Supplemental Information

Particle Size-Control Enables Extraordinary Activity of Ruthenium Nanoparticles/Multiwalled Carbon Nanotubes Catalysts towards Oxygen Reduction Reaction

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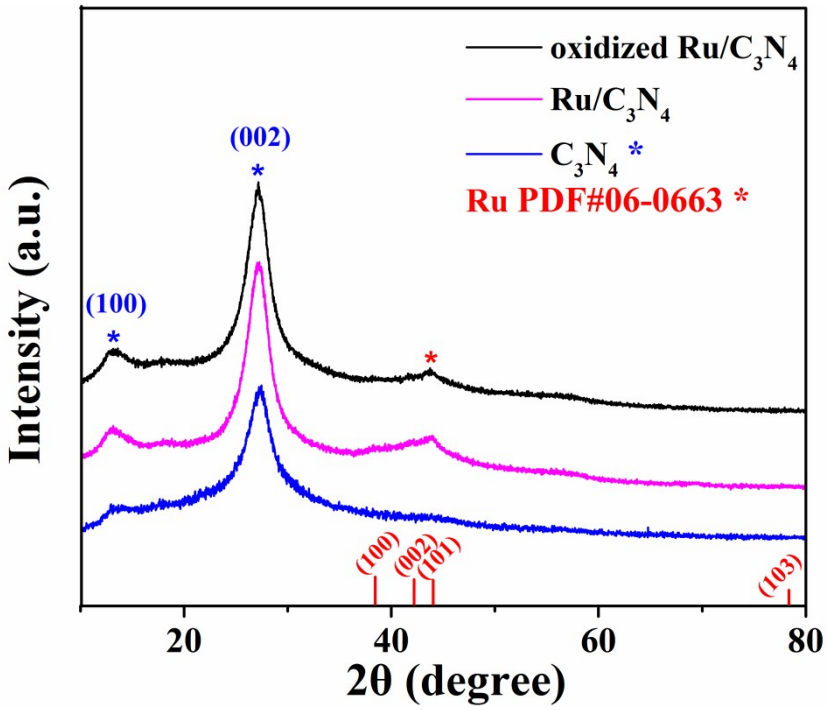

Figure S1 XRD patterns of C_3N_4, Ru/C_3N_4, oxidized Ru/C_3N_4.

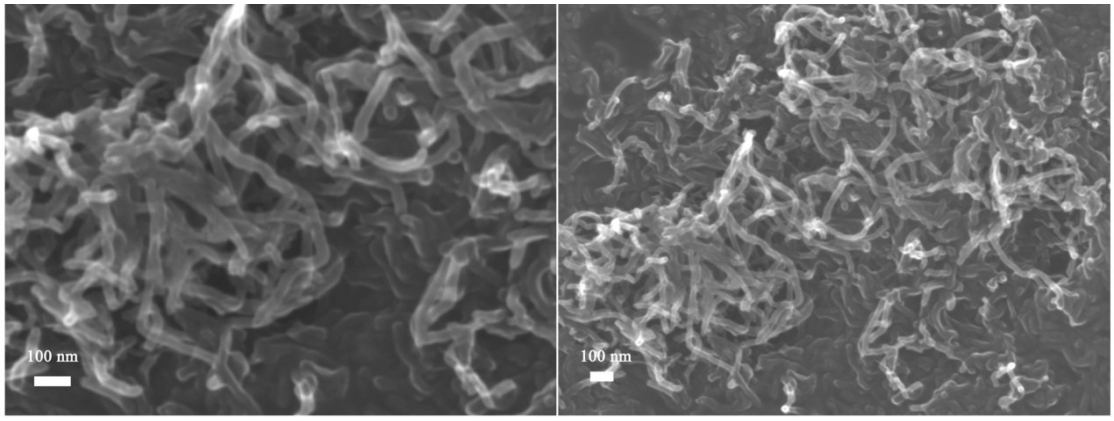

Figure S2 SEM images of Ru/MWCNTs.

