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Supporting information

for the article "**Oxidation, defunctionalization and catalyst life cycle of carbon nanotubes: Raman spectroscopy view**" by Sergei A. Chernyak, Anthon S. Ivanov, Konstantin I. Maslakov, Alexander V. Egorov, Zexiang Shen, Serguei S. Savilov, Valery V. Lunin

S-1. TGA data for pristine CNTs and those oxidized in nitric acid for 12 h

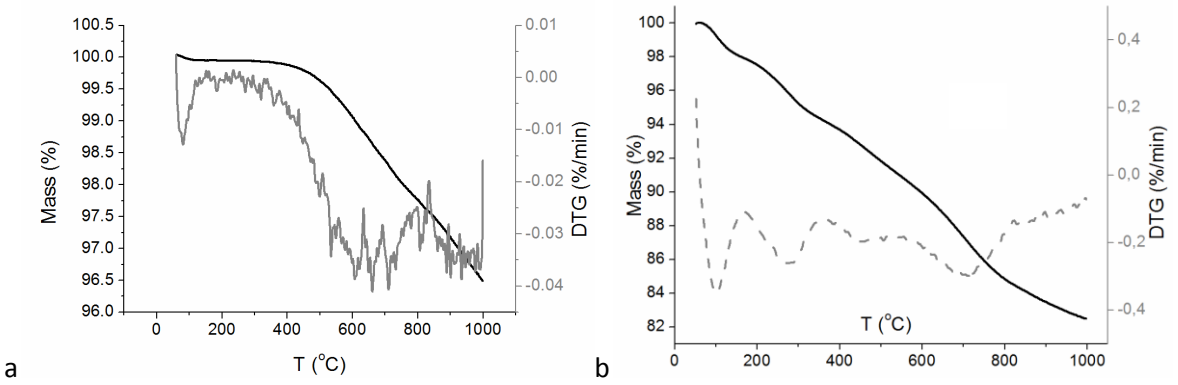
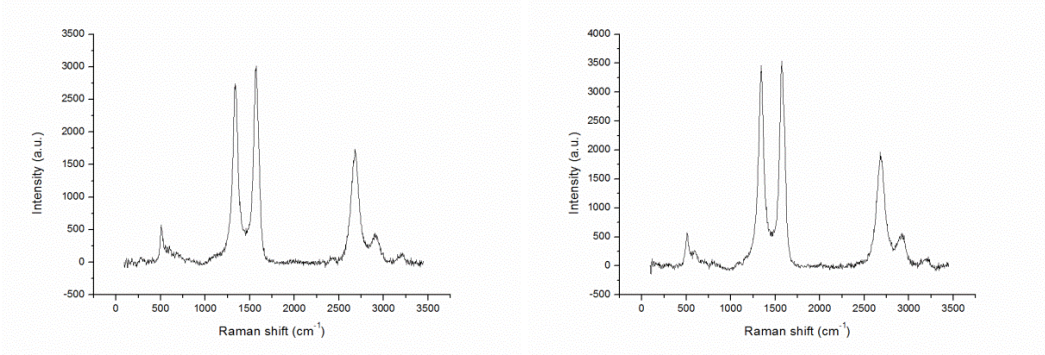
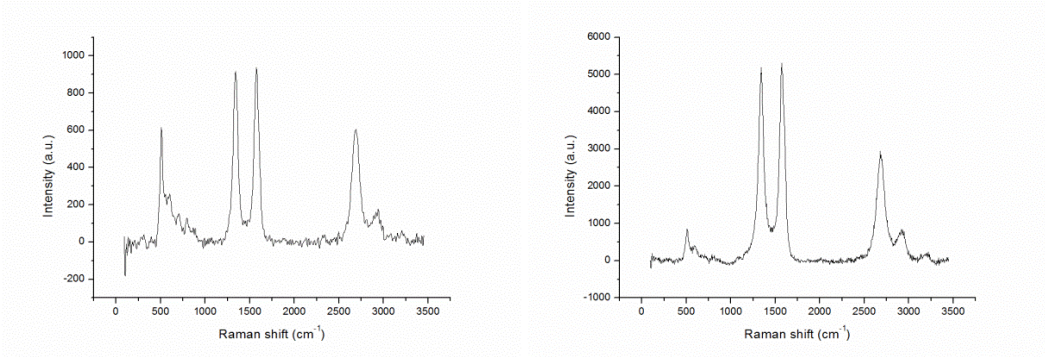


Figure S-1. a – TG and DTG curves for CNTp obtained in air flow at heating rate of 10°/min ; b – TG and DTG curves for CNT12 obtained in Ar flow at heating rate of 10°/min

S-2. Raman spectra

a





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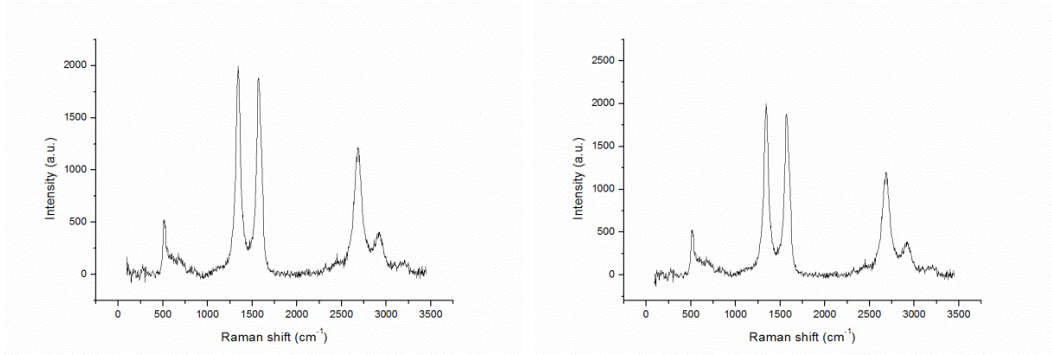

