

Pyrrolic nitrogen-doped carbon nanotubes: Physicochemical properties, interactions with Pd and their role in the selective hydrogenation of nitrobenzophenone

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Supplementary Information S1

Materials used to synthesize 3-ferrocenyl-2-(4-cyanophenyl)acrylonitrile and the synthetic procedure

Ferrocenecarboxaldehyde 98%, 4-cyanophenylacetonitrile 97%, piperidine 99%, diethyl ether 99.8% and hexane 97% were purchased from Sigma Aldrich. All reagents and solvents were of analytical grade and were used as received from the suppliers. Aluminium-backed silica gel 60 F₂₅₄ plates purchased from Merck were used to carry out thin layer chromatography in solvents of varying polarity. Column chromatography was accomplished by using Merck silica gel 60, 0.063-0.2 mm.

The catalyst, 3-ferrocenyl-2-(4-cyanophenyl)acrylonitrile, was synthesized *via* a mechanochemical approach under solvent-free conditions following the procedure outlined by Imrie *et al.* Ferrocenecarboxaldehyde (200.0 mg, 0.93 mmol) and 4-cyanophenylacetonitrile (132.0 mg, 0.93 mmol) were ground together in the presence of 2 drops of piperidine to yield a maroon paste. The paste was first dried in air, then under vacuum to obtain a maroon product. The maroon product was purified by means of column chromatography on silica gel with a solvent system of (1:1) hexane/diethyl ether to obtain 3-ferrocenyl-2-(4-cyanophenyl)acrylonitrile as dark red crystals. Yield (311.0 mg; yield of 98%); m. p. 139 °C (lit [Imrie *et al.*]: 140 °C). IR (cm⁻¹) 3099, 3050, 2943, 2225, 2207, 1609, 1585, 1452, 1408, 1367, 1312, 1252, 1178, 1103, 1032, 998, 920, 833, 826, 543, 501, 487, 432; ¹H-NMR (ppm) in CDCl₃: 7.68 (4H, s, ArH), 7.50 (1H, s, CH), 4.99 (2H, t, *J* 1.9, C₅H₄), 4.61 (2H, t, *J* 1.8, C₅H₄), 4.24 (5H, s, C₅H₅); ¹³C-NMR (ppm) in CDCl₃ 132.85, 125.45, 146.60, 139.12, 118.56, 118.34, 111.36, 104.52, 77.18, 72.56, 70.68, 70.10. MS (C₂₀H₁₄FeN₂) ES: [M]⁺ *m/z* calcd 338.050638, found 338.0500.

Conditions for GC-FID and GC-MS analysis

Quantitative analysis of 4-nitrobenzophenone (NBP) and 4-aminobenzophenone (ABP) was conducted on the GC-FID. The GC-FID was fitted with a SGE BP X5 column (0.25 mm inner diameter, 30 m length, 0.25 μM film thickness). The carrier gas used was nitrogen and it was pumped at a flow rate of 30.0 mL min⁻¹. The oven temperature used for NBP and ABP analysis was 250 °C. A splitless injection mode was used, and for each analysis 3 μL of the quenched product was injected at a temperature of 110 °C. The identities of NBP and ABP were determined by comparing their retention times with that of purchased commercial samples used as external standards. The integrated peak areas of each sample was used to determine the concentration of NBP and ABP at different time intervals. The calibration range used for both NBP and ABP was 5, 20, 40, 80 and 100 ppm. The NBP calibration curve had an R² value of 0.9884, while the ABP calibration curve had an R² value of 0.9981.

Further qualitative analysis of the hydrogenation product was conducted on the GC-MS. The GC-MS was fitted with an InertCap 5MS/Sil column (0.25 mm inner diameter, 30 m length, 0.25 μM film thicknesses). The carrier gas used was helium and it was pumped at a flow rate of 30.0 mL min⁻¹. The oven temperature used for NBP and ABP analysis was 250 °C. A splitless injection mode was used, for each analysis, 1 μL of the quenched product was injected at a temperature of 110 °C. The identity of NBP and ABP was determined by comparing their masses with the hit-targets obtained from the mass spectrometer library.

ICP-OES analysis

Triplicate analyses were performed for each catalyst. For all analyses, an external standard was used to create a calibration line ($R^2 = 0.994$). The calibration standards used were prepared in nitric acid solutions at concentrations of 0, 20, 40, 60 and 100 ppm from a palladium ICP-OES standard stock solution (Johnson Matthey, prepared in South Africa, guaranteed to be 1000 ppm \pm 0.2% Pd in 0.5 M HNO₃). For each ICP-OES measurements, three measurements were conducted. The results were analysed using a Perkin Elmer WinLab 32 software.

Raman analysis

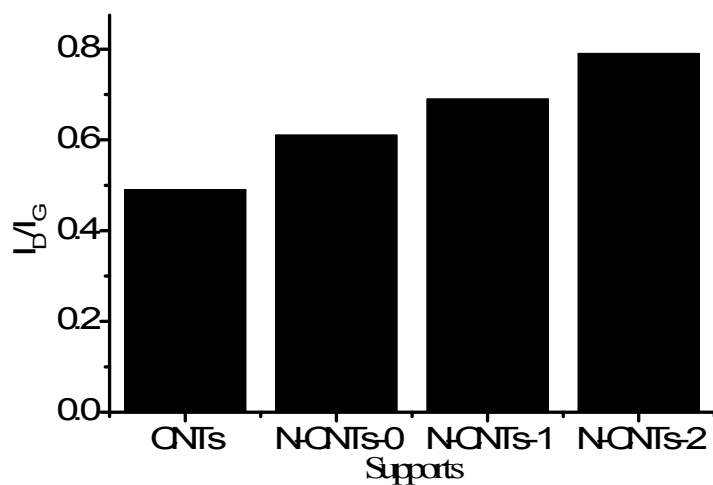


Figure S1: I_D/I_G ratios of N-CNTs and CNTs: Note the higher ratios indicate more disordered materials

Supplementary Information S2

Table S2. Summary of oxygen and nitrogen percentages in acetonitrile solution used to synthesize N-CNTs.

Sample	Mass of ethylbenzoate (g) in 10 g of solution	Moles of oxygen in 10 g of solution	Oxygen (%) in acetonitrile solution	Moles of nitrogen in 10 g of solution	nitrogen (%) in acetonitrile solution
N-CNTs-0	0	0	0	0.239	33.5
N-CNTs-1	0.50	0.009	1	0.226	31.7
N-CNTs-2	1.00	0.018	2	0.211	29.6

Supplementary Information S3

S3 (1). Summary of XPS analysis of all Pd/CNTs and Pd/N-CNTS

Sample	Element	Atomic Concentration (%)	Binding energy (eV)
Pd/N-CNTs-0	O	10.48	532
	N	4.36	398.5 (21.43%) 400.3 (63.08%) 404.1 (15.49%)
	Pd	1.31	335
	C	83.85	284
Pd/N-CNTs-1	O	8.34	532
	N	3.48	398.4 (16.68%) 400.6 (72.87%) 404.7 (10.46%)
	Pd	0.67	336
	C	87.51	284
Pd/N-CNTs-2	O	13.46	534
	N	2.53	398.4 (11.64%) 400.3 (80.37%) 405.1 (7.98%)
	Pd	0.94	337
	C	83.07	285
Pd/CNTs	O	6.66	532
	Pd	1.13	335
	C	92.22	284

S3(2). XPS analysis of Pd/N-CNTs-0

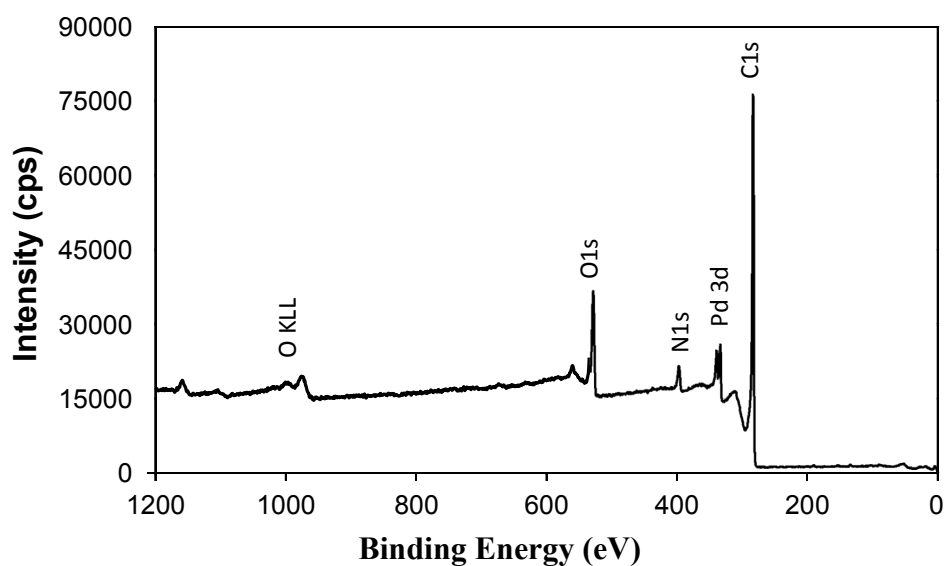


Figure S3 (2a). XPS spectra of Pd/N-CNTs-0

Table S3 (2a). Summary of XPS spectra of Pd/N-CNTs-0

Peak	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conn %
C 1s	285	2.610	254430.0	0.278	12.011	83.85	73.24
N 1s	399	4.222	23168.0	0.477	14.007	4.36	4.44
Pd 3d	335	3.291	77012.0	5.356	106.534	1.31	10.13
O 1s	532	4.082	92125	0.780	15.999	10.48	73.24

