.75

1 E. Lee, J.-H. Jang and Y.-U. Kwon, *Journal of power sources*, 2015, **273**, 735-741.
2 C. Li, X. Han, F. Cheng, Y. Hu, C. Chen and J. Chen, *Nature communications*, 2015, **6**, 7345.

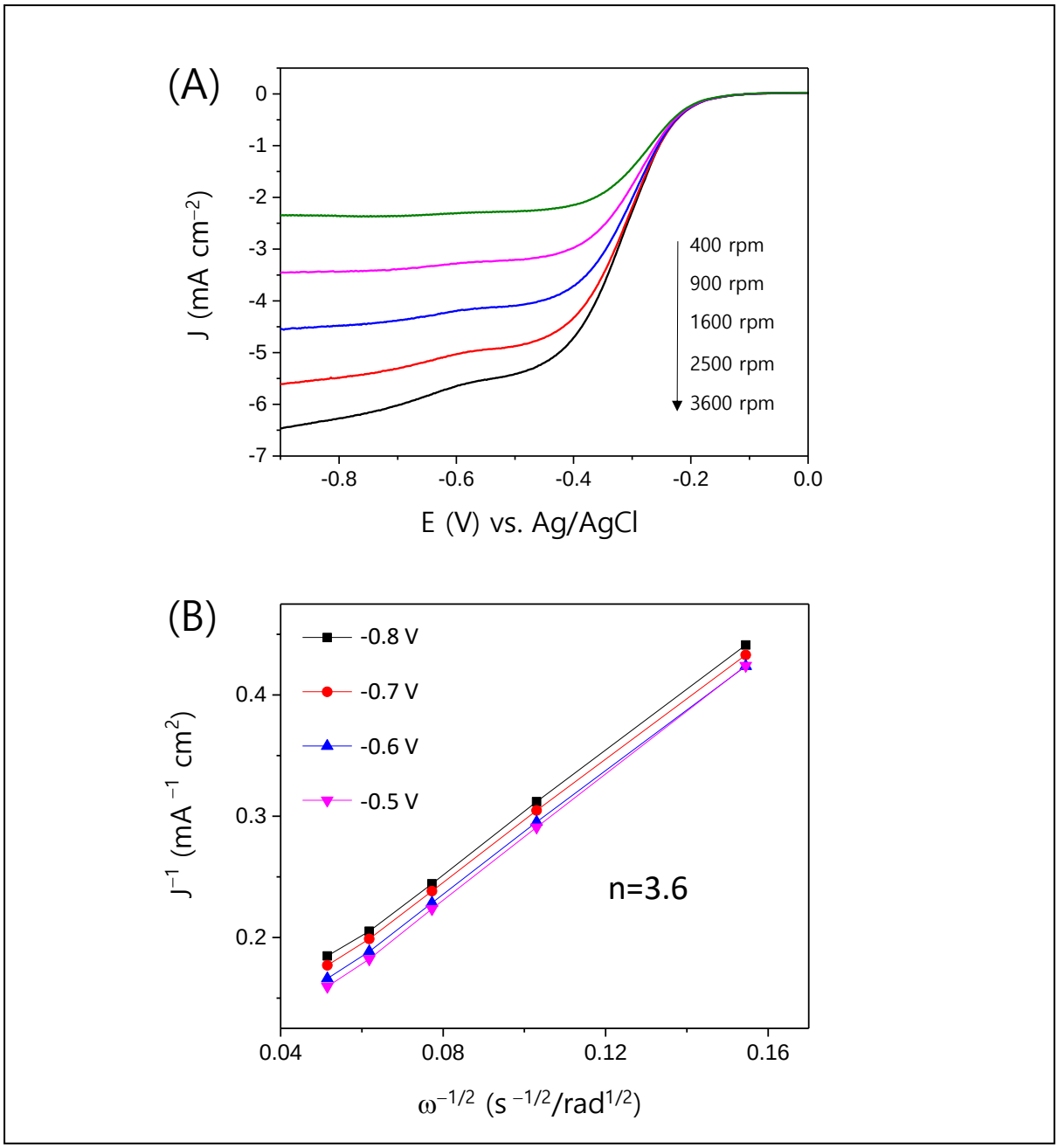

Figure S8. ORR polarization curves (A) for GC electrode modified with spinel $Mn_xCo_{3-x}O_4$ (x=0.005) nanocubes on carbon black. K-L plots (B) for the ORR polarization curves. The curves were performed in O_2-saturated KOH (0.1 M) solution.