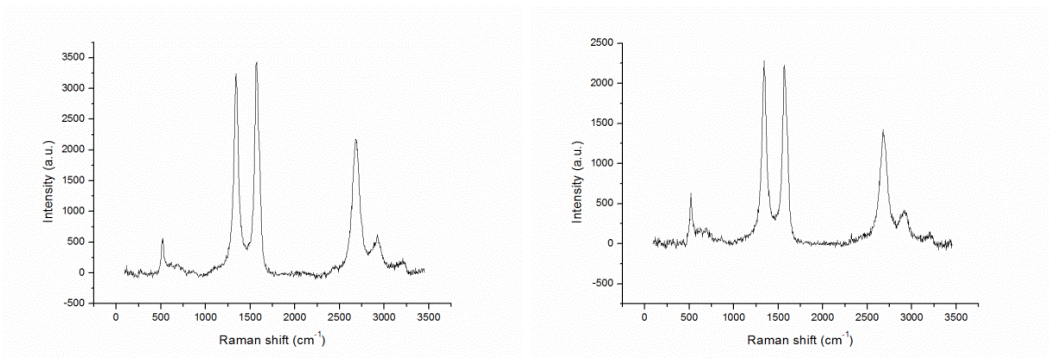

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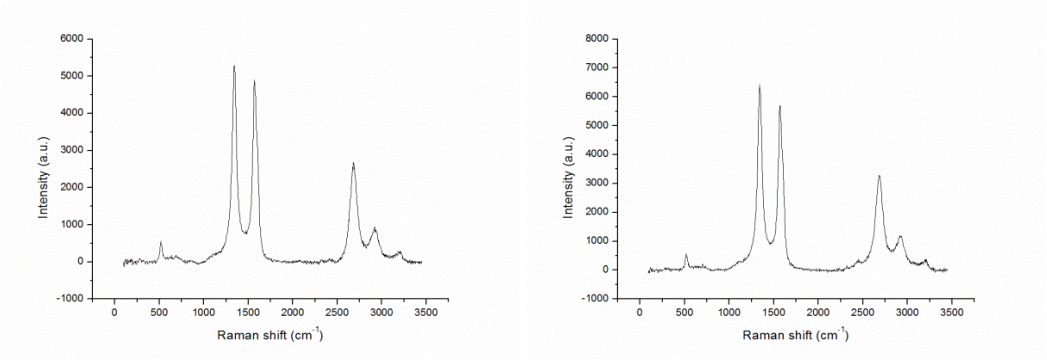
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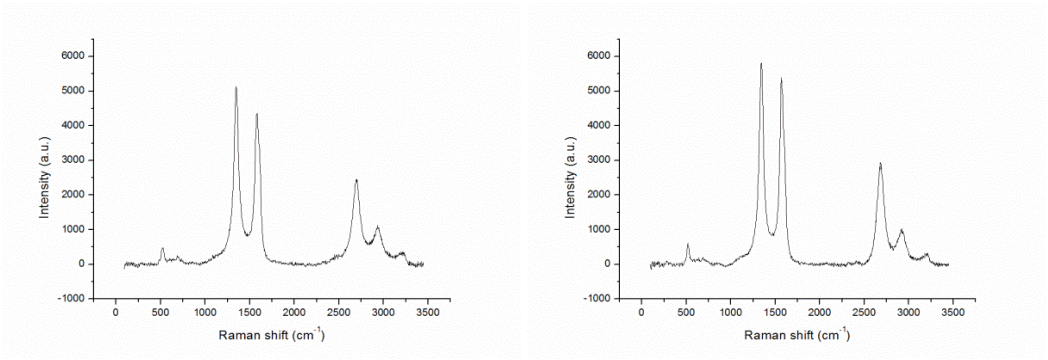
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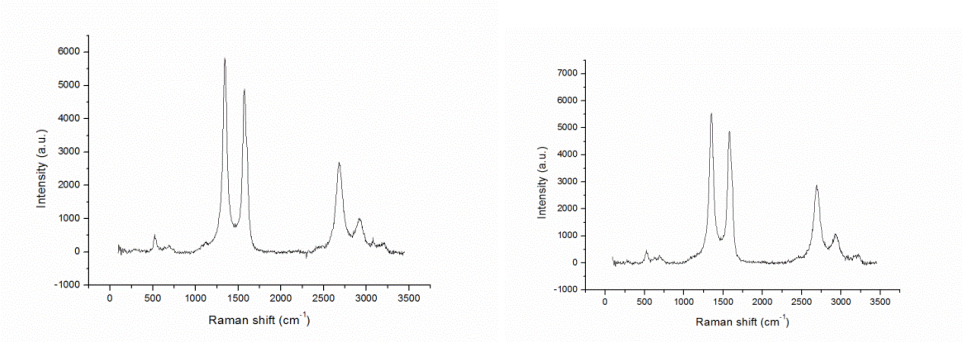
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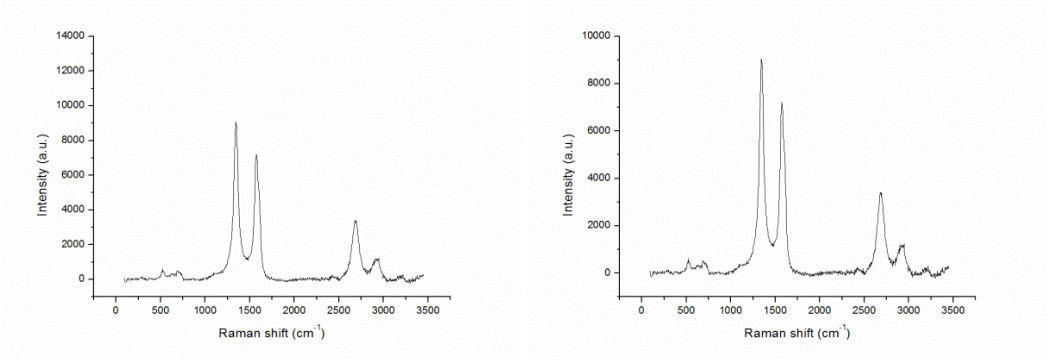
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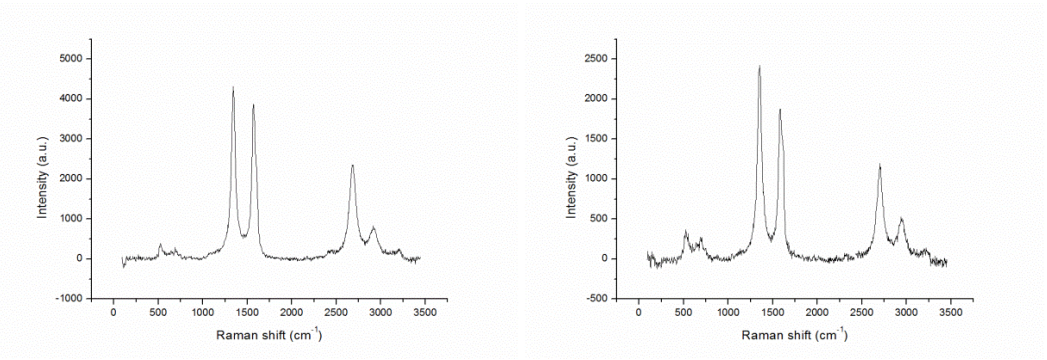
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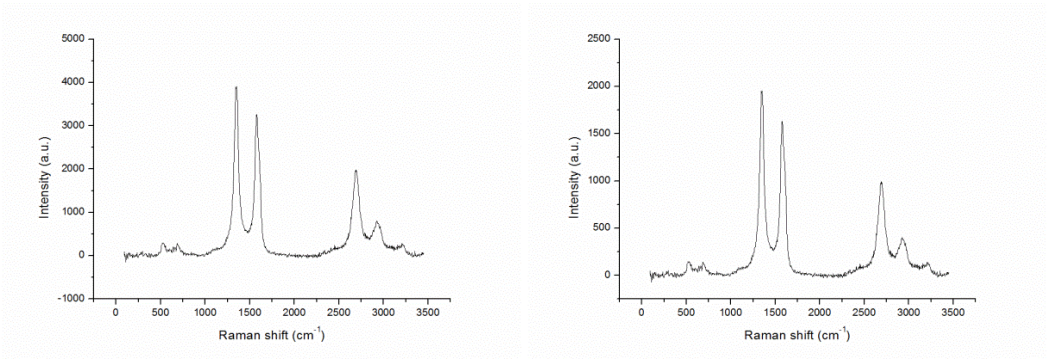
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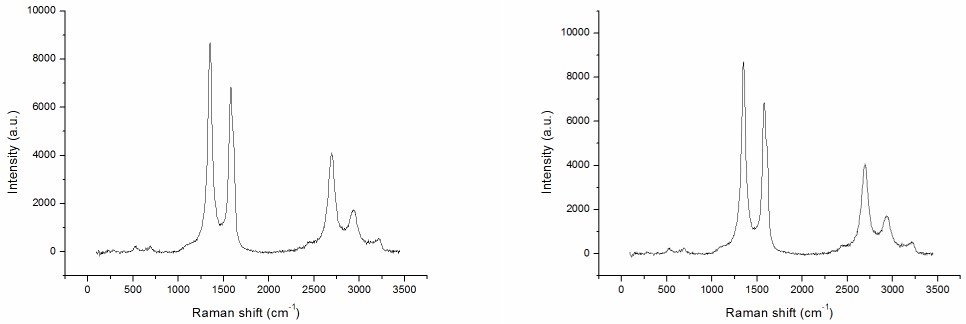
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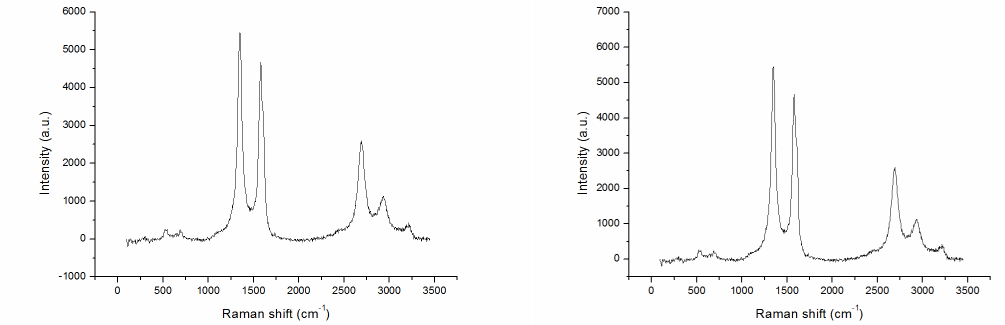
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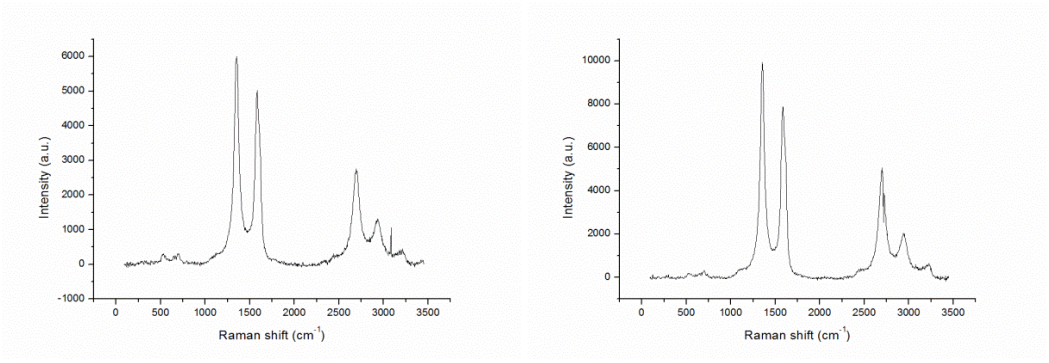