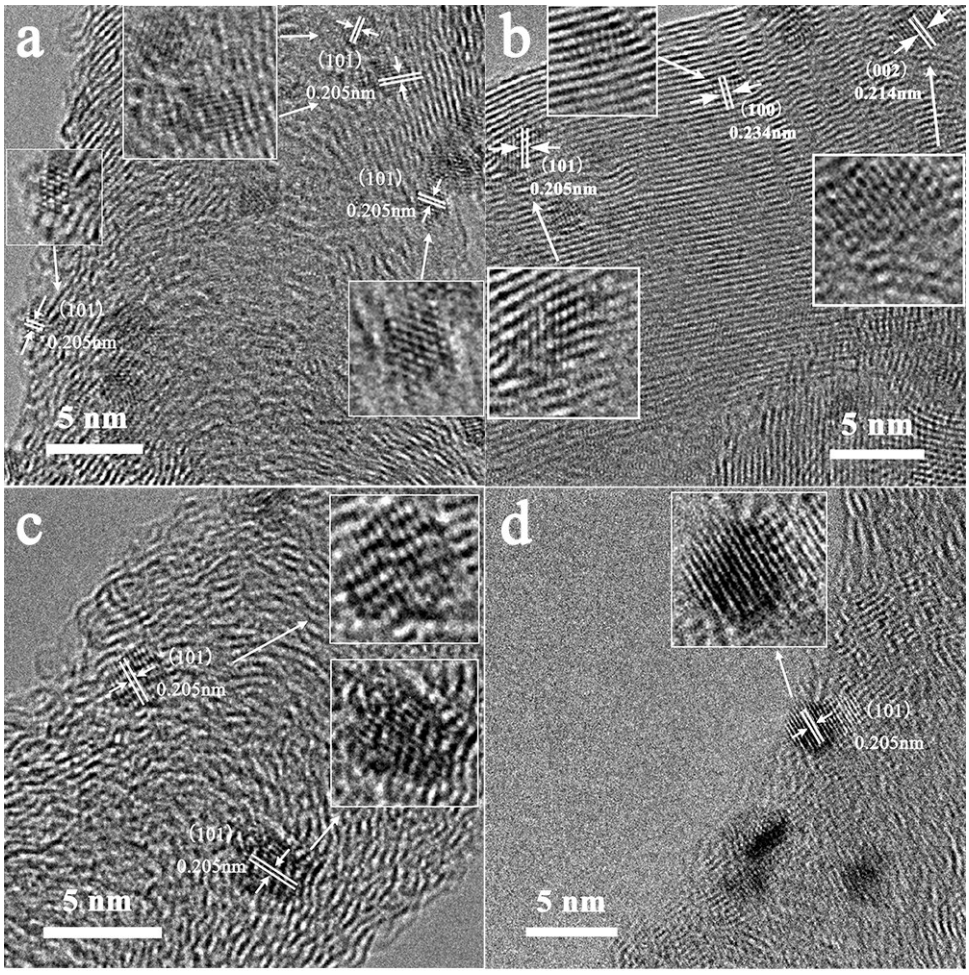

Figure S3 HRTEM image of Ru/MWCNTs catalysts with the mean particle diameter is 1.4 nm (a), 2.1 nm (b), 2.6 nm (c), and 3.3 nm (d), respectively.