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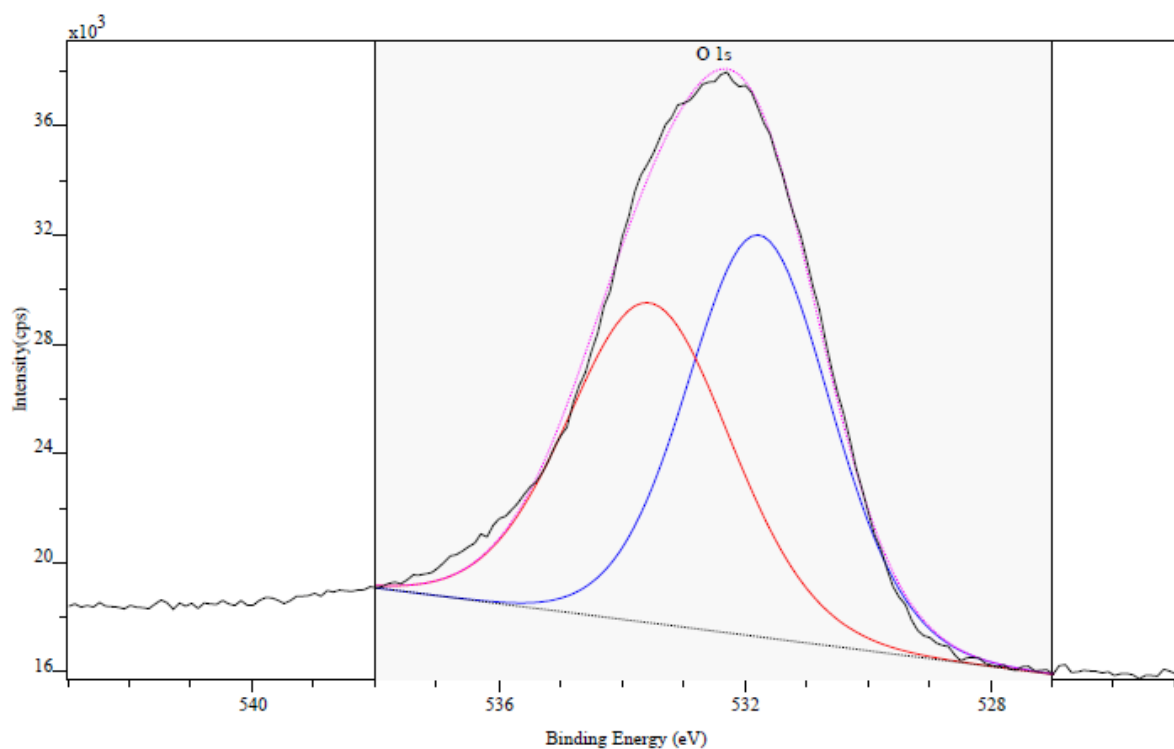


Figure S3 (2b). O 1s spectra of Pd/N-CNTs-0

Table S3 (2b). Summary of O 1s spectra of Pd/N-CNTs-0

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	531.883	2.817	44351.3	0.780	15.999	53.03	53.03
2	533.520	3.322	39294.8	0.780	15.999	46.97	46.97

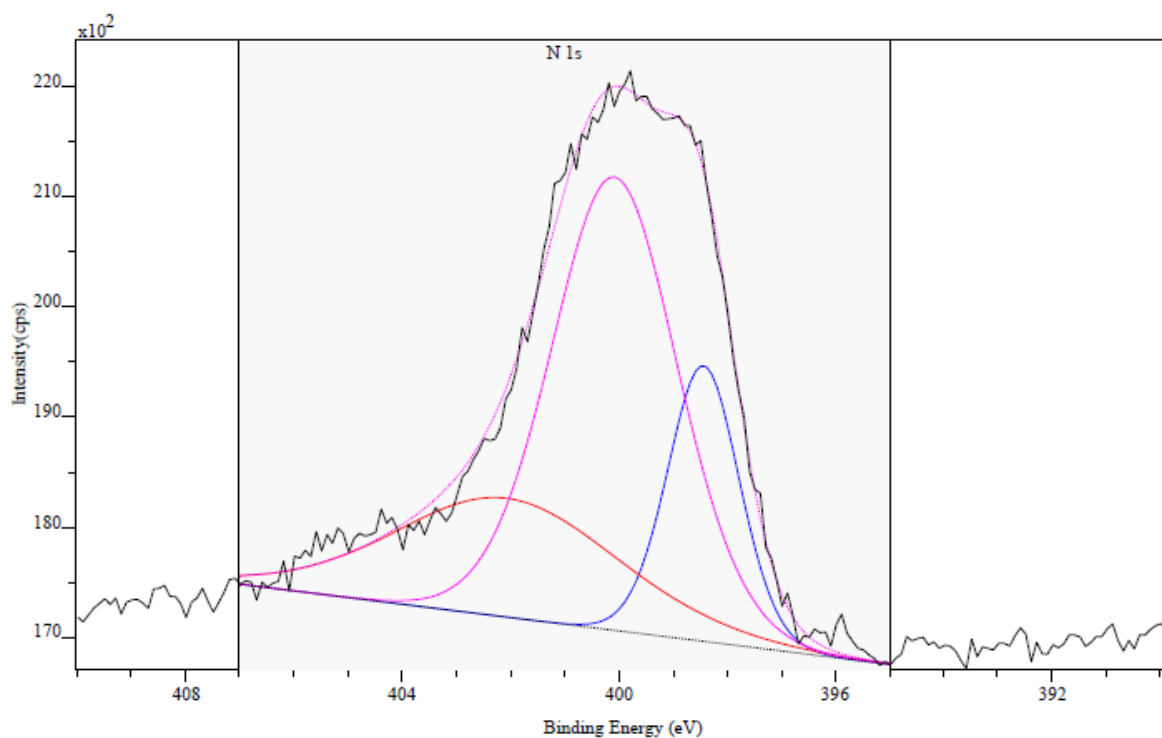


Figure S3 (2c). N 1s spectra of Pd/N-CNTs-0

Table S3 (2c). Summary of N 1s spectra of Pd/N-CNTs-0

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	398.512	1.687	5031.7	0.477	14.007	21.43	21.43
2	404.059	4.149	3636.6	0.477	14.007	15.49	15.49
3	400.291	2.898	14809.6	0.477	14.007	63.08	63.08

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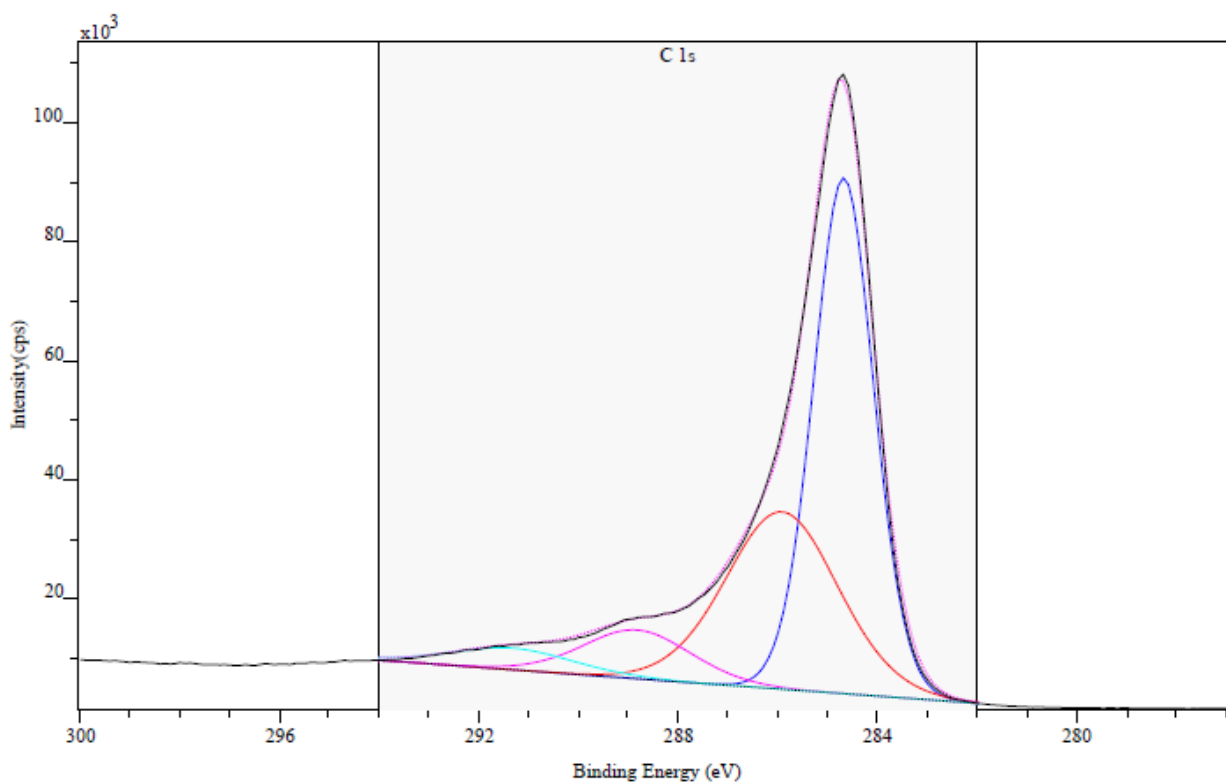


Figure S3 (2d). C 1s spectra of Pd/N-CNTs-0

Table S3 (2d). Summary of C 1s spectra of Pd/N-CNTs-0

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	284.683	1.400	133171.5	0.278	12.011	52.74	52.74
2	285.939	2.606	85347.5	0.278	12.011	33.81	33.81
3	288.826	2.510	22557.5	0.278	12.011	8.94	8.94
4	291.336	2.860	11371.4	0.278	12.011	4.51	4.51