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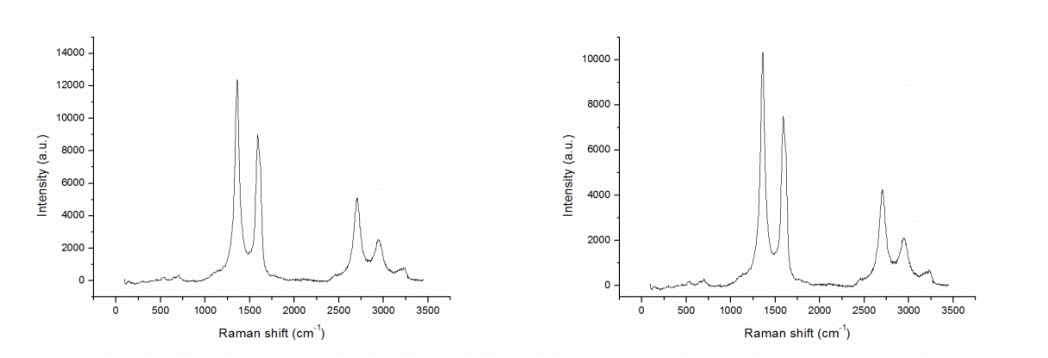
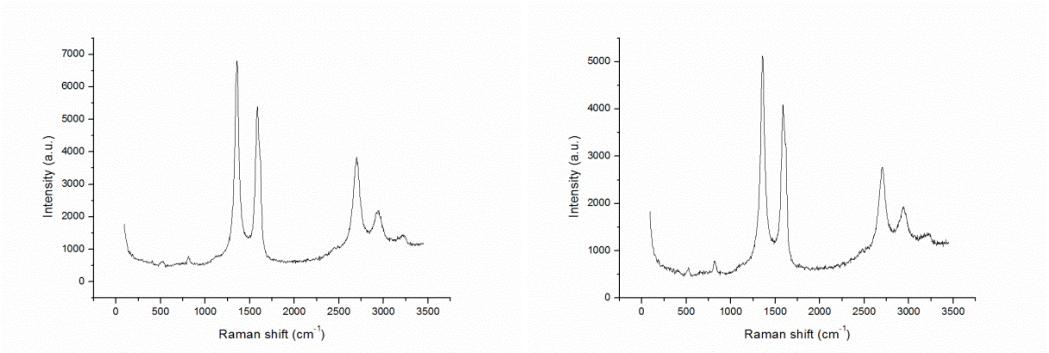
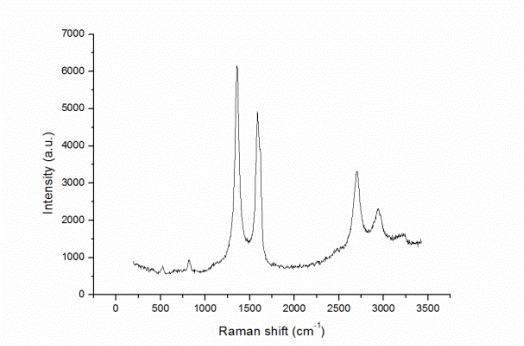
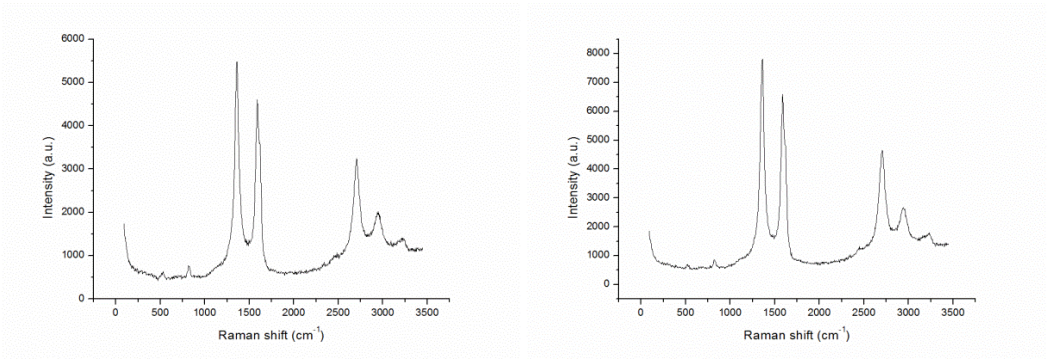


