Supporting Information

Local electrocatalytic activity of PtRu supported on nitrogen doped carbon nanotubes towards methanol oxidation by scanning electrochemical microscopy

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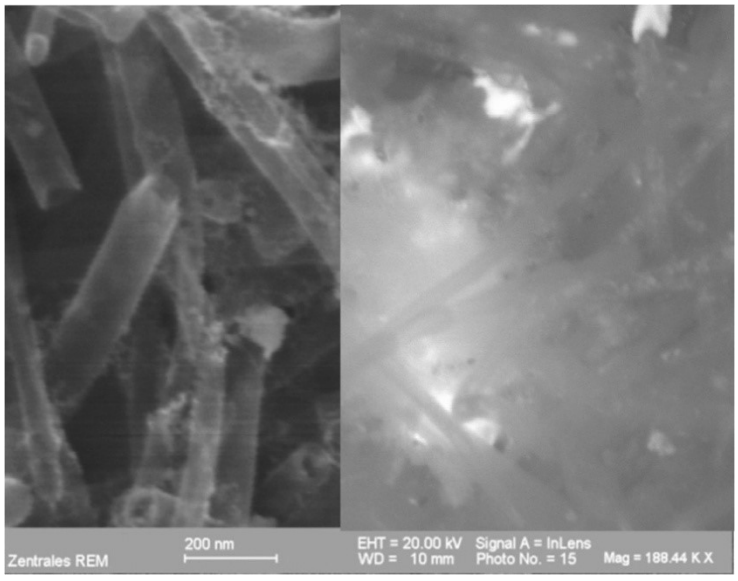

Fig. S1: SEM images of the PtRu/NCNT-200 catalyst in the secondary electron (SE, left) and back scattered electron (BSE, Right) mode.

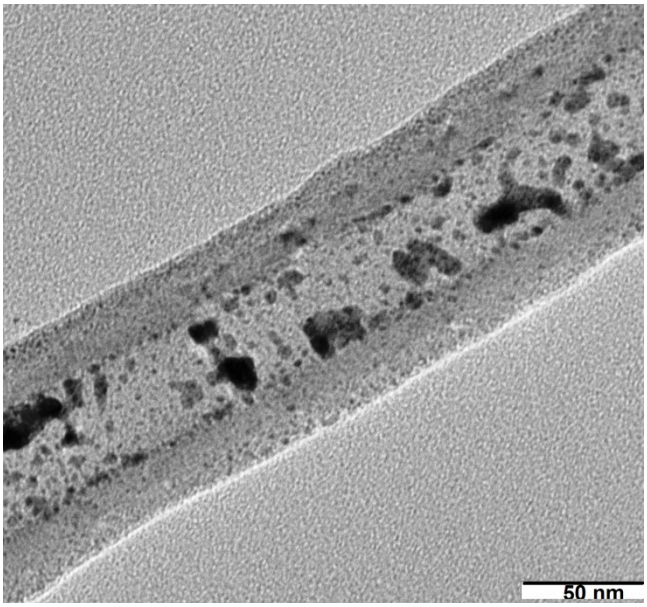

Fig. S2: TEM images of the PtRu/NCNT-200 catalyst.