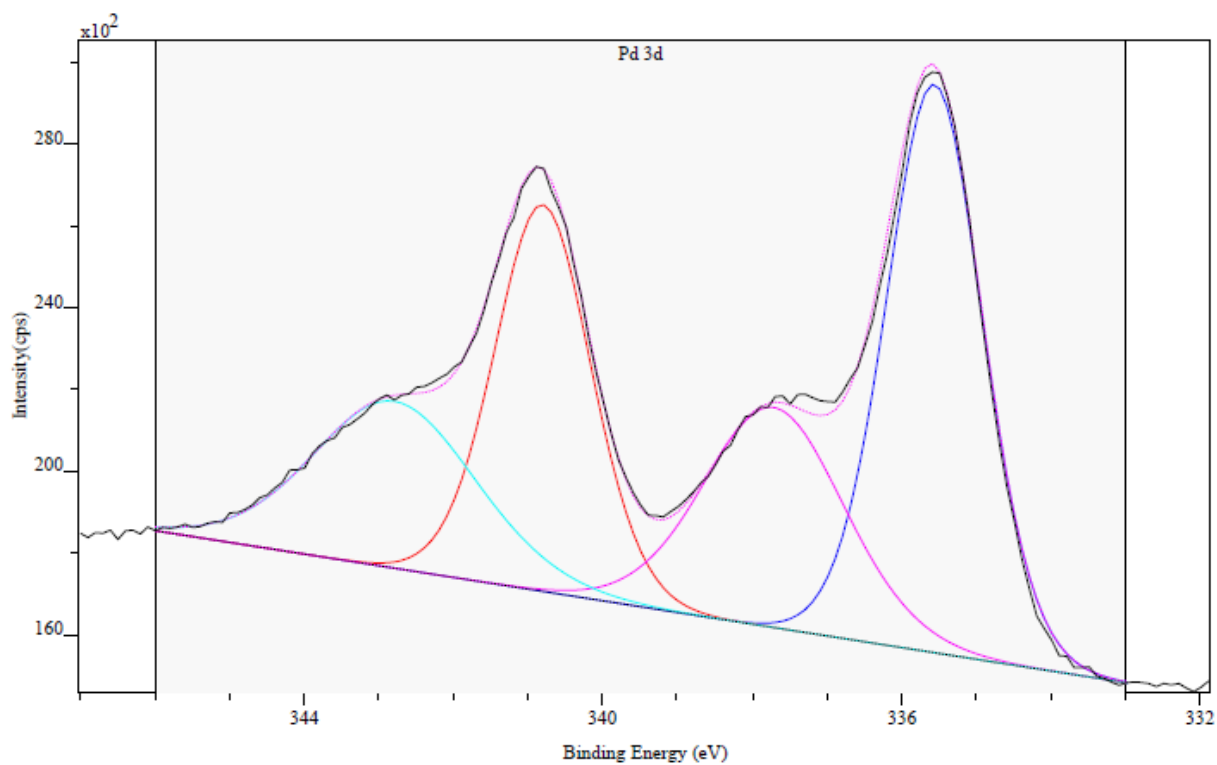


Figure S3 (2e). Pd 3d spectra of Pd/N-CNTs-0

Table S3 (2e). Summary of Pd 3d spectra of Pd/N-CNTs-0

Band	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	335.555	1.500	22918.0	5.356	106.534	36.53	36.53
2	340.796	1.500	15600.5	5.356	106.534	24.83	24.83
3	337.746	2.178	12918.9	5.356	106.534	20.58	20.58
4	342.795	2.532	11353.2	5.356	106.534	18.06	18.06

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S3(3). XPS spectra of Pd/N-CNTs-1

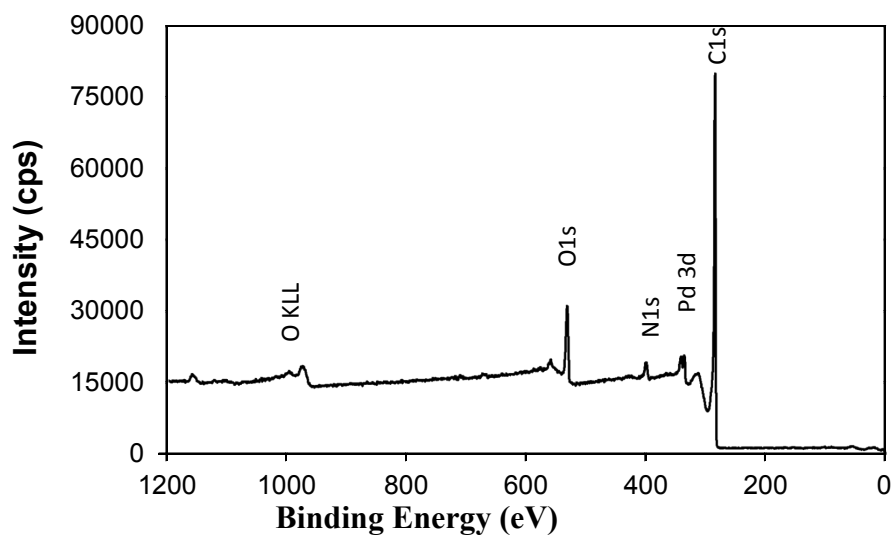


Figure S3 (3a). XPS spectra of Pd/N-CNTs-1

Table S3 (3a). Summary of XPS spectra of Pd/N-CNTs-1

Peak	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conn %
C 1s	284	2.573	278652.0	0.278	12.011	87.51	80.53
N 1s	400	4.944	19421.0	0.477	14.007	3.48	3.74
Pd 3d	336	4.460	41703.0	5.356	106.534	0.67	5.51
O 1s	532	4.646	76876.0	0.780	15.999	8.34	10.22

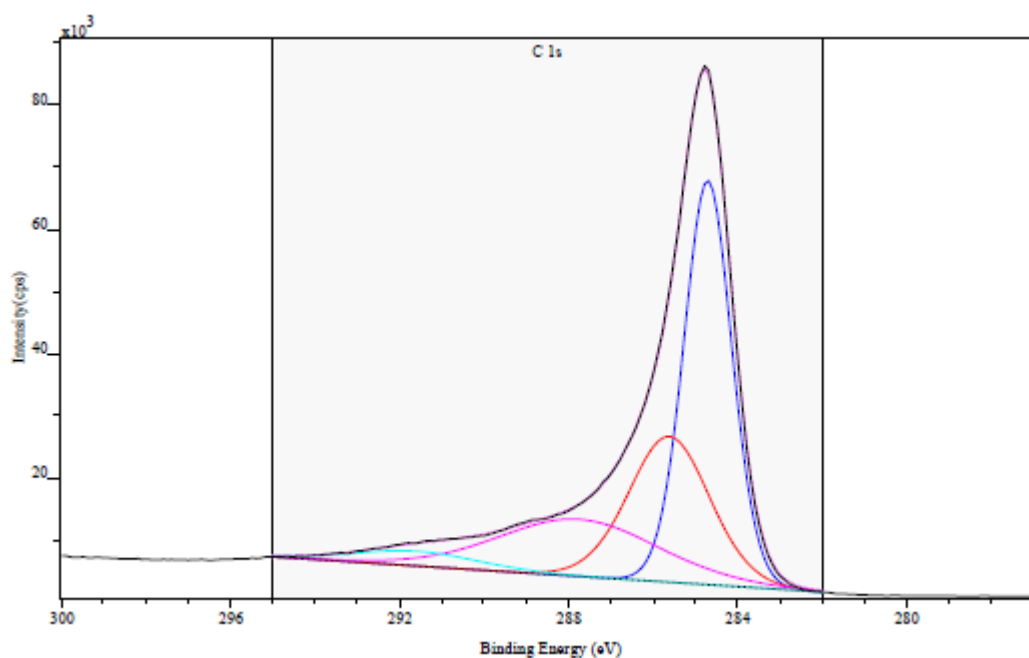


Figure S3 (3b). C 1s spectra of Pd/N-CNTs-1

Table S3 (3b). Summary of C 1s spectra of Pd/N-CNTs-1

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	284.743	1.297	92897.4	0.278	12.011	45.87	45.87
2	285.625	2.213	56818.4	0.278	12.011	28.06	28.06
3	287.777	4.371	43967.5	0.278	12.011	21.73	21.73
4	291.599	3.391	8777.8	0.278	12.011	4.34	4.34

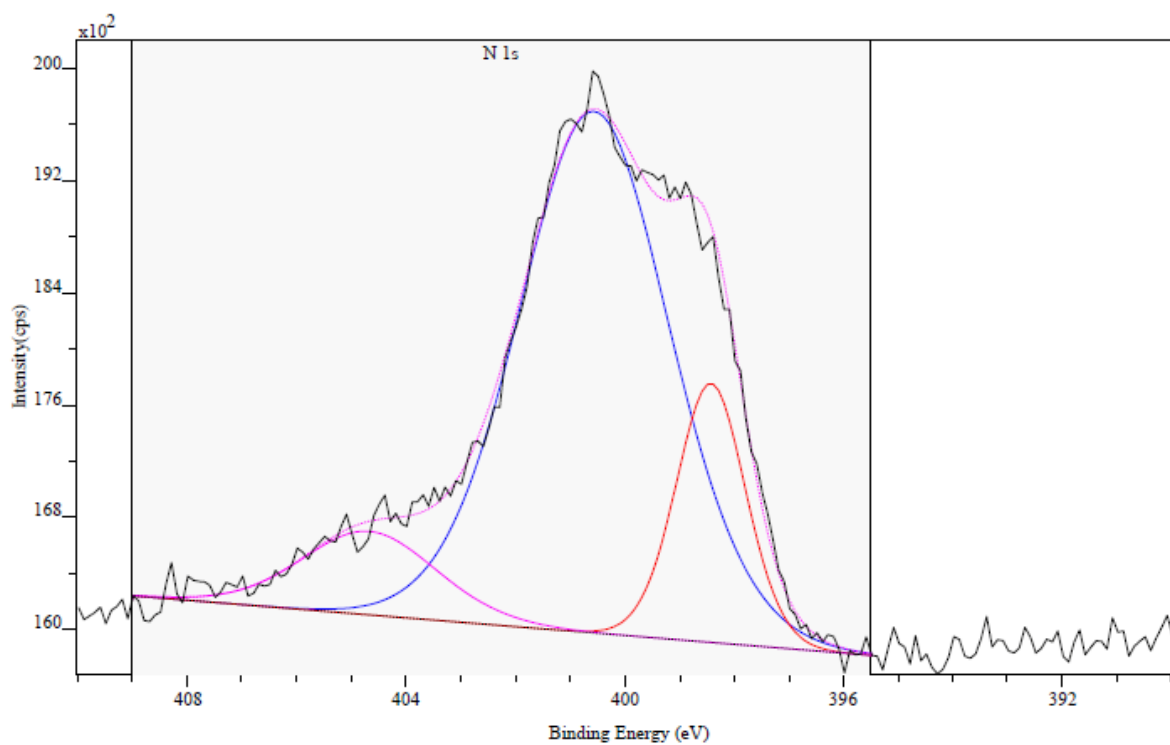


Figure S3 (3c). N 1s spectra of Pd/N-CNTs-1

Table S3 (3c). Summary of N 1s spectra of Pd/N-CNTs-1

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	400.595	3.182	12996.5	0.477	14.007	72.87	72.87
2	398.416	1.471	2974.7	0.477	14.007	16.68	16.68
3	404.712	2.854	1864.9	0.477	14.007	10.46	10.46