Figure S-2.1. Raman spectra of the samples: a – CNTp, b – CNT1, c – CNT3, d – CNT6, e – CNT9, f – CNT12, g – CNT15.



a





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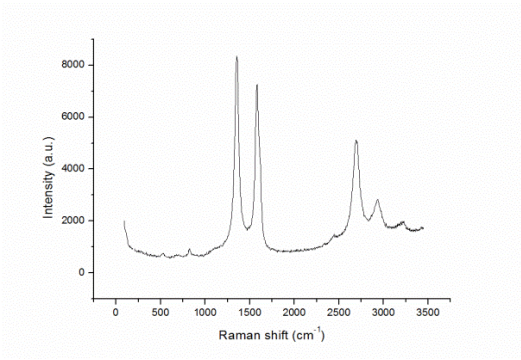

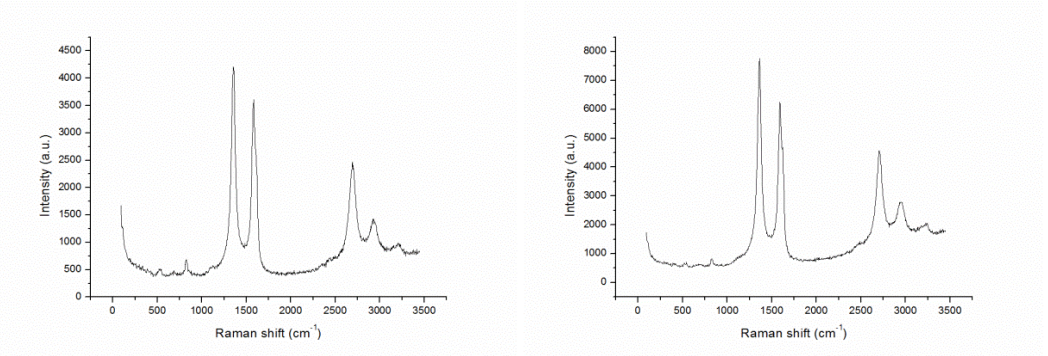

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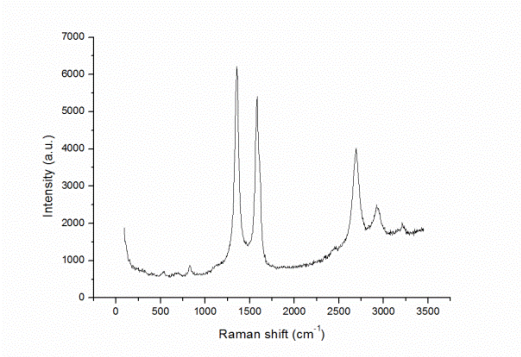
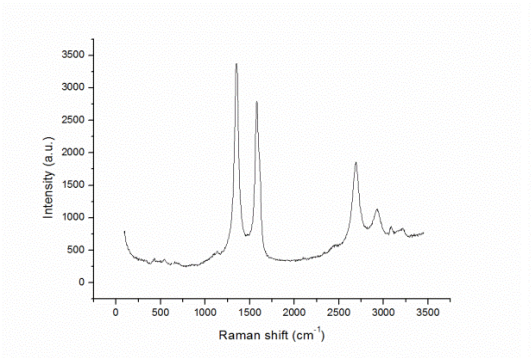


Figure S-2.2. Raman spectra of the annealed CNT samples. Annealing temperature: a – 160, b – 370, c – 530.