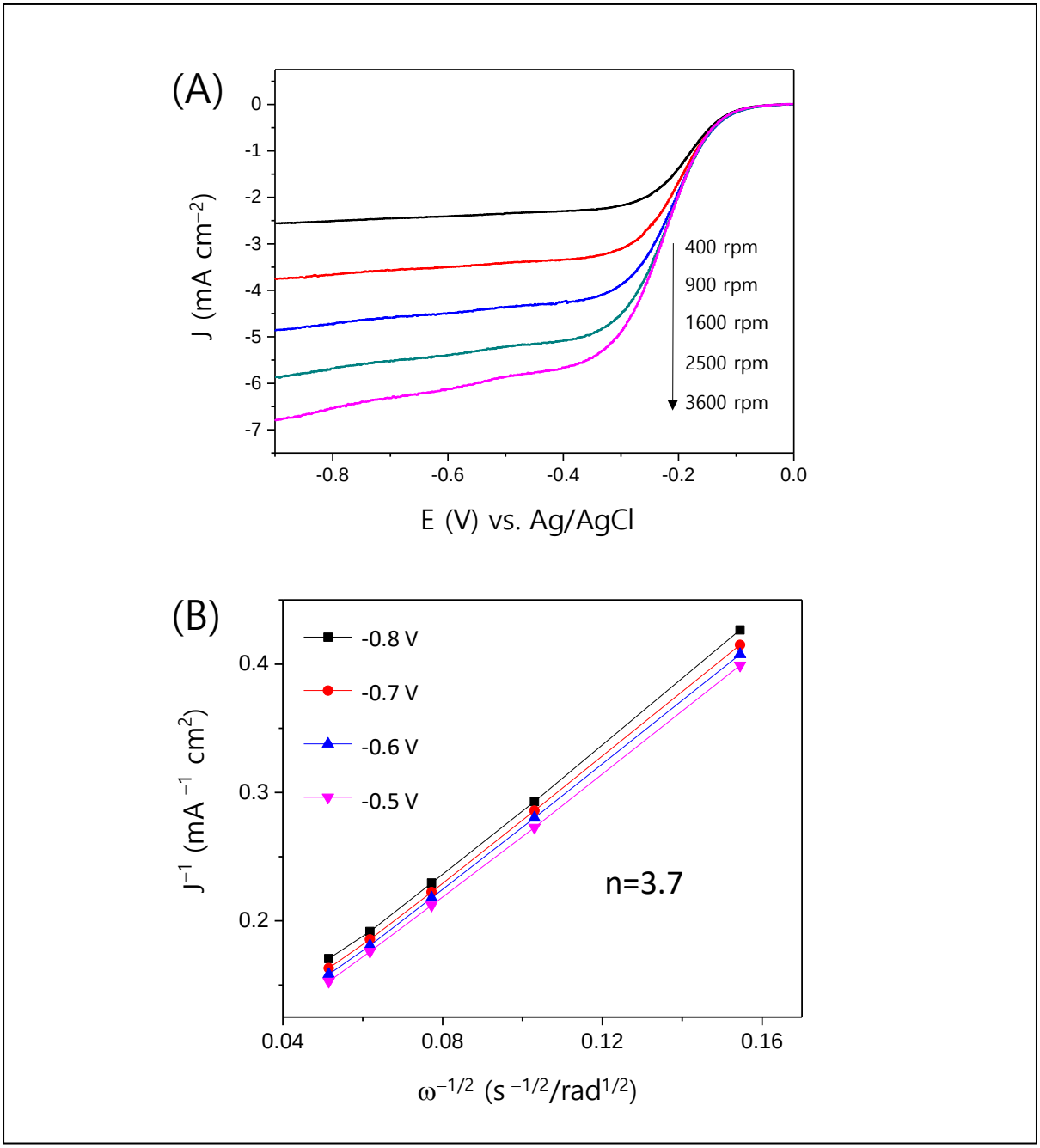

Figure S9. ORR polarization curves (A) for GC electrode modified with spinel $Mn_xCo_{3-x}O_4$ (x=0.05) nanocubes on carbon black. K-L plots (B) for the ORR polarization curves. The curves were performed in O_2-saturated KOH (0.1 M) solution.