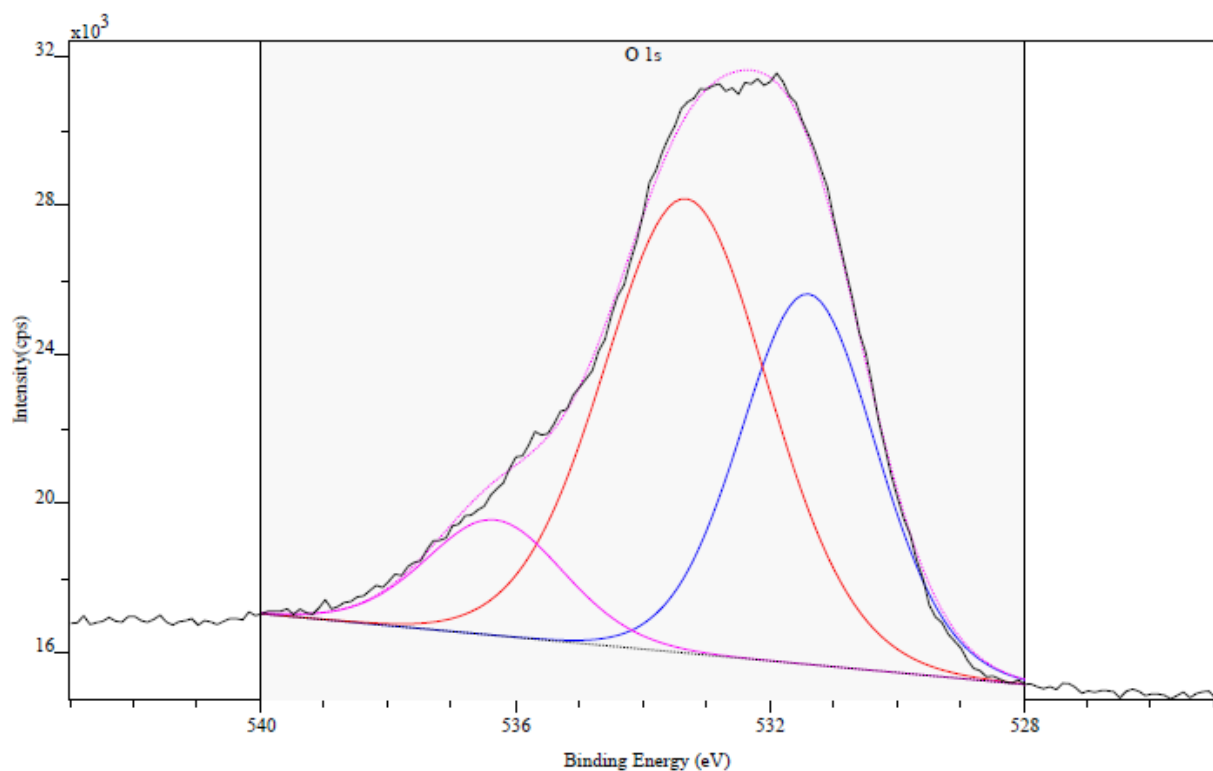


Figure S3 (3d). O 1s spectra of Pd/N-CNTs-1

Table S3 (3d). Summary of O 1s spectra of Pd/N-CNTs-1

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	531.393	2.487	27160.2	0.780	15.999	35.68	35.68
2	533.329	3.017	40417.0	0.780	15.999	53.08	53.08
3	536.334	2.516	8564.2	0.780	15.999	11.24	11.24

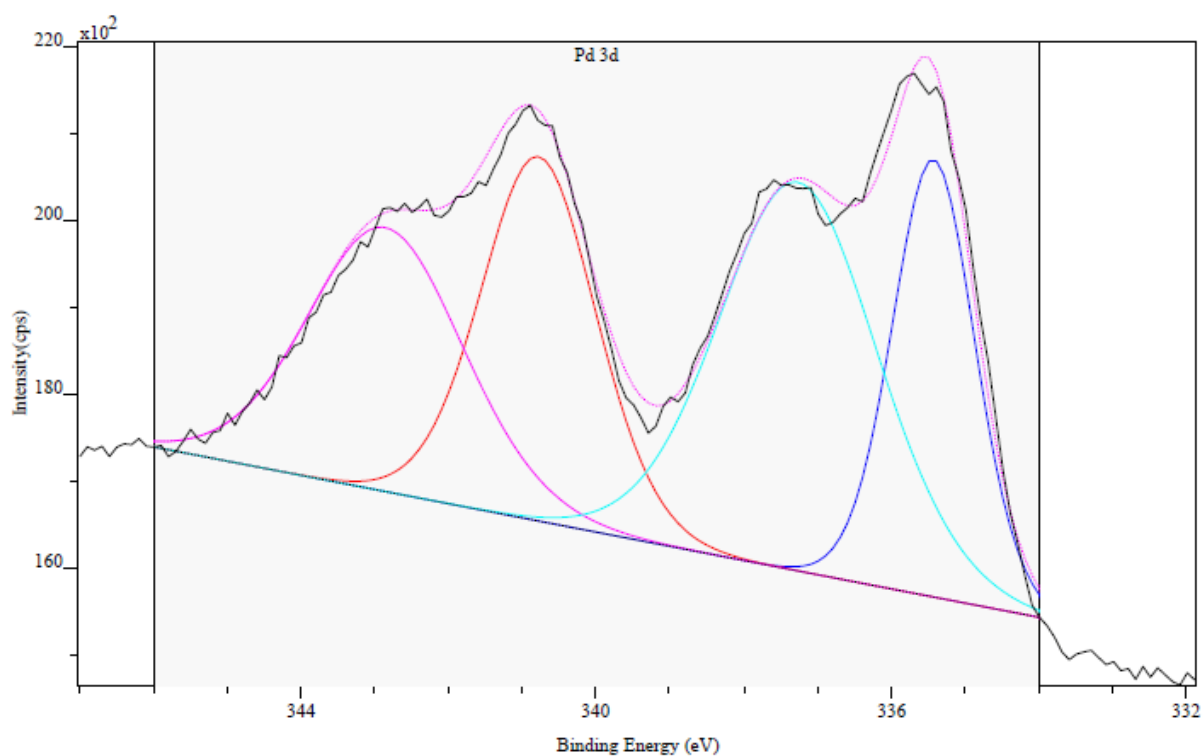


Figure S3 (3e). Pd 3d spectra of Pd/N-CNTs-1

Table S3 (3e). Summary of Pd 3d spectra of Pd/N-CNTs-1

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	335.435	1.300	7198.1	5.356	106.534	20.01	20.01
2	340.779	1.810	8332.6	5.356	106.534	23.13	23.13
3	342.848	2.458	8193.3	5.356	106.534	22.73	22.73
4	337.289	2.499	12289.0	5.356	106.534	34.14	34.14

S3(4). XPS spectra of Pd/N-CNTs-2

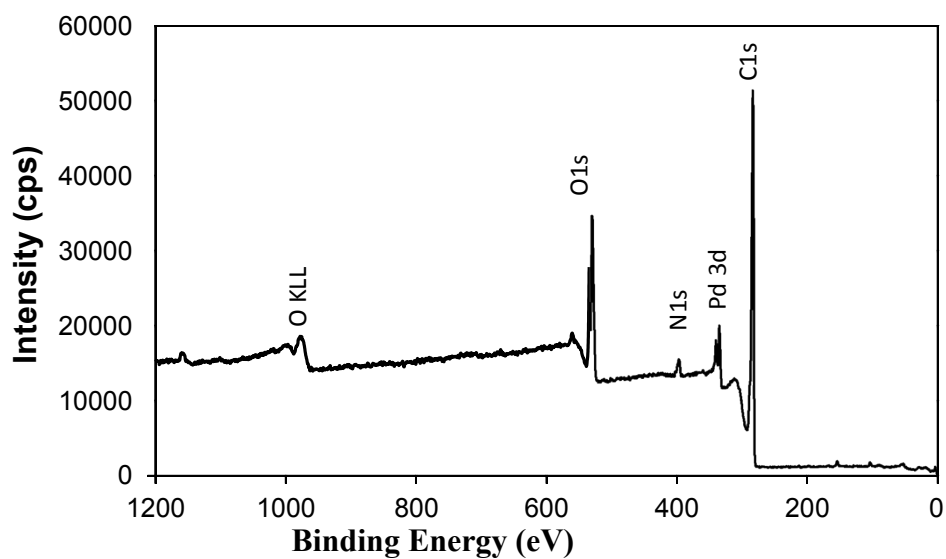


Figure S3 (4a). XPS spectra of Pd/N-CNTs-2

Table S3 (4a). Summary of XPS spectra of Pd/N-CNTs-2

Peak	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conn %
C 1s	285	3.653	200690.0	0.278	12.011	83.07	73.96
N 1s	399	4.828	10807.0	0.477	14.007	2.53	2.62
Pd 3d	337	2.678	44772.0	5.356	106.534	0.94	7.46
O 1s	532	4.082	92125.0	0.780	15.999	10.48	10.22