a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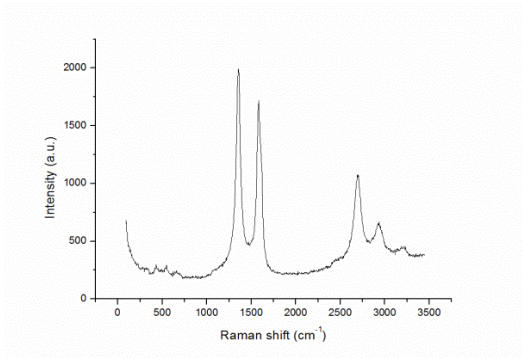
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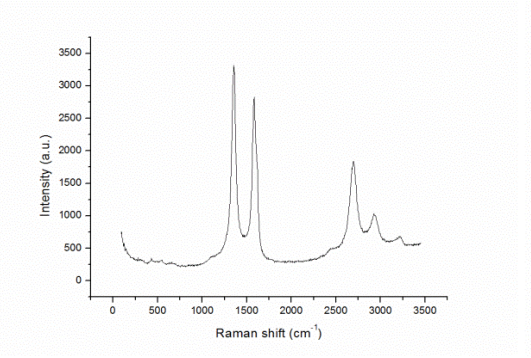
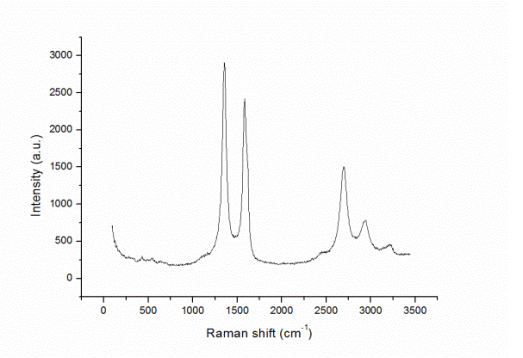
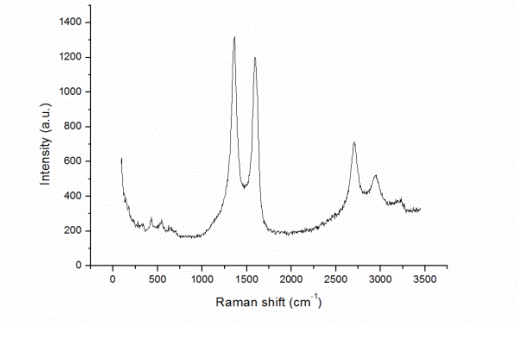
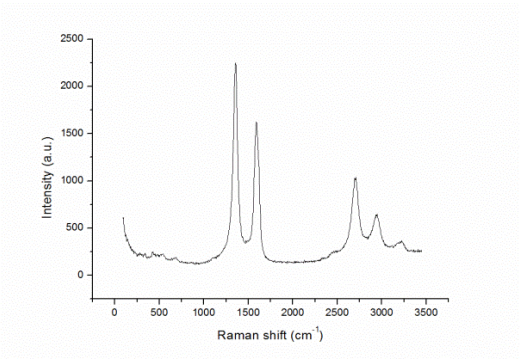
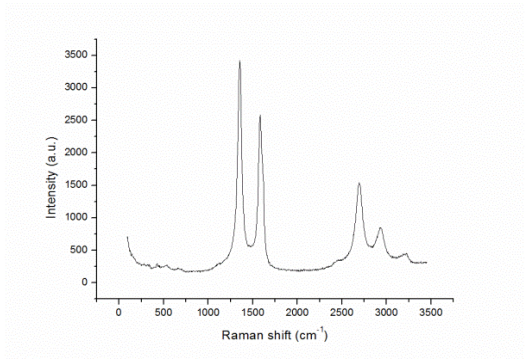

Intensity (a.u.)
Raman shift (cm-1)

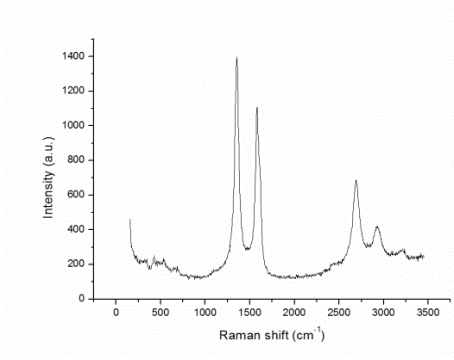

Intensity (a.u.)
Raman shift (cm-1)


Intensity (a.u.)
Raman shift (cm-1)


Intensity (a.u.)
Raman shift (cm-1)


Intensity (a.u.)
Raman shift (cm-1)

b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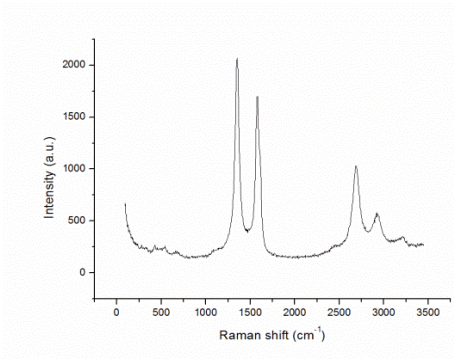
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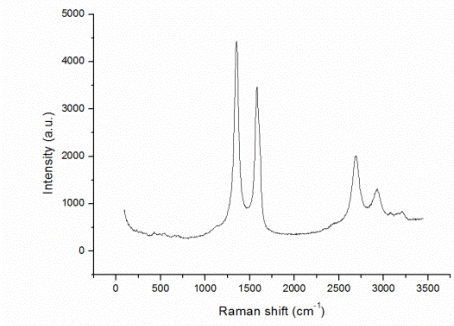
Raman shift (cm-1)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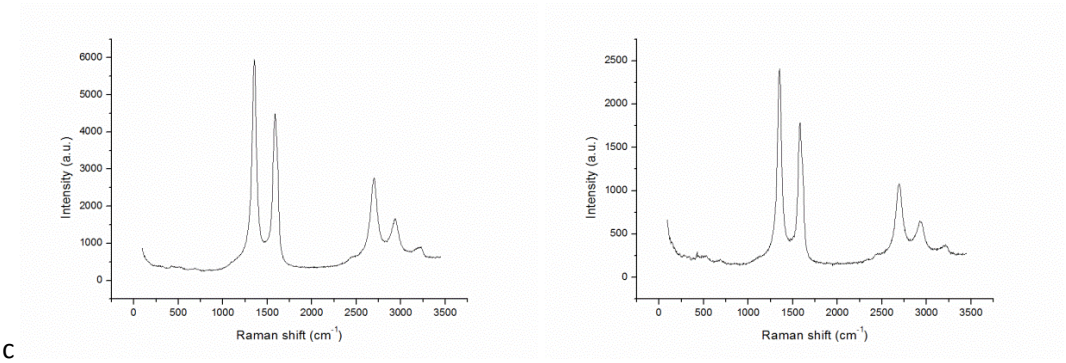
Raman shift (cm-1)



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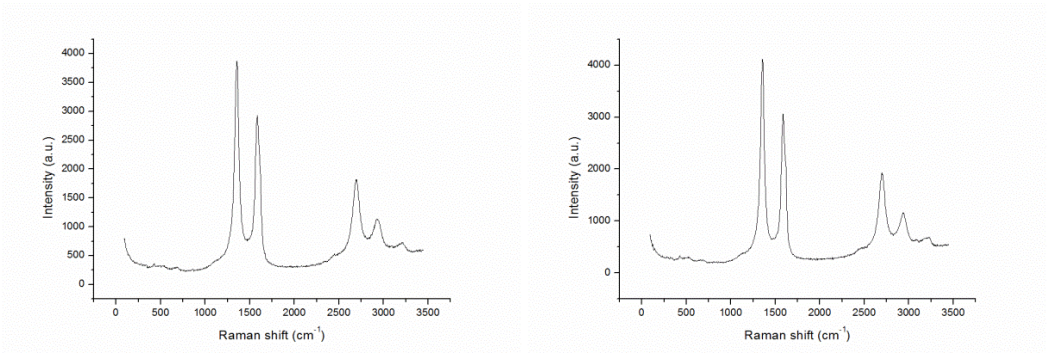