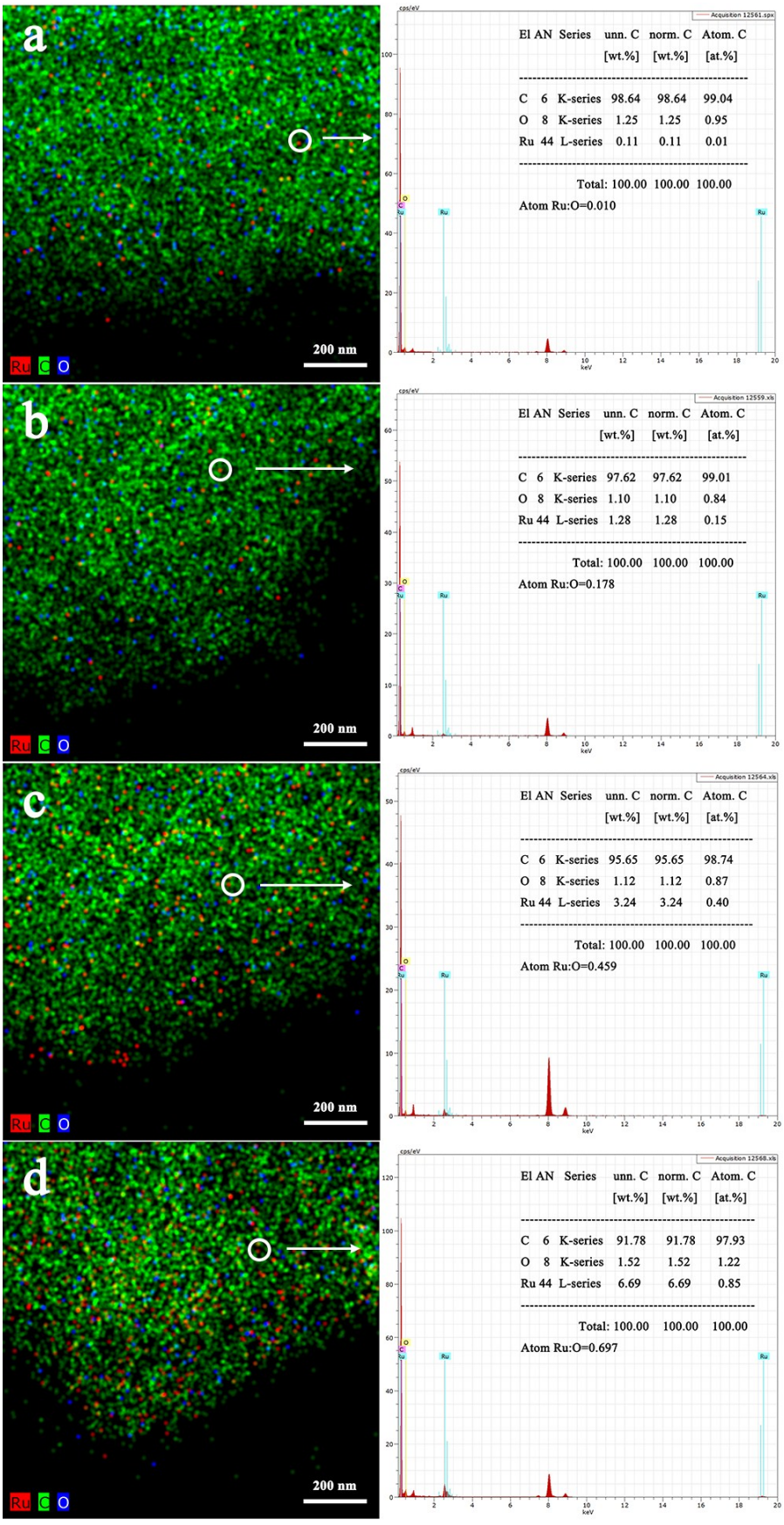

Figure S4 EDS mapping and cumulative spectrum of Ru/MWCNTs catalysts with the mean particle diameter is 1.4 nm (a), 2.1 nm (b), 2.6 nm (c), and 3.3 nm (d), respectively.

