Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information for "Understanding the role of post-CCVD synthetic impurities, functional groups and functionalization-based oxidation debris on the behavior of carbon nanotubes as a catalyst support in cyclohexene hydrogenation over Pd nanoparticles"

R. Puskas,[a] A. Sápi,[*a] Á. Kukovecz,[a,b] and Z. Kónya[a,c]

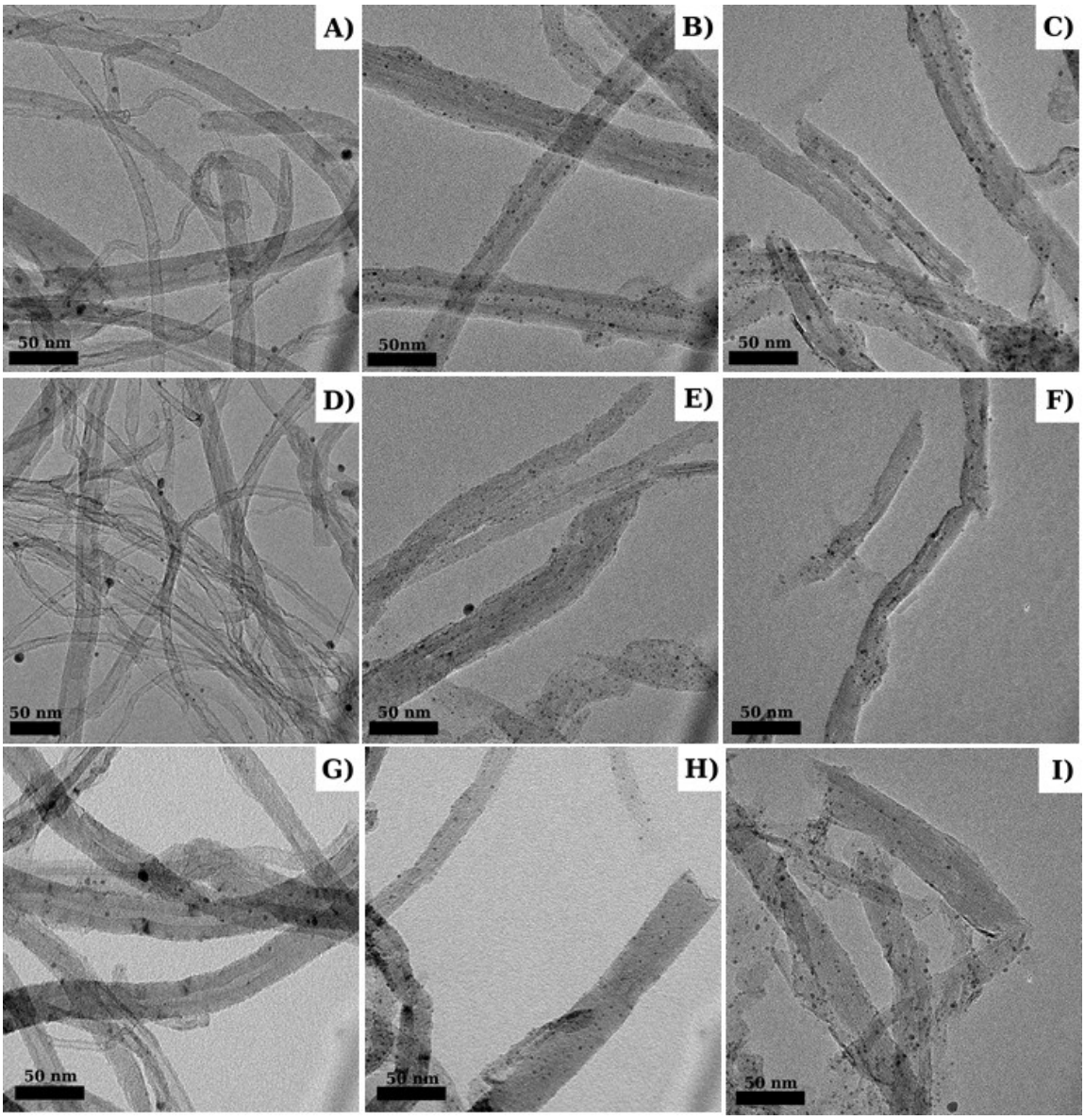


Fig. S1 TEM micrographs of A) Pd-CNT-BW-0h; B) Pd-CNT-BW-12h; C) Pd-CNT-BW-24h; D) Pd-CNT-NW-0h; E) Pd-CNT-NW-12h; F) Pd-CNT-NW-24h; G) Pd-CNT-AW-0h; H) Pd-CNT-AW-12h; I) Pd-CNT-AW-24h

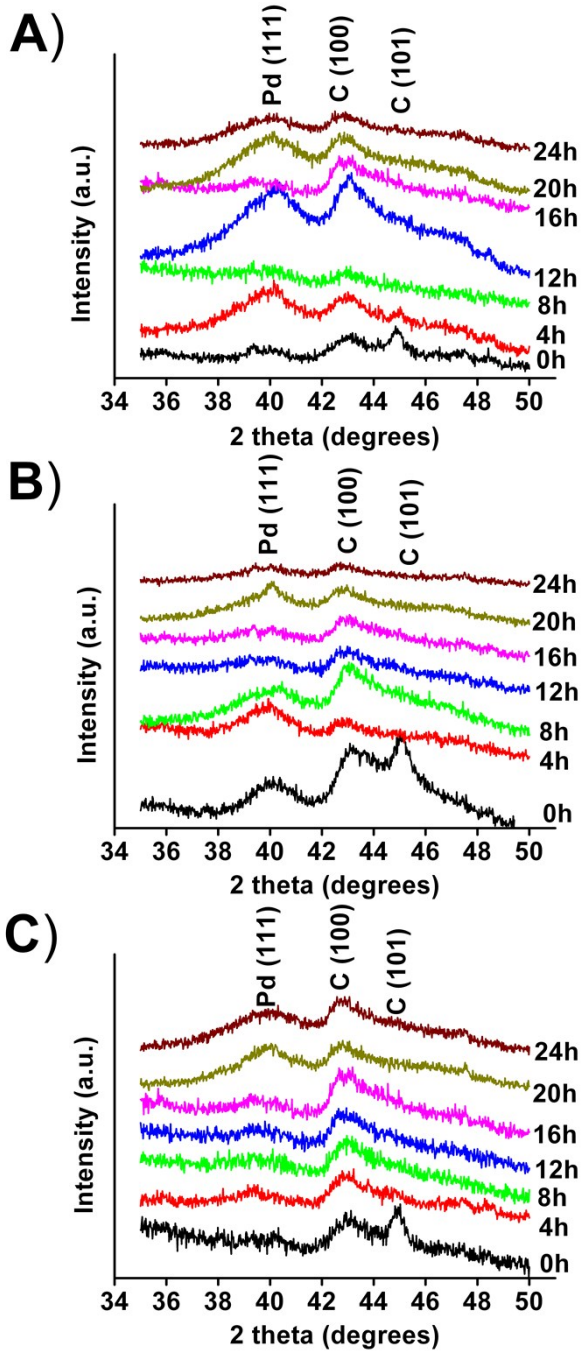
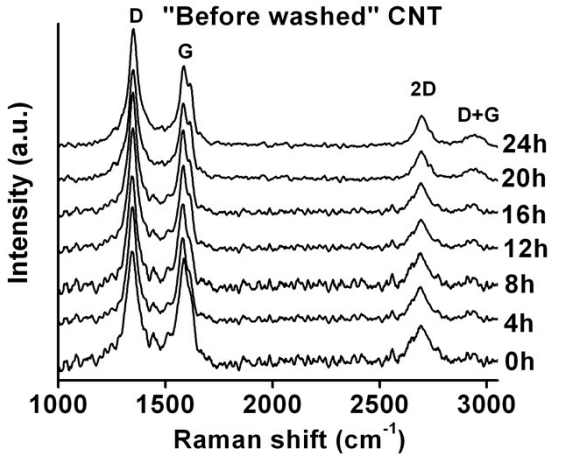
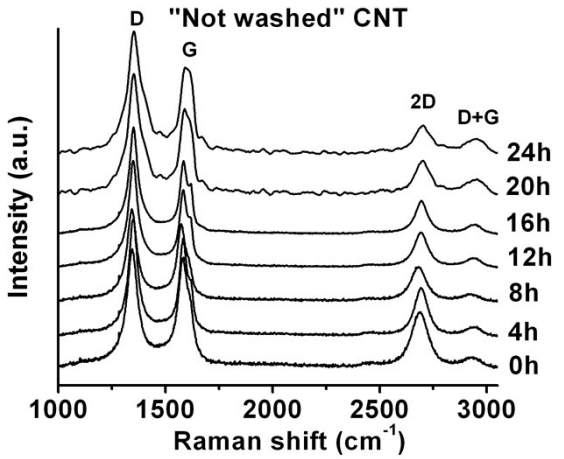