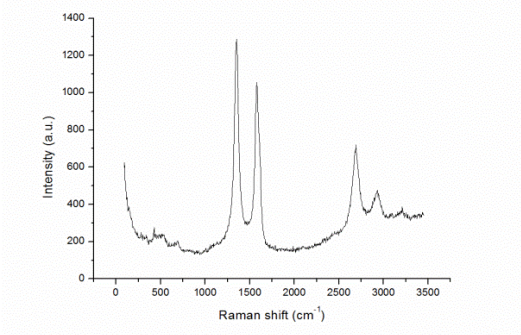
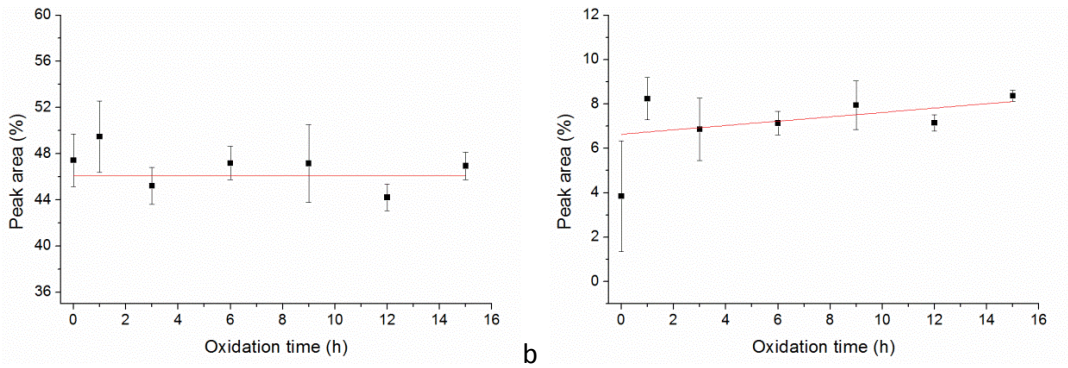
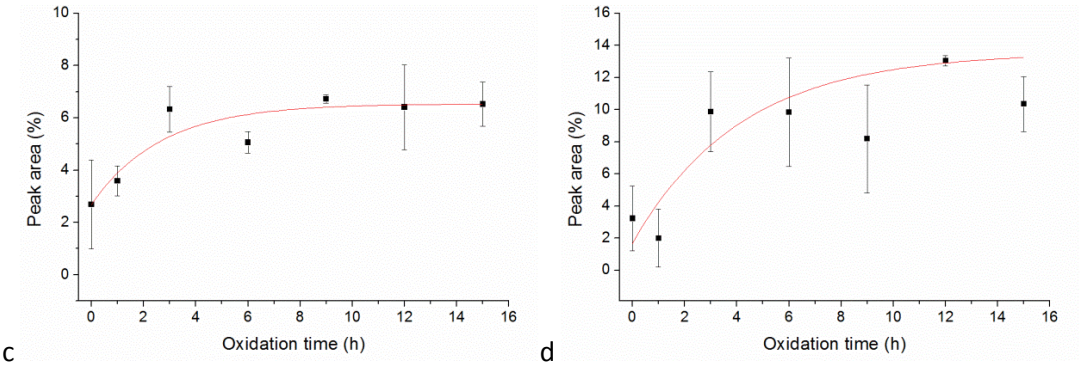


Figure S-2.3. Raman spectra of the samples: a – N2-CNT, b – H2-CNT, c – FTS-CNT.

S-3. Effect of the oxidation time on the relative areas of D bands and G band



a b



c d

Figure S-3 Relative areas of D1 (a), D2 (b), D3 (c), and D4 (d) bands in Raman spectra of oxidized CNTs in percentage of total area under 900–1800 cm^{-1} region.

The equations used for curve fitting and obtained best-fit parameters:

D1: $y = y_0$, $y_0 = 46.1$

D2: $y = A + B*x$, $A = 6.6$ $B = 0.1$

D3: $y = A_1*\exp(x/t_1) + A_2*\exp(x/t_2) + A_3*\exp(x/t_3) + y_0$, $y_0 = 6.5$ $A_1 = -1.3$ $t_1 = -2.7$ $A_2 = -1.3$ $t_2 = -2.7$ $A_3 = -1.3$ $t_3 = -2.7$

D4: $y = y0 + A*\exp(k*x)$, $y0 = 13.6$ $A = -11.9$ $k = -0.2$

G: $y = A_1*\exp(x/t_1) + A_2*\exp(x/t_2) + y_0$, $y_0 = -351503$ $A_1 = 12.8$ $t_1 = 1.2$ $A_2 = 351535$ $t_2 = 1.7$

S-4. BET and XPS data

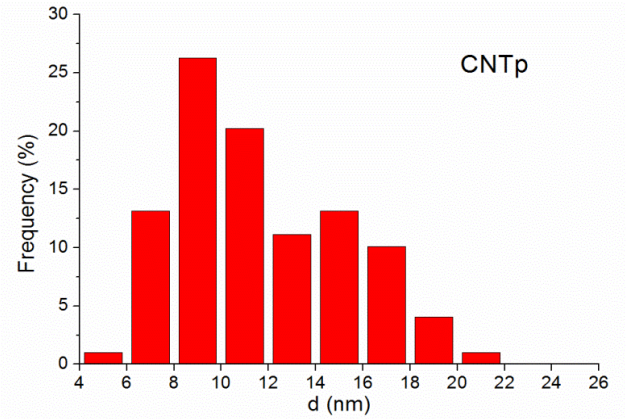
Table S-4. BET specific surface area and XPS oxygen content in pristine and oxidized CNTs.

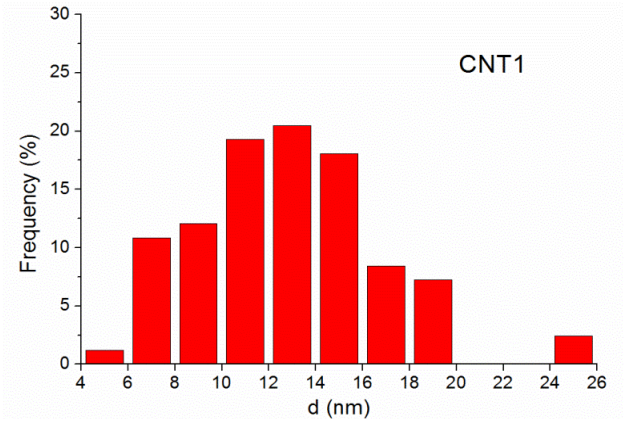
Oxidation time (h)	S_{BET} (m^2/g)	O_{XPS} (at.%)
0	192_5	0.3
1	225_5	6.5
3	233_5	8.0
6	237_5	8.6
9	249_5	8.9
12	246_5	8.7