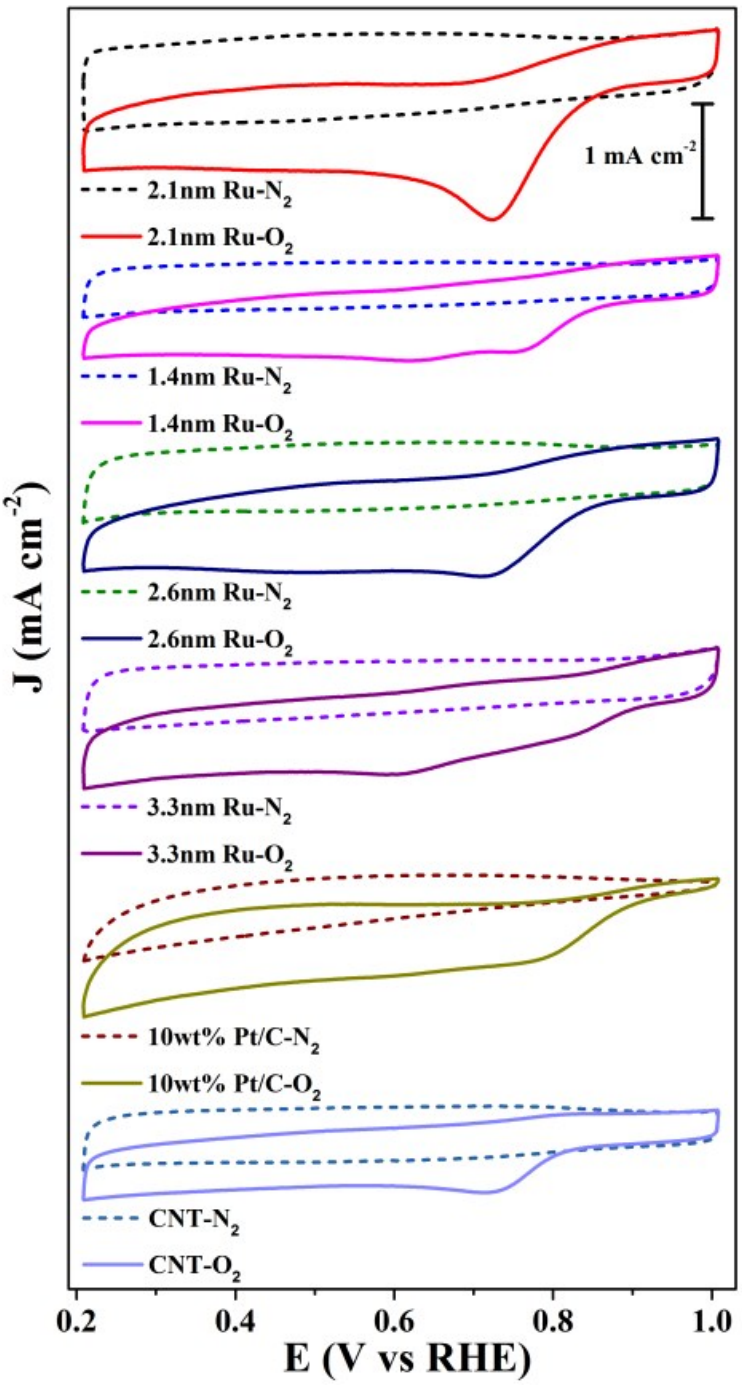

Figure S5 CV curves of Ru/MWCNTs with different mean particle size of Ru NPs, Pt/C and MWCNTs in 0.1 M KOH saturated with N_2 or O_2.

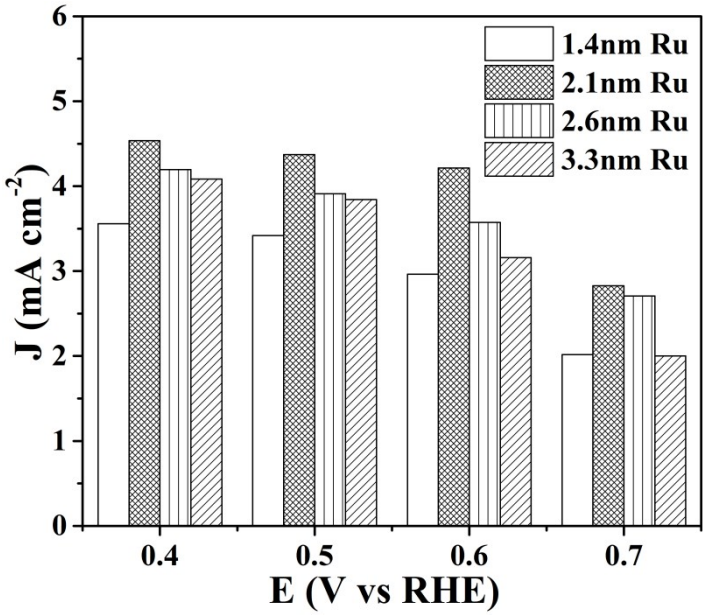

Figure S6 Comparison of current density (mA cm^{-2}) at the potential of 0.4, 0.5, 0.6, and 0.7 V (vs. RHE)

From the figure S6, it is clearly seen that the Ru/MWCNTs catalysts with the particle size of 2.1 nm exhibit the best ORR activity although its loading is only higher than that for the Ru/MWCNTs catalysts with the size of 1.4 nm. The catalytic activity of Ru NPs with different loading present the following tendency: 1.2 wt% > 1.4 wt% > 3.0 wt% > 0.8wt%.