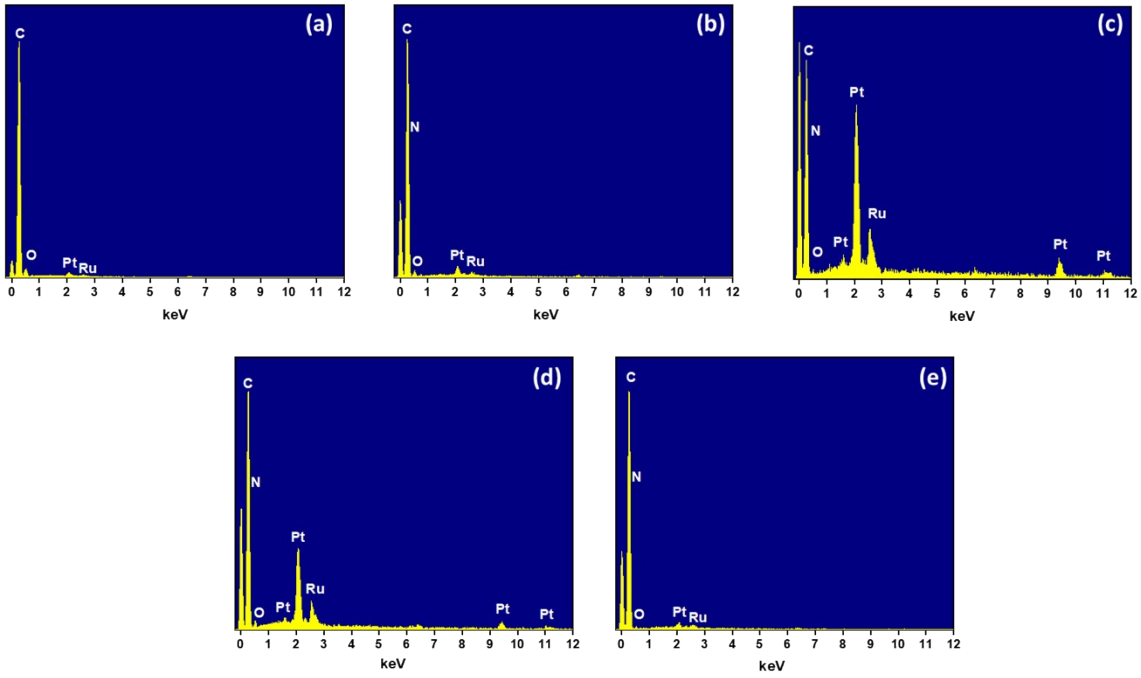

Fig. S3: EDAX spectrum of (a) PtRu/OCNT, (b) PtRu/NCNT-200, (c) PtRu/NCNT-400, (d) PtRu/NCNT-600 and (e) PtRu/NCNT-800 catalyst extracted from TEM images respectively.

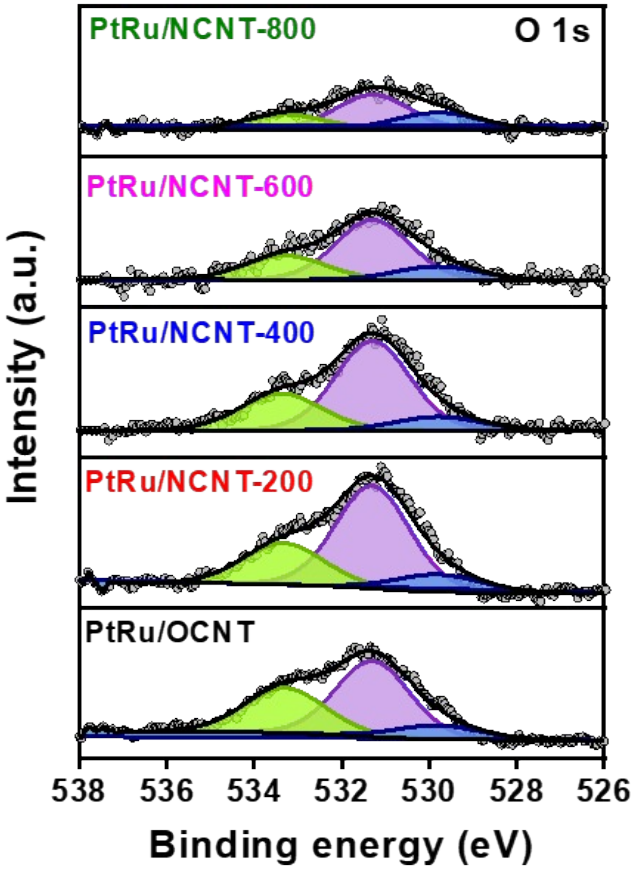

Fig. S4: Deconvoluted O 1s XP spectra of PtRu catalyst on different CNTs supports *i.e.* OCNT, NCNT-200, NCNT-400, NCNT-600 and NCNT-800.

Table S1: XPS surface atomic concentration of PtRu catalyst on different CNTs support.

Catalyst	C at.%	O at.%	N at.%	Pt at.%	Ru at.%
OCNTs	91.6	6.6	N/A	0.9	0.9
NCNT- 200	89.6	6.2	2.0	1.1	1.1
NCNT- 400	88.8	6.0	2.7	1.2	1.3
NCNT- 600	91.0	4.8	2.7	1.2	1.3
NCNT- 800	94.1	3.2	1.3	0.7	0.7

Table S2: Species and relative concentration of N as obtained from XPS N 1s spectra. N1: pyridinic and nitrile, at 398.6eV; N2: pyrrolic and amine, at 400.2eV; N3: quaternary, at 401.2eV; N4: pyridine oxide, at 403.0-404.0 eV.