Fig. S2 XRD patterns of A) CNT-BW; B) CNT-NW; and C) CNT-AW sample series


"Before washed" CNT
D
G
2D
D+G
24h
20h
16h
12h
8h
4h
0h
Intensity (a.u.)
1000
1500
2000
2500
3000
Raman shift (cm-1)


"Not washed" CNT
D
G
2D
D+G
24h
20h
16h
12h
8h
4h
0h
Intensity (a.u.)
1000
1500
2000
2500
3000
Raman shift (cm-1)

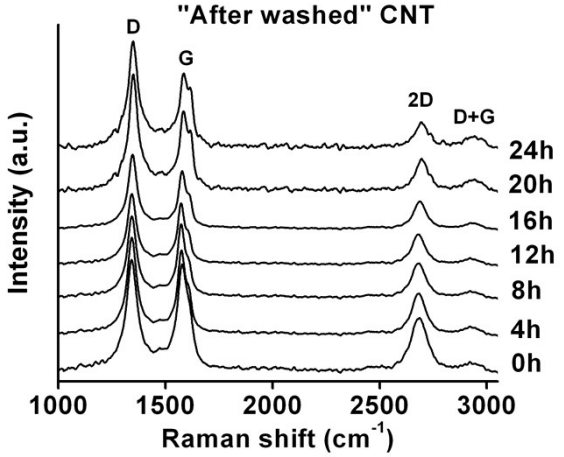

"After washed" CNT
D
G
2D
D+G
24h
20h
16h
12h
8h
4h
0h
Intensity (a.u.)
1000
1500
2000
2500
3000
Raman shift (cm-1)

Fig. S3 Raman spectra of “Before washed”, “Not washed” and “After washed” sample series

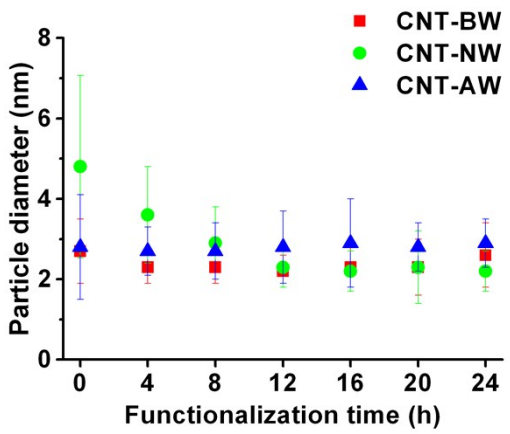


Fig. S4 Plotted average Pd nanoparticle diameters scaled manually on TEM micrograhs