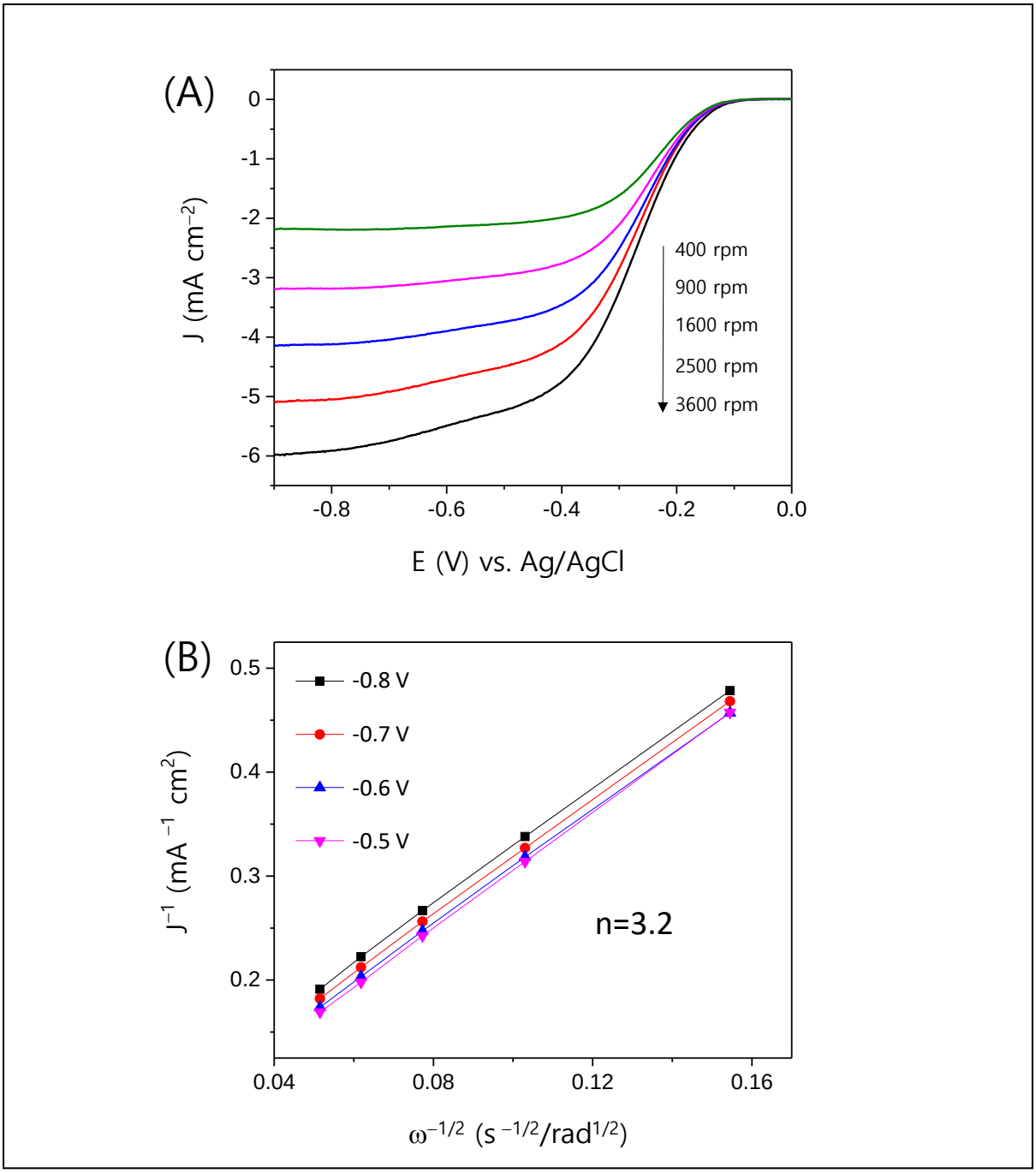

Figure S10. ORR polarization curves (A) for GC electrode modified with spinel $Mn_xCo_{3-x}O_4$ (x=1.0) nanocubes on carbon black. K-L plots (B) for the ORR polarization curves. The curves were performed in O_2-saturated KOH (0.1 M) solution.