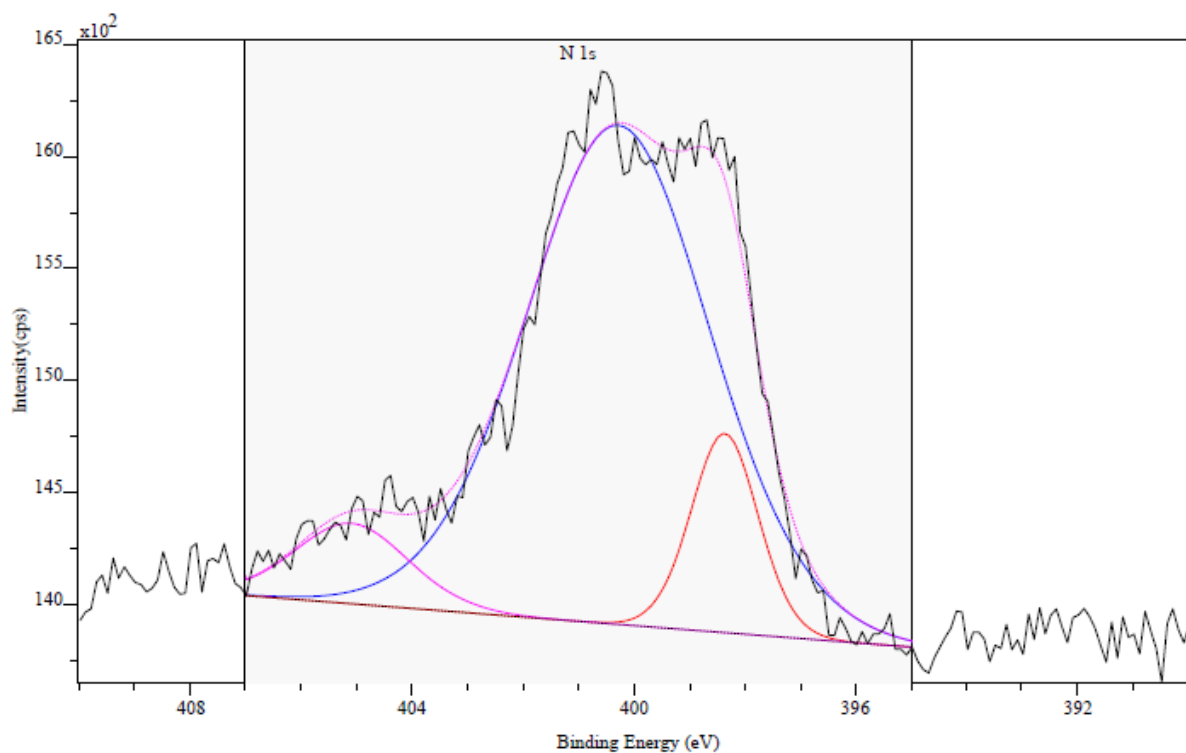


Figure S3 (4b). N 1s spectra of Pd/N-CNTs-2

Table S3 (4b). Summary of N 1s spectra of Pd/N-CNTs-2

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	400.312	3.859	9431.7	0.477	14.007	80.37	80.37
2	398.387	1.397	1366.6	0.477	14.007	11.64	11.64
3	405.125	2.377	936.7	0.477	14.007	7.98	7.98

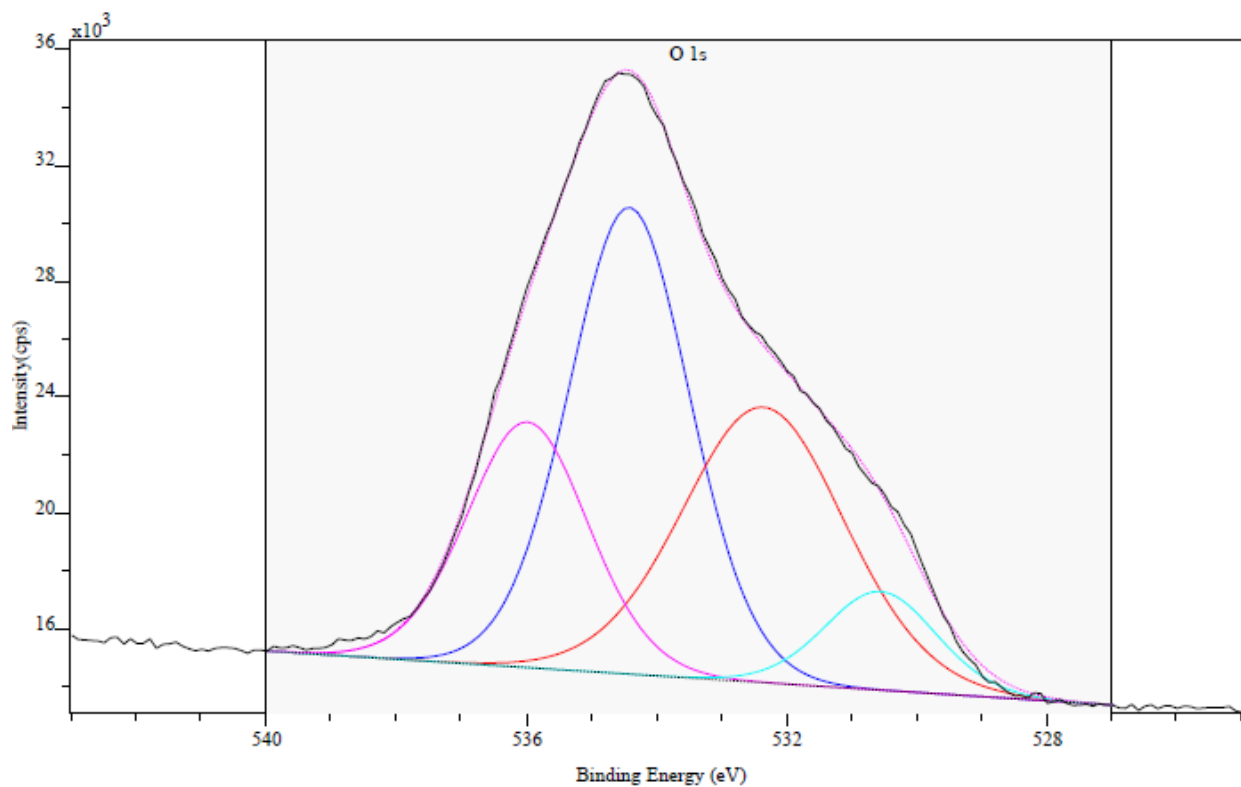


Figure S3 (4c). O 1s spectra of Pd/N-CNTs-2

Table S3 (4c). Summary of O 1s spectra of Pd/N-CNTs-2

Band	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc
1	534.431	2.165	38249.0	0.780	15.999	39.77	39.77
2	532.370	2.911	30330.1	0.780	15.999	31.55	31.55
3	536.000	2.165	20134.2	0.780	15.999	20.93	20.93
4	530.559	2.000	7454.0	0.780	15.999	7.75	7.75

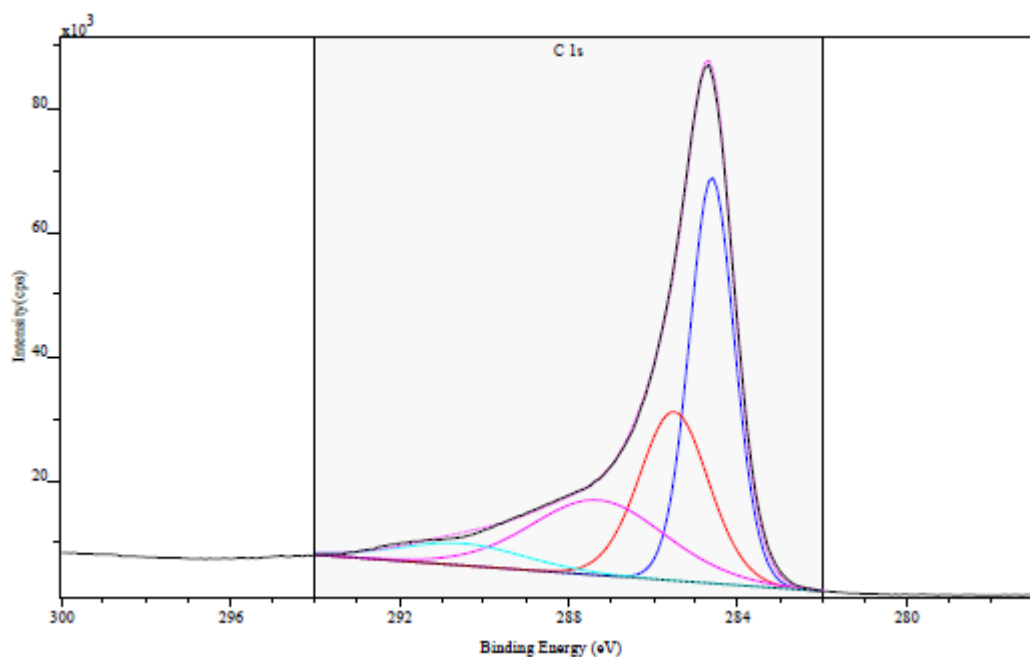


Figure S3 (4d). C 1s spectra of Pd/N-CNTs-2

Table S3 (4d). Summary of C 1s spectra of Pd/N-CNTs-2

Band	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	284.626	1.231	88666.3	0.278	12.011	42.62	42.62
2	285.524	1.900	56800.8	0.278	12.011	27.31	27.31
3	287.319	3.687	48917.9	0.278	12.011	23.53	23.53
4	290.561	3.500	13561.4	0.278	12.011	6.53	6.53