Fig. S5 Photograph of the acetone after CNT washing process

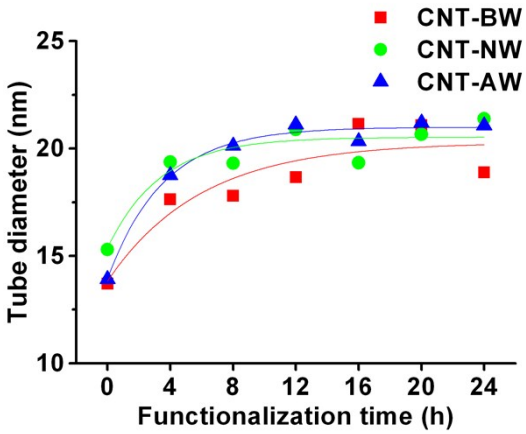


Fig. S6 The change in nanotube diameters as a function of functionalization time as scaled manually on TEM micrographs

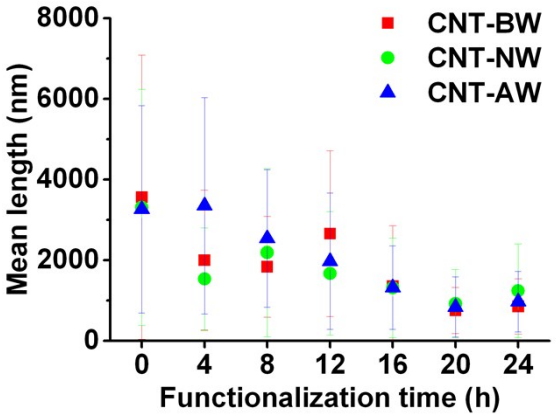


Fig. S7 The change in nanotube lengths as a function of functionalization time as scaled manually on TEM micrographs