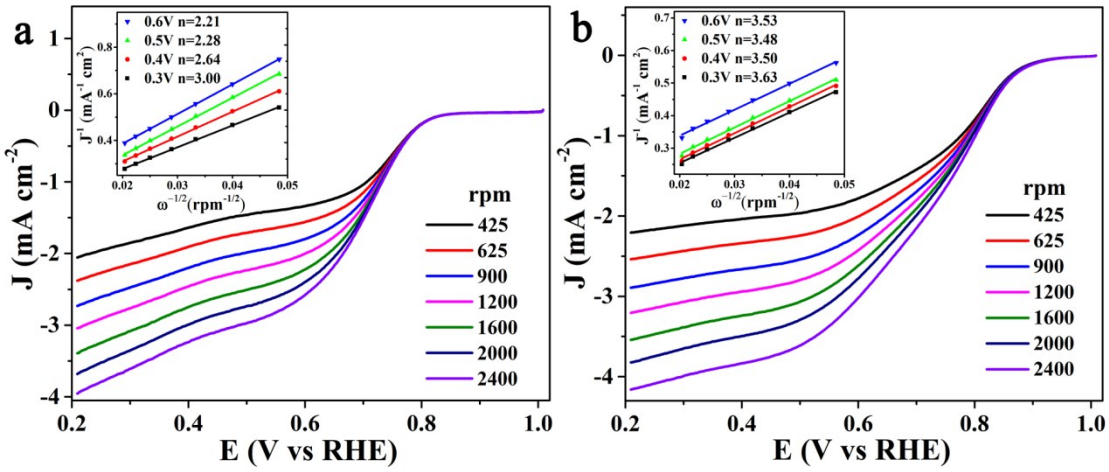

Figure S7 LSV curves in O_2-saturated electrolyte under different rotation rates and Koutecky-Levich plots under different potentials (inset) of (a) MWCNTs and (b) 10 wt% Pt/C.

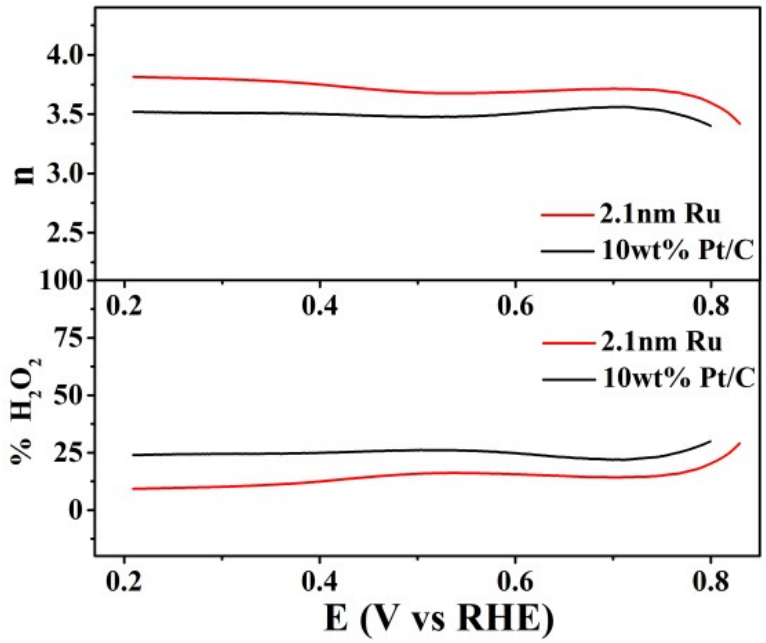

Figure S8 Electron transfer number (n) and H_2O_2 yield of the Ru/MWCNTs with the particle size of 2.1 nm and 10 wt% Pt/C measured by RRDE at 1600 rpm in 0.1 M KOH saturated with O_2.