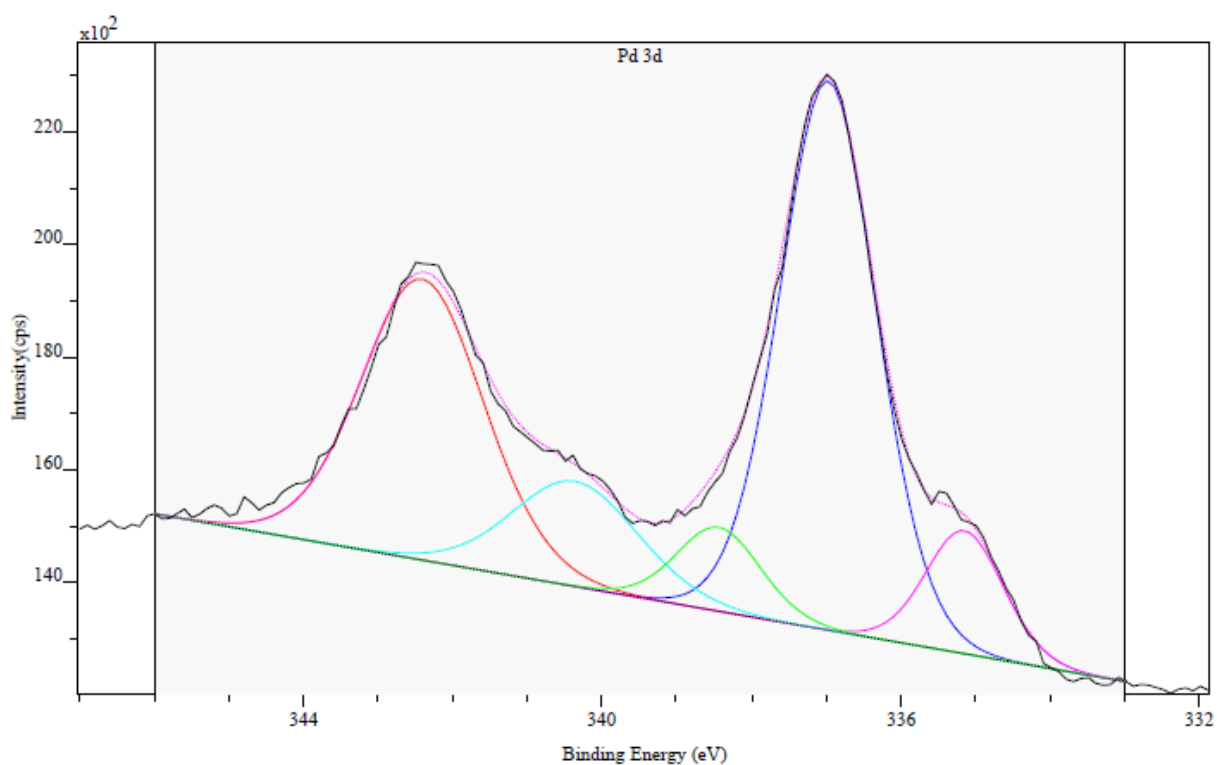


Figure S3 (4e). Pd 3d spectra of Pd/N-CNTs-2

Table S3 (4e). Summary of Pd 3d spectra of Pd/N-CNTs-2

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	336.966	1.500	16093.2	5.356	106.534	45.29	45.29
2	342.409	1.902	10429.3	5.356	106.534	29.30	29.30
3	335.166	1.200	2897.6	5.356	106.534	8.16	8.16
4	340.372	1.953	4010.6	5.356	106.534	11.27	11.27
5	338.455	1.291	2125.9	5.356	106.534	5.98	5.98

S3(5). XPS spectra of Pd/CNTs

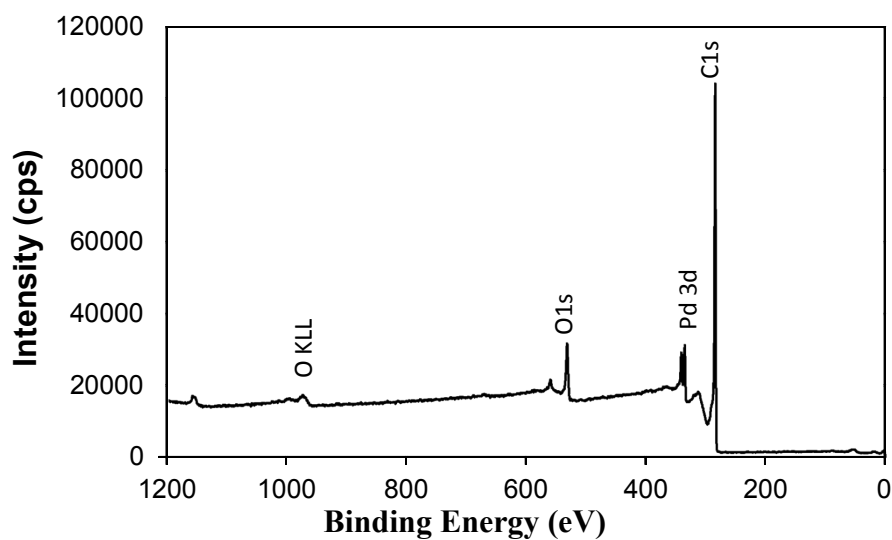


Figure S3 (5a). XPS spectra of Pd/CNTs

Table S3 (5a). Summary of XPS spectra of Pd/CNTs

Peak	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conn %
C 1s	284	2.144	293844.0	0.278	12.011	92.22	83.03
Pd 3d	335	2.383	69642.0	5.356	106.534	1.13	8.99
O 1s	532	3.860	61397.0	0.780	15.999	6.66	7.98

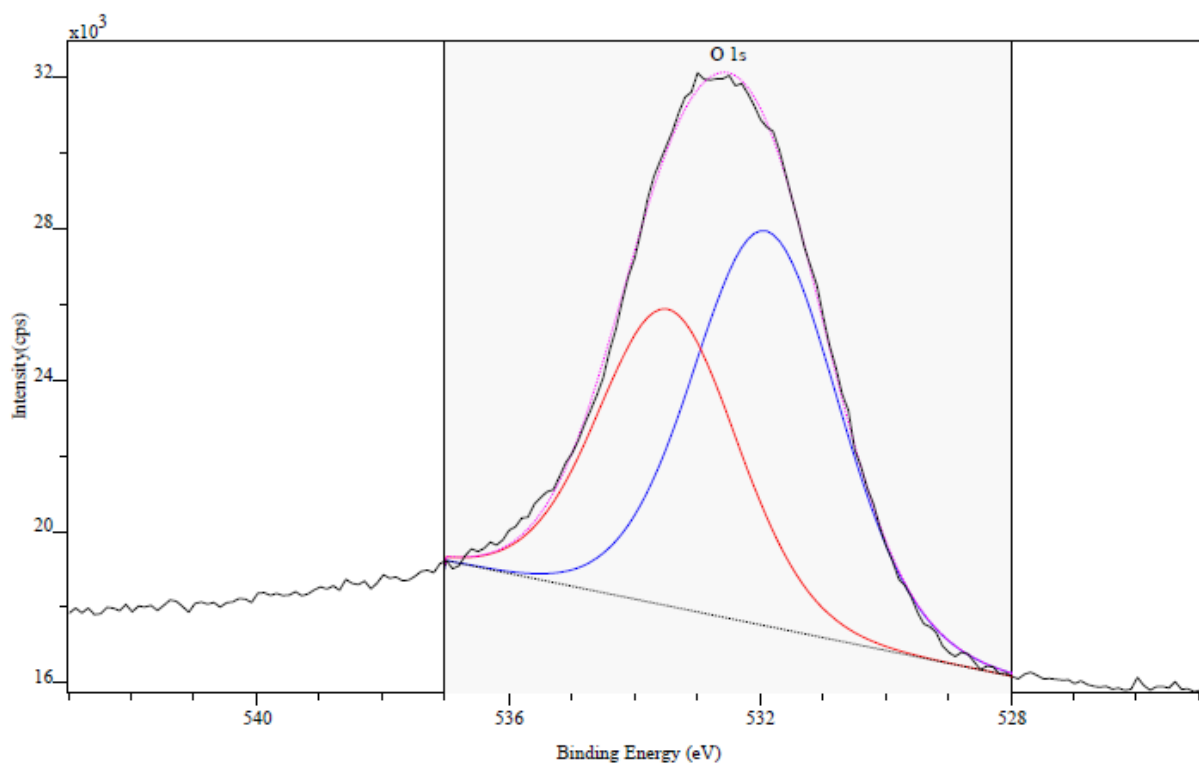


Figure S3 (5b). O 1s spectra of Pd/CNTs

Table S3 (5b). Summary of O 1s spectra of Pd/CNTs

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	531.925	2.690	30860.6	0.780	15.999	58.24	58.24
2	533.486	2.568	22129.1	0.780	15.999	41.76	41.76

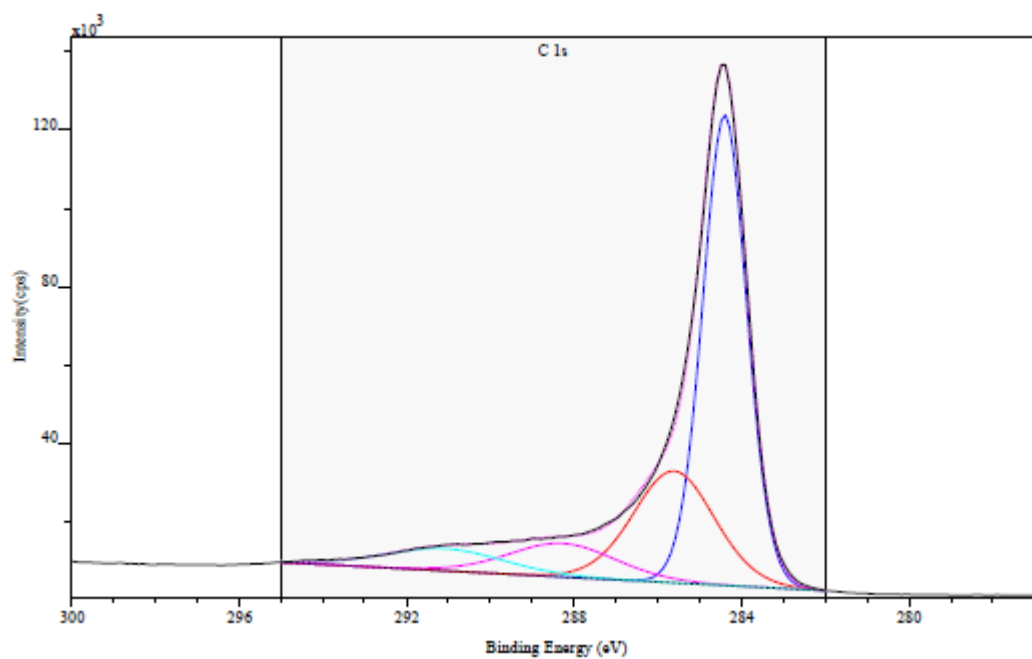


Figure S3 (5c). C 1s spectra of Pd/CNTs

Table S3 (5c). Summary of C 1s spectra of Pd/CNTs

Band	Position BE (eV)	FWHM (ev)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	284.418	1.208	159796.3	0.278	12.011	57.48	57.48
2	285.627	2.235	69976.4	0.278	12.011	25.18	25.18
3	288.298	2.948	27689.2	0.278	12.011	9.97	9.97
4	291.105	3.301	20465.8	0.278	12.011	7.37	7.37