Samples	N1 at.%	N2 at.%	N3 at.%	N4 at.%
NCNTs200C	32.9	42.2	12.2	12.7
NCNTs400C	39.5	40.6	12.7	7.2
NCNTs600C	42.2	35.8	13.6	8.4
NCNTs800C	34.9	28.9	22.0	14.2

Table S3: Species and relative concentration of Pt as obtained from XPS Pt 4f spectra. The spectra were deconvoluted into three pairs of peaks which are assigned to Pt^0 (71.4, 74.8 eV), $Pt^{\delta+}$ (72.1, 75.5 eV), and PtO (73.8, 77.5 eV) species.

Catalyst	Pt^0 at.%	$Pt^{\delta+}$ at.%	PtO at.%
OCNTs	60.2	31.0	8.8
NCNT-200	55.2	26.1	9.8
NCNT-400	55.2	36.0	8.8
NCNT-600	59.7	32.4	7.9
NCNT-800	56.2	31.5	12.3

Table S4: Species and relative concentration of Ru as obtained from XPS Ru 3p spectra. The spectra were deconvoluted into three peaks which are attributed to Ru0 (461.9 eV), RuO_2 (463.9 eV), and RuO_2•xH_2O (467.3 eV) species.

Catalyst	Ru^0 at.%	RuO_2 at.%	RuO_2·xH_2O at.%
OCNTs	64.4	19.1	16.5
NCNT-200	55.4	25.2	19.4
NCNT-400	56.5	23.1	20.4
NCNT-600	56.4	22.8	20.8
NCNT-800	60.0	27.5	13.5

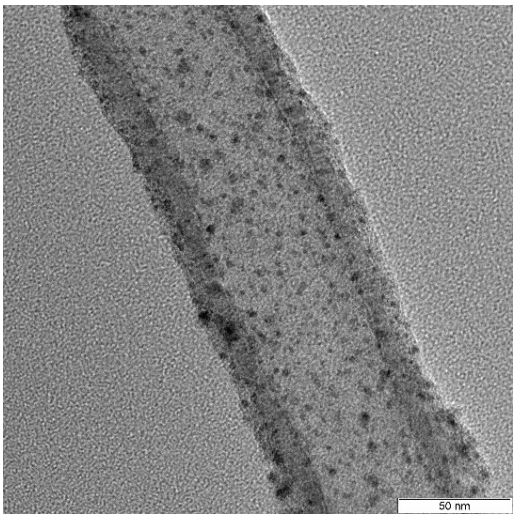

Fig. S5: TEM images of the PtRu/NCNT-400 catalyst after the stability studies.

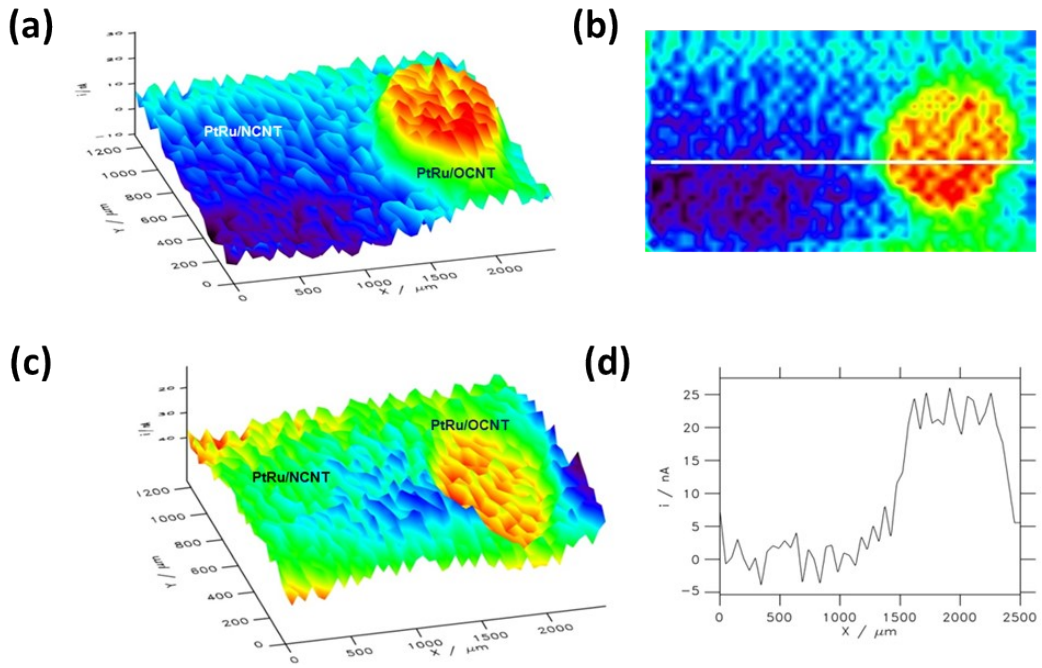

Fig. S6: (a) RC-SECM 3D-images of PtRu/OCNT and PtRu/NCNT-400 catalyst spots in 1 M CH_3OH + 0.5 M H_2SO_4 at an applied sample potential of +0.3 V. The tip (Pt-microelectrode, 25 µm) was polarized at +0.05 V during P1 and at +0.3 V during P2. (b) RC-SECM 2D-image of 'a', (c) at an applied sample potential of +0.5 V (d) Line scan extracted from 2D-image 'b'. Images taken after 368 ms of the detection pulse.