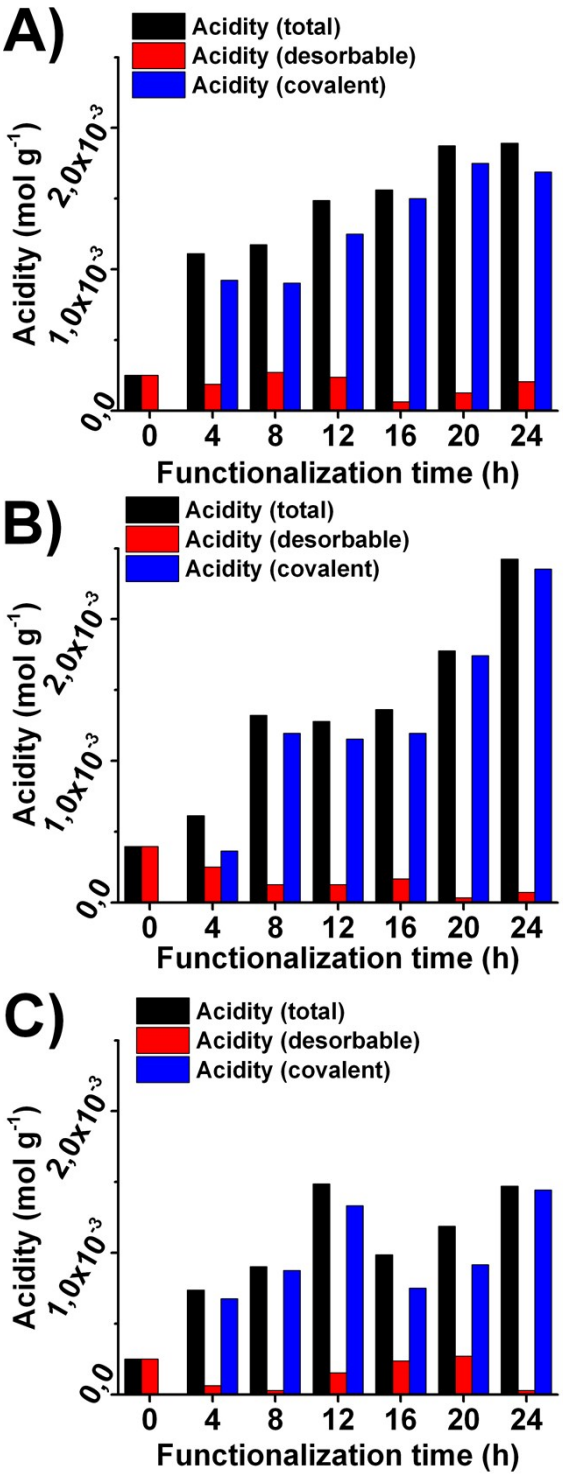


Fig. S8 Measured amount of different acidities on samples A) CNT-BW, B) CNT-NW and C) CNT-AW

Table S1: Pd content of samples measured by EDS

Oxidation time (h)	CNT-BW (wt%)	CNT-NW (wt%)	CNT-AW (wt%)
0	1.2	1.1	1.9
4	4.8	4.9	3.4
8	3.5	4.9	4.3
12	3.7	4.7	4.1
16	3.5	3.9	4.1
20	4.6	4.7	4.5
24	4.7	4.5	5

Table S2: Average particle diameters determined from manual scaling on TEM micrographs

Oxidation time (h)	CNT-BW (nm)	CNT-NW (nm)	CNT-AW (nm)
0	2.7 ± 0.8	4.8 ± 2.3	2.7 ± 0.8
4	2.3 ± 0.4	3.6 ± 1.2	2.7 ± 0.6
8	2.3 ± 0.4	2.9 ± 0.9	2.7 ± 0.7
12	2.2 ± 0.4	2.3 ± 0.5	2.8 ± 0.9
16	2.3 ± 0.5	2.2 ± 0.5	2.9 ± 0.9
20	2.3 ± 0.7	2.3 ± 0.6	2.8 ± 0.6
24	2.6 ± 0.8	2.2 ± 0.5	2.9 ± 0.6

Method for calculating turnover frequency (TOF):

The loading of the Pd on the supported catalysts was determined by an Energy Dispersive Spectroscope integrated to a Scanning Electron Microscope (SEM-EDS). The size of the Pd nanoparticles were determined by using TEM images. The number of the Pd nanoparticles loaded into the test samples were calculated by the results of TEM and SEM-EDS. The calculation of the number of the active sites was based on these results assuming Pd nanoparticles with spherical shape and Pd (111) surfaces and that of every surface Pd atom is active in the reaction. The calculation is as follows:

1. Calculation of the number of surface atoms in a particle:

    a. Calculate average volume of individual Pd nanoparticles:

$$V_{total} = \frac{4}{3}\pi\left(\frac{d_{Pd-NP}}{2}\right)^3$$

b. Calculate average volume of individual Pd nanoparticles minus the surface shell of nanoparticles

$$V_{core} = \frac{4}{3}\pi\left(\frac{d_{Pd-NP}}{2} - \frac{d_{lattice}}{2}\right)^3$$

c. Calculate the volume of a single unit cell

$$V_{unit} = (d_{lattice})^3$$

d. Calculate the number of unit cells in the surface shell of nanoparticles

$$Unitcells_{shell} = \frac{V_{shell}}{V_{unit}}$$

e. Calculate the number of atoms per unit cell

$$Atoms_{surface} = Unitcells_{shell} \times 4$$

2. Calculate the number of particles

   a. Calculate average particle volume from average particle diameters

   b. Calculate the average particle mass using the density of Pd

   c. Calculate the total mass of Pd in 0.005 g Pd-carbon sample using EDS data

   d. Calculate the number of particles ($m_{total}/m_{particle}$)

3. Calculate TOF

   a. Calculate the total number of surface atoms ($Atoms_{surface}$ x particle number)

   b. Calculate the moles of cyclohexene converted in a minute

   c. Calculate the number of conversions on a single surface atom