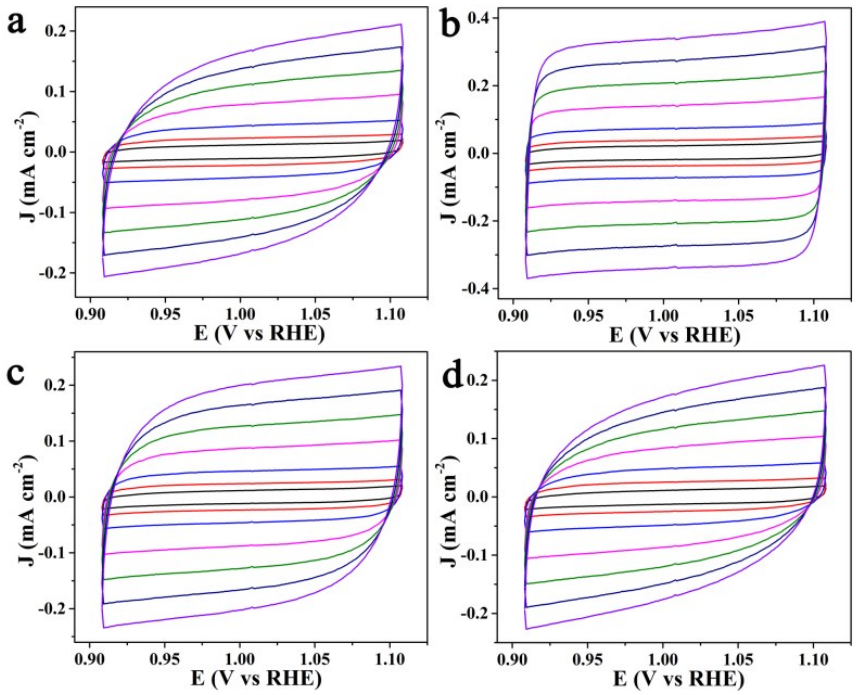

Figure S9 CV curves of Ru/MWCNTs with the particle size was 1.4 nm (a), 2.1 nm (b), 2.6 nm (c) and 3.3 nm (d) under different scan rate (5-100 mVs^{-1}).

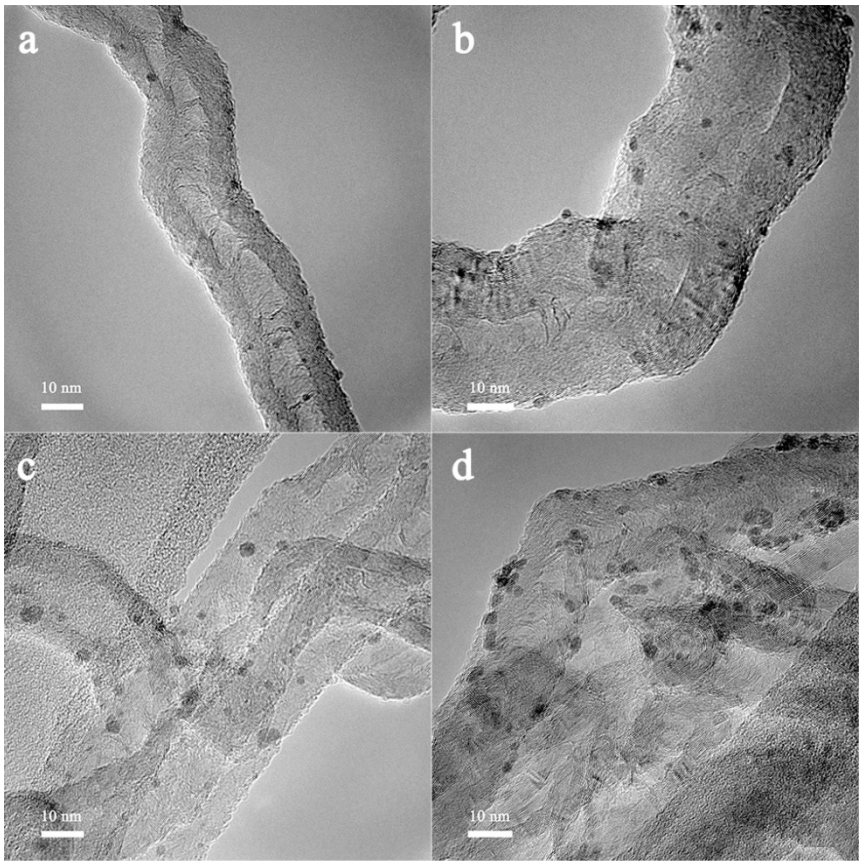

Figure S10 TEM images of Ru/MWCNTs with mean particle size was 1.4 nm (a), 2.1 nm (b), 2.6 nm (c) and 3.3 nm (d) after stability test.