Table S3. Summary of XPS atomic ratio of spinel $Mn_xCo_{3-x}O_4$ nanotubes.

Catalysts	Atomic ratio (XPS)		
	Mn(x)/Co	Mn^{3+}/Mn^{2+}	Co^{3+}/Co^{2+}
$Mn_xCo_{3-x}O_4$ (x=0)	-	-	1.0
$Mn_xCo_{3-x}O_4$ (x=0.005)	0.014/2.986	1.0	0.7
$Mn_xCo_{3-x}O_4$ (x=1)	1.4/1.6	1.1	1.4

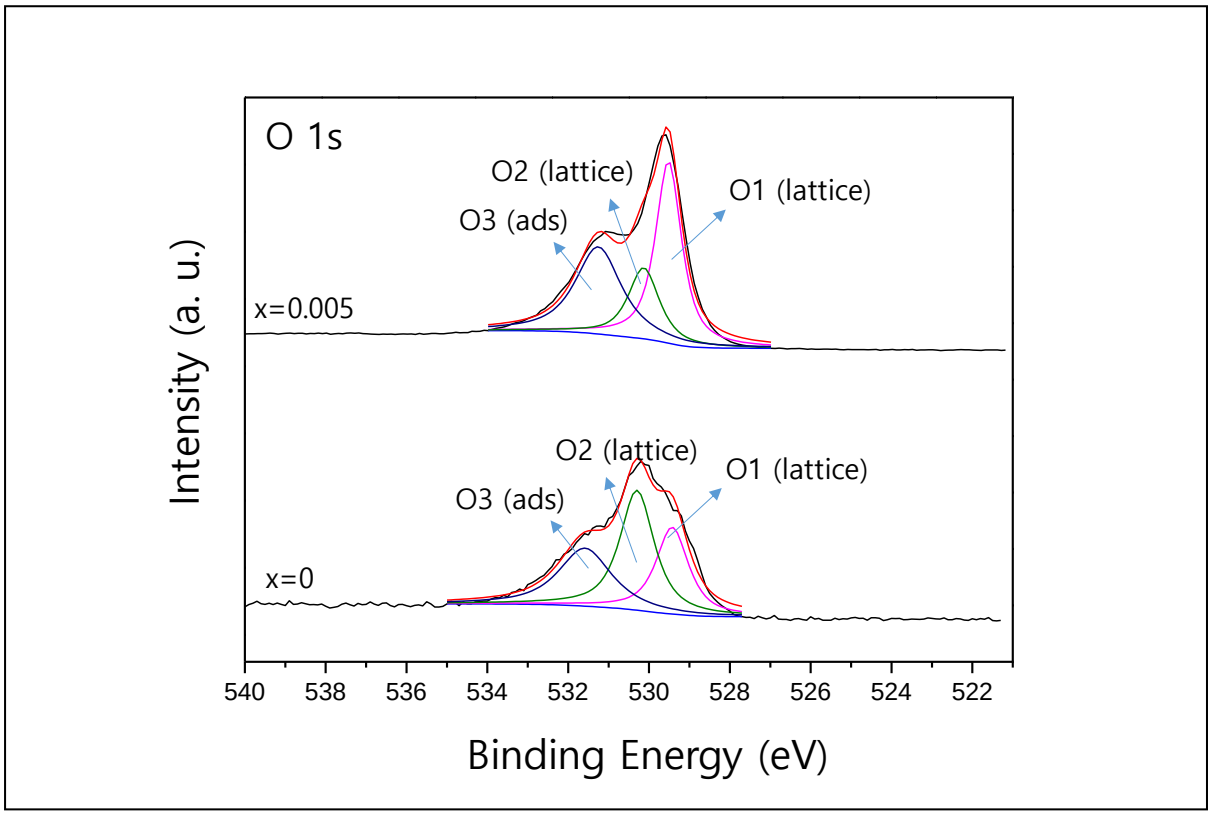

Figure S11. High resolution XPS spectra for O 1s of spinel $Mn_xCo_{3-x}O_4$ nanocubes (x=0 and x=0.005). The O1 and O2 correspond to lattice oxygen, and the O3 corresponds to surface adsorbed oxygen-containing species[ref], respectively.