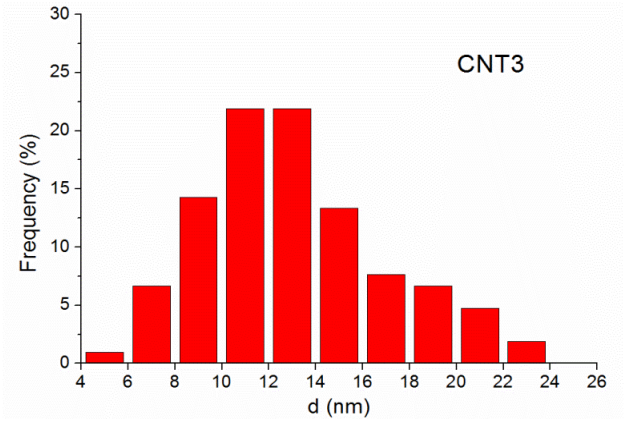
15	232_5	8.8

S-5. TEM study of CNTs

Average CNT diameter and its distribution were calculated from TEM images. At least 100 nanotubes were processed.







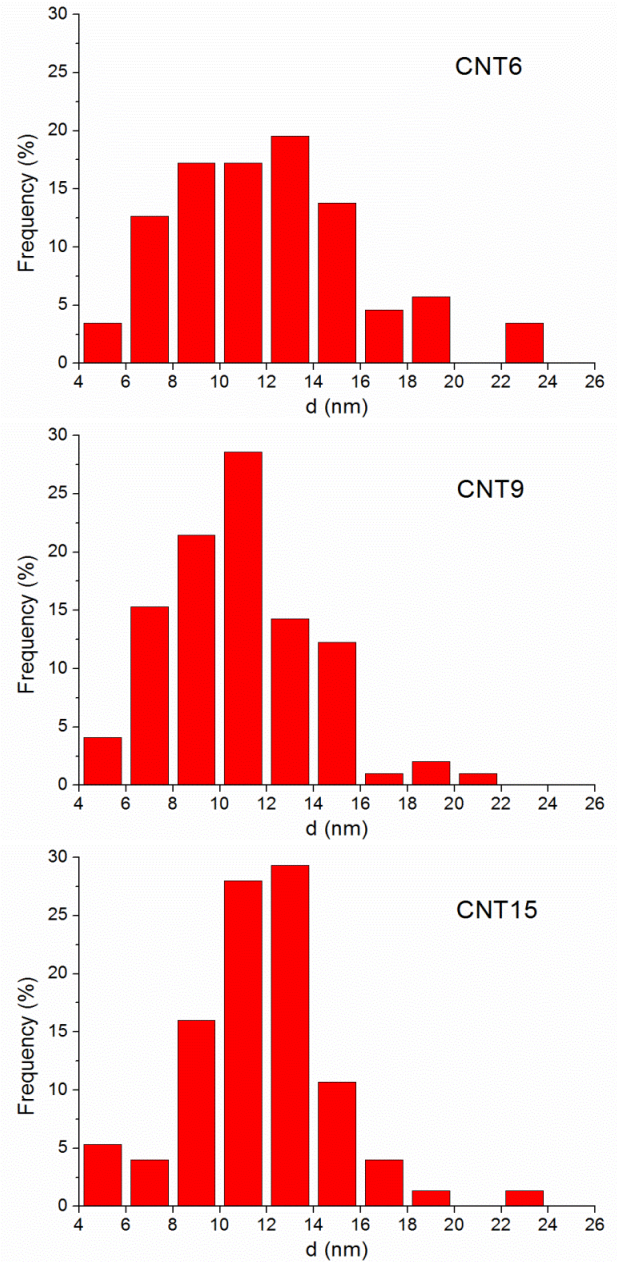
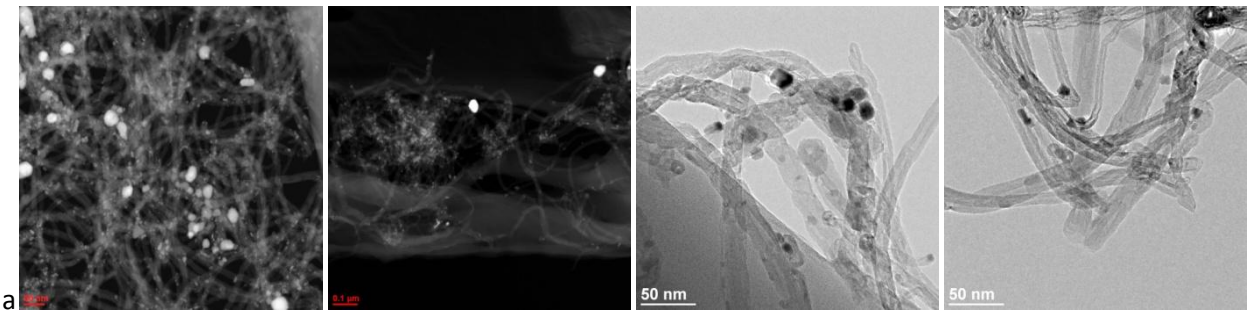