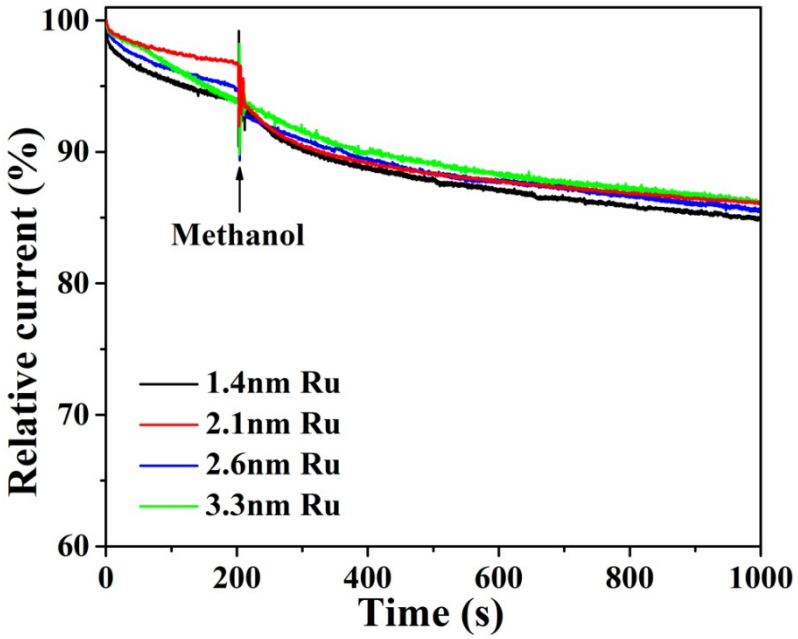

Figure S11 Chronoamperometric curves added methanol of Ru/MWCNT catalysts in O_2-saturated solution at 1600 rpm.

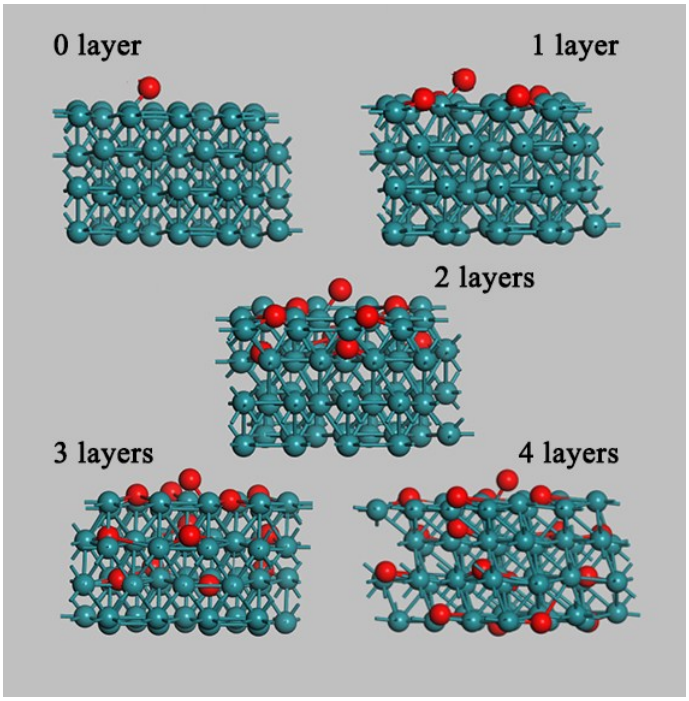

Figure S12 Models of the Ru/MWCNTs with different thicknesses oxidation layer.

Table S1 Comparison of the ORR activity.

Catalysts	Mean particle size (nm)	Oneset potential (V vs RHE)	Half-wave Potential (V vs RHE)	Diffusion-limited current density(mA/cm^2)	Electron-transfer number (n) Potential = 0.3V
MWCNT	-	0.823	0.676	3.1	3.0
10 wt% Pt/C	-	0.902	0.716	3.4	3.6
0.8 wt% Ru/MWCNTs	1.4	0.864	0.709	3.8	2.8
1.2 wt% Ru/MWCNTs	2.1	0.894	0.723	4.7	4.0
1.4 wt% Ru/MWCNTs	2.6	0.872	0.720	4.5	3.8
3.0 wt% Ru/MWCNTs	3.3	0.881	0.689	4.3	3.0
20 wt% Ru/MWCNTs[1]	-	0.770	~0.620	~7.1	2.5
3 wt% Ru/OMC[2]	-	~0.880	~0.700	~3.9	4.0
Ru/NG[3]	-	~0.830	~0.720	~3.2	4.0

References

1. M. G. Hosseini, P. Zardari, Int. J. Hydrogen Energ., 2016, 41, 8803-8818.

2. M. Stojmenović, M. Momčilović, N. Gavrilov, I. A. Pašti, S. Mentus, B. Jokić, B. Babić, Electrochim. Acta, 2015, 153, 130-139.

3. R. Ye, Y. Liu, Z. Peng, T. Wang, A. S. Jalilov, B. I. Yakobson, S-H. Wei, J. M. Tour, ACS Appl. Mater. Interfaces, 2017, 9, 3785-3791.