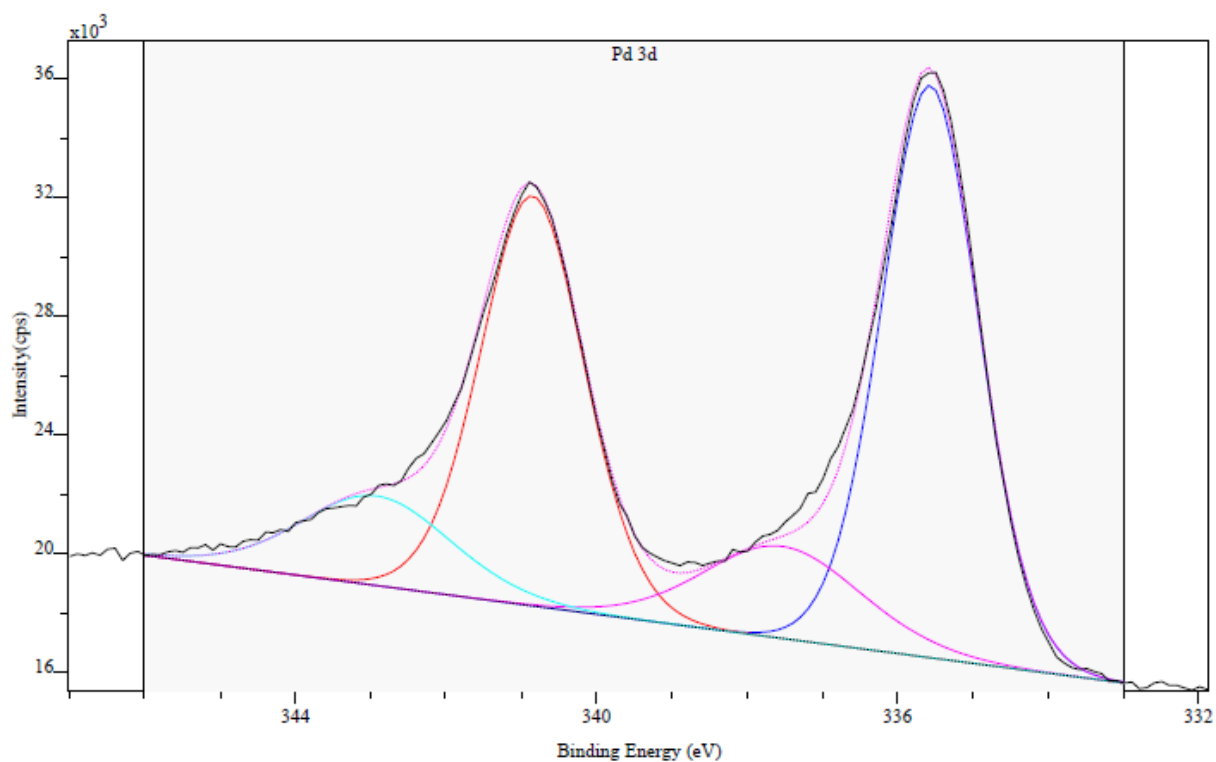


Figure S3 (5d). Pd 3d spectra of Pd/CNTs

Table S3 (5d). Summary of Pd 3d spectra of Pd/CNTs

Band	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
1	335.561	1.500	31746.3	5.356	106.534	44.11	44.11
2	340.882	1.600	24318.1	5.356	106.534	33.74	33.74
3	337.564	2.437	8300.4	5.356	106.534	11.53	11.53
4	342.957	2.307	7658.1	5.356	106.534	10.62	10.62

Supplementary Information S4

O 1s analysis

The O 1s spectra of N-CNTs and CNTs exhibited broad peaks between 531-536 eV as depicted in Figure S4 (1). Deconvolution of these broad peaks revealed that N-CNTs-1 and N-CNTs-2 had an extra peak at 536.0-536.3 eV coded as O1, which was assigned to oxygen present in esters (Supplementary Information S3). Increase in the quantity of C3 directly correlated with the increase of O1 (Table 1). Since both species were only present in N-CNTs-1 and N-CNTs-2, it is possible that they originated from the same compound present in N-CNTs-1 and N-CNTs-2 alone. This compound was possibly a lactone because, C3 was assigned to carbonyls in quinones, lactones or ketones and O1 was ascribed to oxygen in esters. Lactones have been known to be introduced into N-CNTs and CNTs by acid treatment with nitric acid.³² However, in this case, a similar procedure was used in the acid treatment of all supports; therefore, the possibility of introducing lactone groups in N-CNTs-1 and N-CNTs-2 by only acid treatment was ruled out. Thus, we propose that the lactones originated from the reaction between oxygen present in ethylbenzoate and hydrocarbons present in the synthesis precursors.

Table S4 (1). Summary of C 1s and O 1s XPS spectra of Pd/N-CNTs and Pd/CNTs.

Sample	C at.%				O at.%	
	C1	C2	C3	C4	O Total	O1
Pd/N-CNTs-0	52.7	33.8	-	8.9	10.4	-
Pd/N-CNTs-1	45.9	28.6	21.7	-	8.3	11.2
Pd/N-CNTs-2	42.4	27.3	23.5	-	13.5	20.9
Pd/CNTs	57.4	25.1	-	10.0	6.6	-

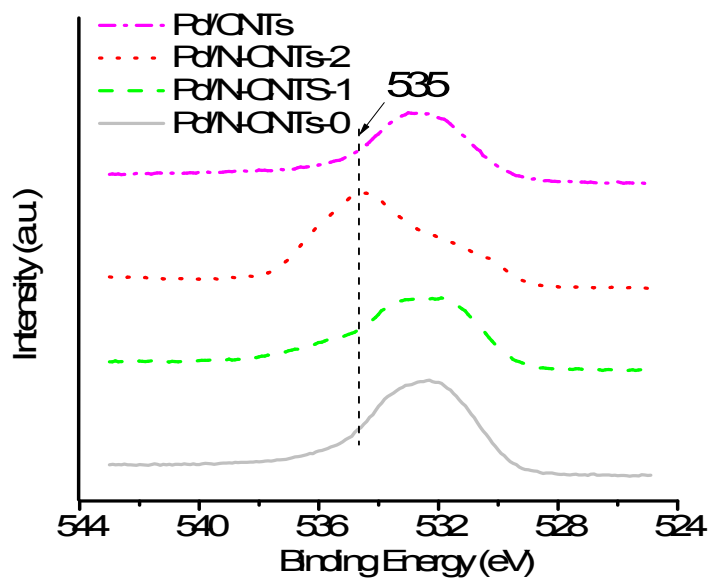


Figure S4 (1). O 1s XPS spectra of CNTs and N-CNTs synthesized by using 0-2 wt.% oxygen in acetonitrile.

N₂-adsorption-desorption analysis

Table S4 (2). Textural properties of as-synthesized and purified supports.

Support	SA of as-synthesized support (m ² g ⁻¹)	SA of purified support (m ² g ⁻¹)	Pore size distribution of as-synthesized support (nm)	Pore size distribution of purified support (nm)
CNTs	14	40	2.8	4.1
N-CNTs-0	24	38	3.8	4.5
N-CNTs-1	14	64	3.9	4.1
N-CNTs-2	15	33	3.9	4.1

SA: surface area

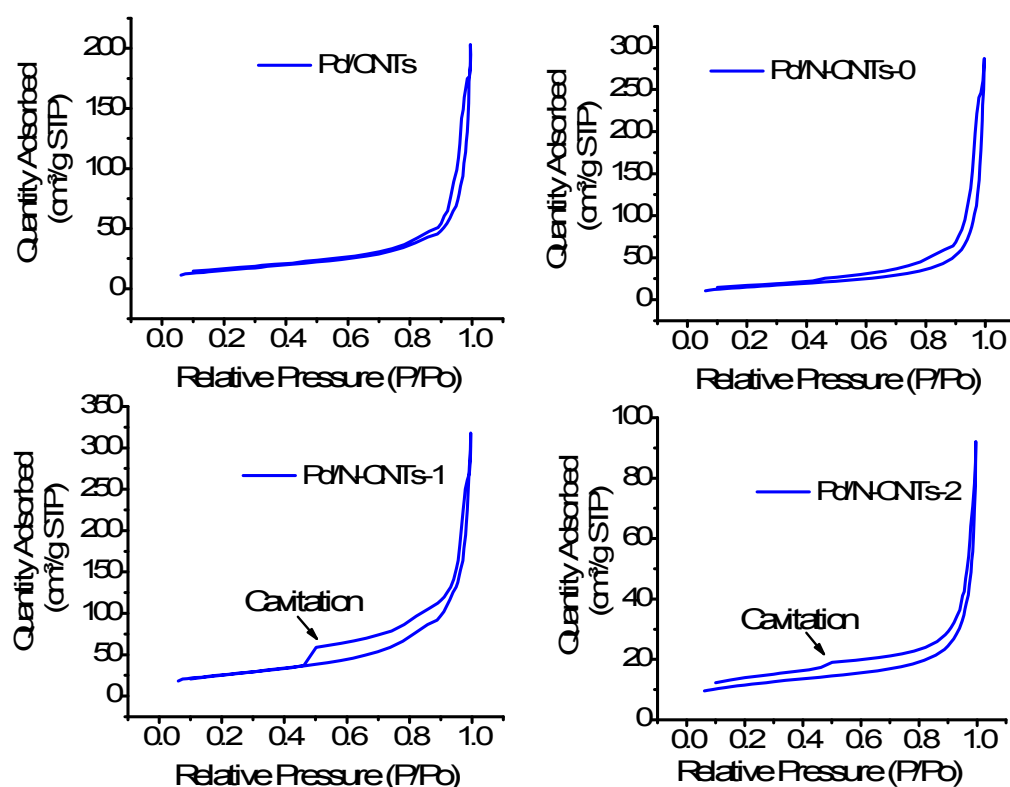


Figure S4 (2). N₂ adsorption–desorption isotherms of Pd/CNTs and Pd/N-CNTs.