Table S5: Binding energy, closest distance of OCNT and NCNT. We also show the C.A (closest atoms) between tube-molecule

	OCNT			NCNT-200			NCNT-400			NCNT-800		
	C.A.	d (Å)	E_b (eV)	C.A.	d (Å)	E_b (eV)	C.A	d (Å)	E_b (eV)	C.A	d (Å)	E_b (eV)
CO	Ru-C	1.895	-2.821	Ru-C	1.881	-3.014	Ru-C	1.928	-2.476	Ru-C	1.923	-2.374
CH3OH	Ru-H	1.898	-0.715	Ru-H	1.879	-0.784	Ru-O (O-H)	2.222 (1.56)	-1.644	Ru-H	2.156	-0.233

Table S6: Comparison of activity with reported Pt-Ru based catalysts for methanol oxidation

S.No.	Composite	Electrolyte	Mass Activity (A mg^{-1})	Ref.
1.	PtRu/rGO	0.5 M H_2SO_4 + 1 M CH_3OH	0.74	1
2.	Pt@mPtRu YSs	0.5 M H_2SO_4 + 1 M CH_3OH	0.56	2
3.	mPtRu NCs	0.5 M H_2SO_4 + 1 M CH_3OH	0.41	2
4.	PtRu/ RGO/TNTs	0.5 M H_2SO_4 + 1 M CH_3OH	0.32	3
5.	PtRuCu NFs-HAc/C	0.1 M $HClO_4$ and 1 M CH_3OH	0.37	4
6.	$Pt_{66}Ni_{27}Ru_7$ DNSs	0.5 M H_2SO_4 + 0.5 M CH_3OH	0.81	5
7.	d-Pt@Ru	0.5 M H_2SO_4 + 1 M CH_3OH	0.8	6
8.	Ru/Pt NWs	0.1M $HClO_4$ + 1 M CH_3OH	0.57	7
9.	Pt_1Ru_1/C@NC	0.1M $HClO_4$ + 0.5 M CH_3OH	0.67	8
10.	PtRu NWs	0.1M $HClO_4$ + 0.5 M CH_3OH	0.82	9
12.	PtRu nanodendrites	0.1 M $HClO_4$ + 1.0 M CH_3OH	0.52	10
13.	PtRu coreshell	0.5 M H_2SO_4+ 1.0 M CH_3OH	0.4	11
14.	PtRuCu hexapod	0.1 M $HClO_4$ + 1.0 M CH_3OH	0.55	12
15.	PtRu/PPDA-MWCNTs	0.5 M H_2SO4 + 1.0 M CH3OH	0.731	13
16.	PtRu/TiO_2-CNF	0.5 M H_2SO_4 + 2.0 M CH_3OH	0.603	14
17.	PtRu/C* PtRu20/TECNF	0.5 M H_2SO_4 + 0.5 M CH_3OH	0.076 0.10	15
18.	PtRu icosahedra	0.5 M H_2SO_4 + 0.5 M CH_3OH	0.074	16
19.	PtRuCuW	0.5 M H_2SO_4 and 0.5 M CH_3OH	0.47	17
20.	PtRuCu/C	0.5 M H_2SO_4 + 1 M CH_3OH	0.79	18
21.	PtRu/N-doped C	0.5 M H_2SO_4 + 1 M	0.15	19

		CH_3OH		
22.	PtRu/C-TiN-10%	0.5 mol L^{-1} H_2SO_4+0.5 mol L^{-1} CH_3OH	0.81	20
23.	$PtRuWO_x/C$	0.5 mol L^{-1} H_2SO_4+0.5 mol L^{-1} CH_3OH	0.06	21
24.	PtRu/PANI/CNTs	0.5 M H_2SO_4 + 1 M CH_3OH	0.4	22
25.	PtRu/NCNT-400	0.5 M H_2SO_4 + 1 M CH_3OH	0.85	This work

PtRu/C* (commercial catalyst)

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