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Supplementary Information S5

Table S5(a): The surface area and pore size distribution of Pd/AC.

Catalyst	Surface area (m ² g ⁻¹)	Pore size distribution (nm)
Pd/AC	890	3.9

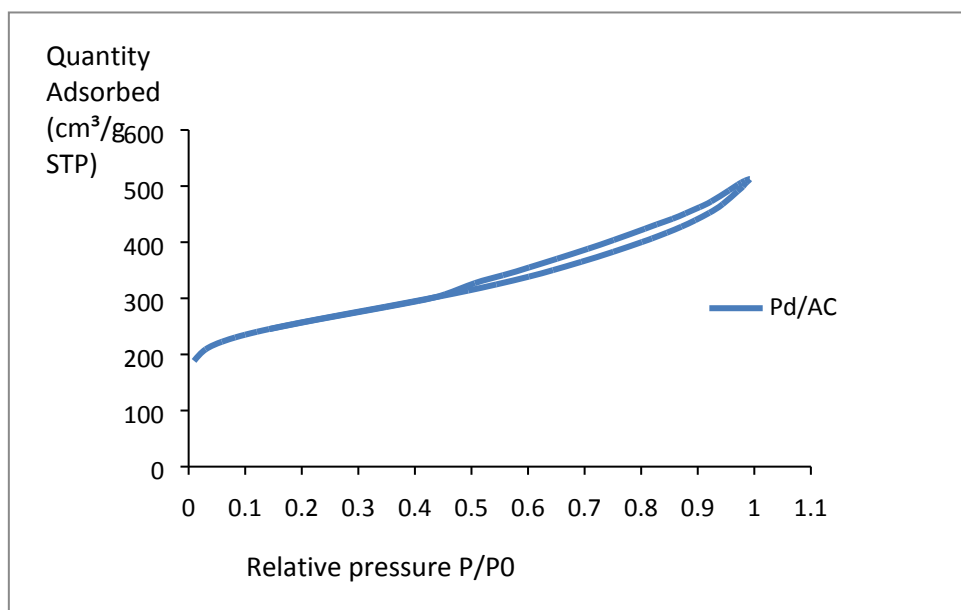


Figure S5 (b): The N₂ adsorption–desorption isotherms of Pd/AC.

Supplementary Information S6

TEM analysis of Pd/AC

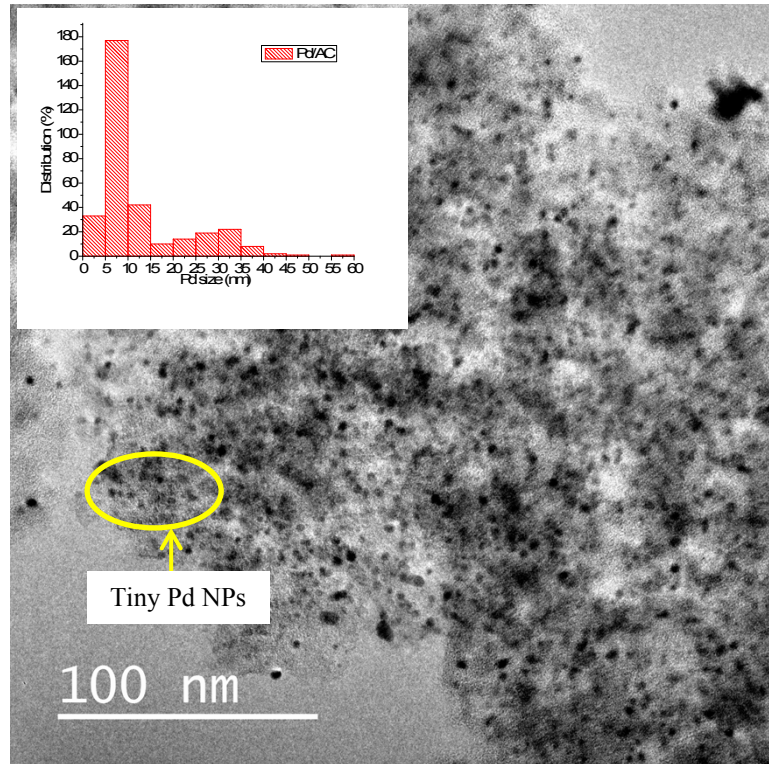


Figure S6 (a): TEM image of Pd/AC.

Hydrogenation over Pd/AC

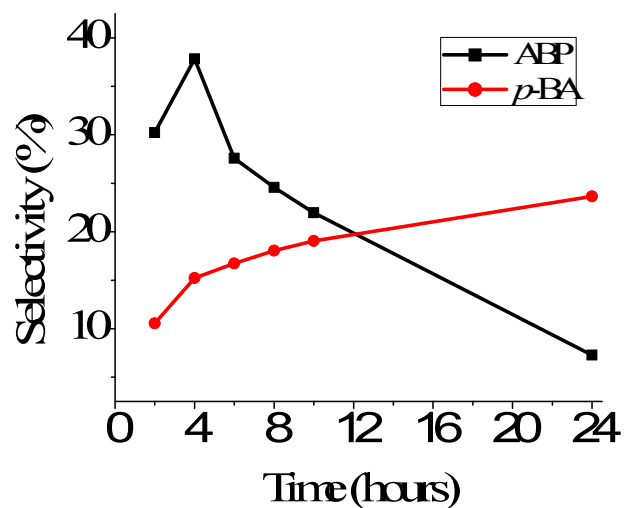


Figure S6 (b): Selectivity towards aminobenzophenone (ABP) and *p*-benzylaniline (*p*-BA) over Pd/AC.

Supplementary Information S7

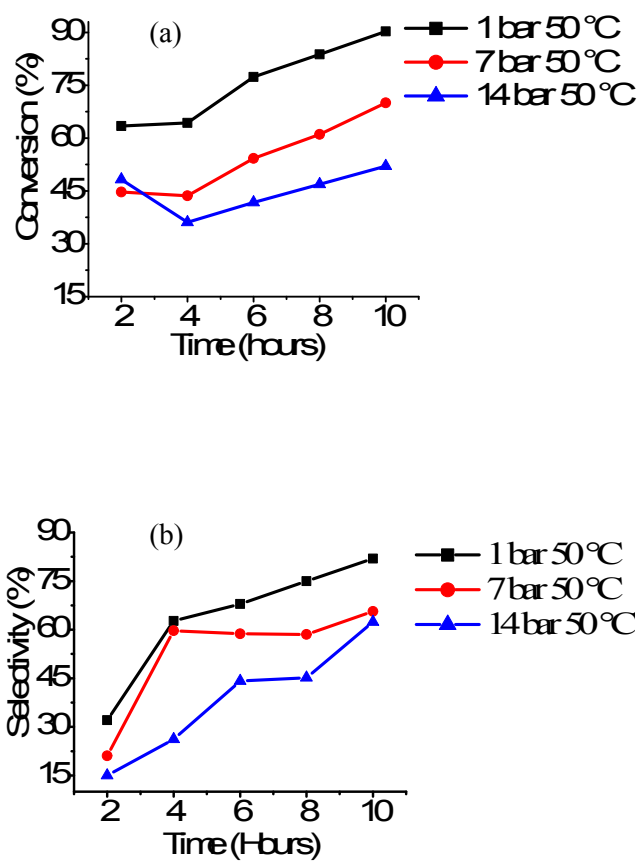


Figure S7. The effect of pressure on (a) catalytic activity of Pd/N-CNTs-2 and (b) selectivity over Pd/N-CNTs-2.

Supplementary Information S8

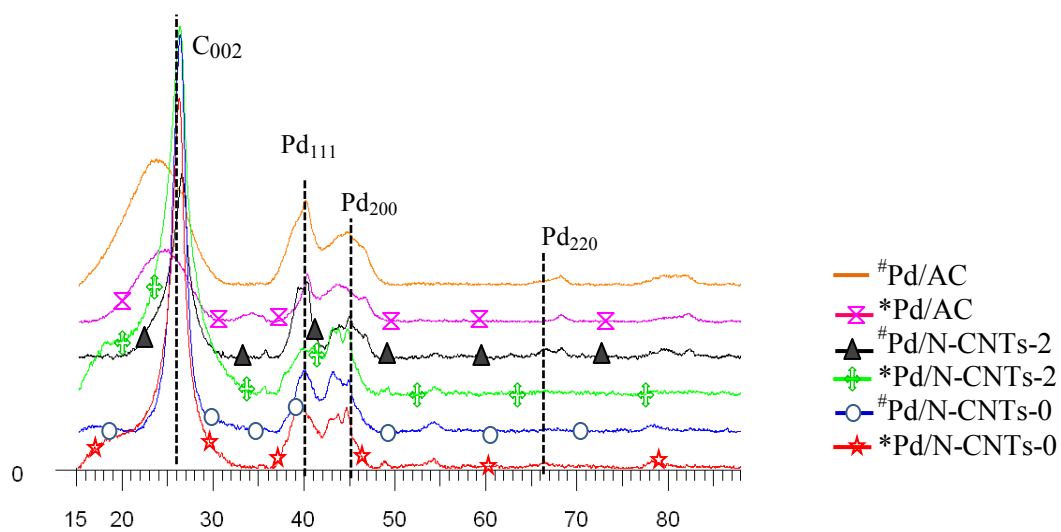


Figure S8. XRD diffractograms of used and unused Pd/AC, Pd/N-CNTs-0 and Pd/N-CNTs-2.

(*): Fresh catalyst and (#): used catalyst.