Figure S-5.1. CNT diameter distribution after different time of oxidation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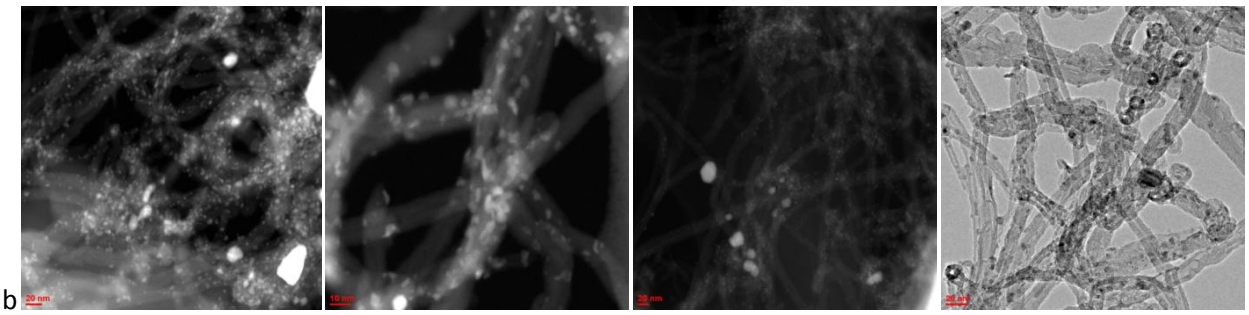
50 nm
50 nm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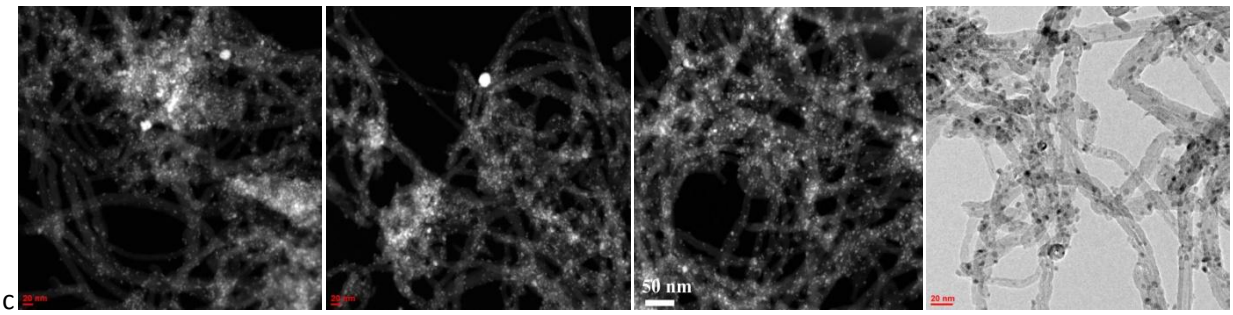
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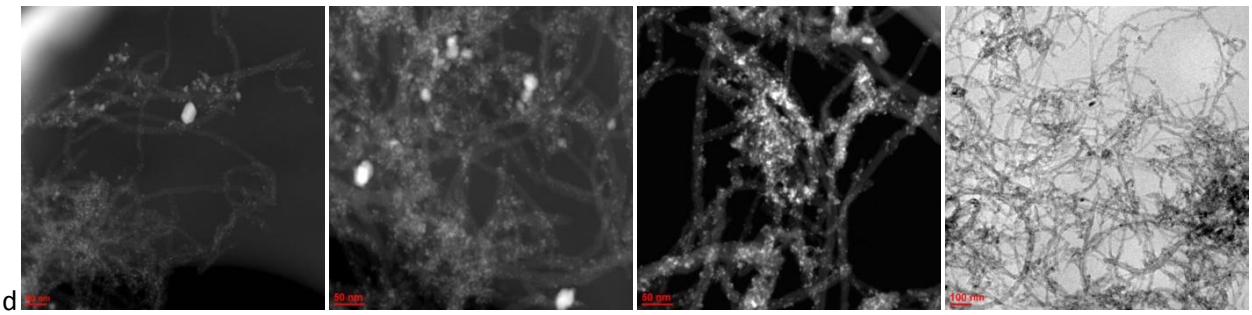
50 nm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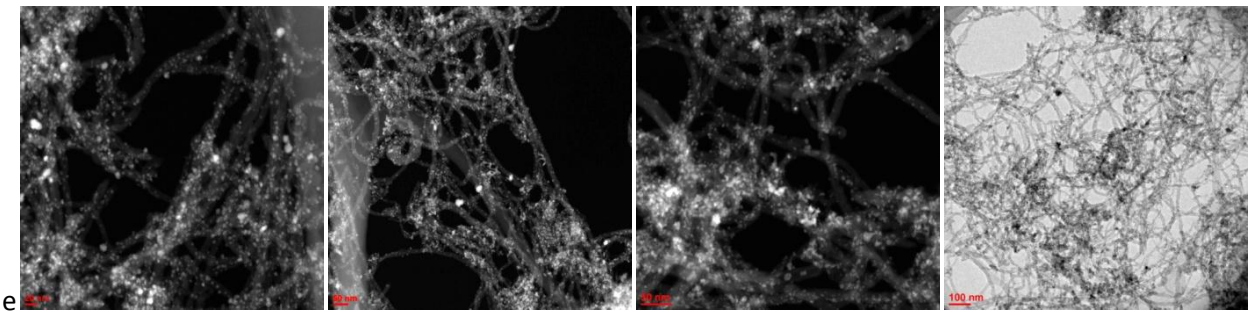
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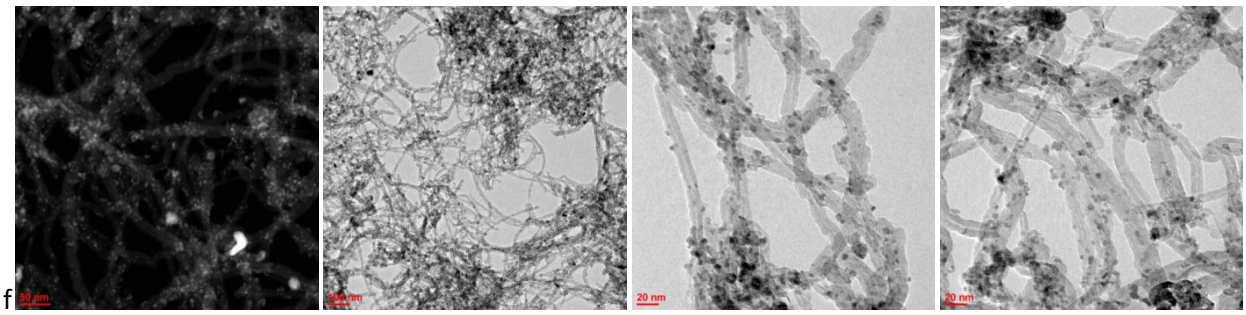
f 

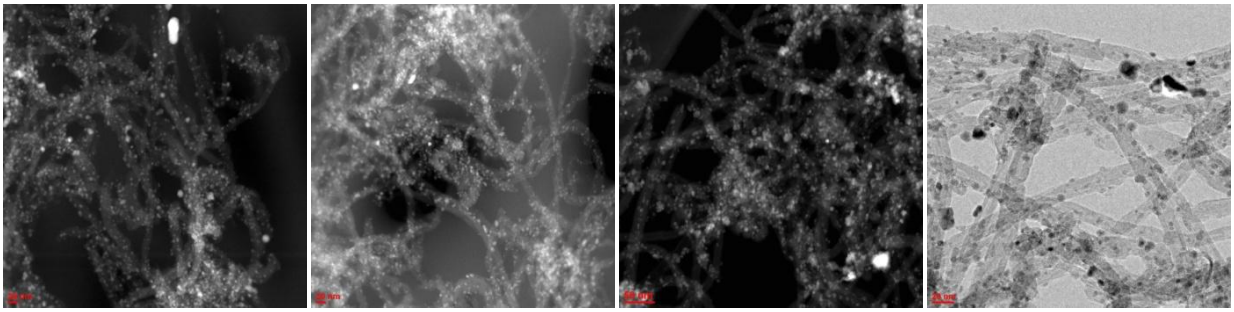
g 

Figure S-5.2. TEM images used for the calculation of CNT diameters. Images are from Co based catalyst supported on appropriate nanotubes: a – CNTp, b – CNT1, c – CNT3, d – CNT6, e – CNT9, f – CNT12, g – CNT15.

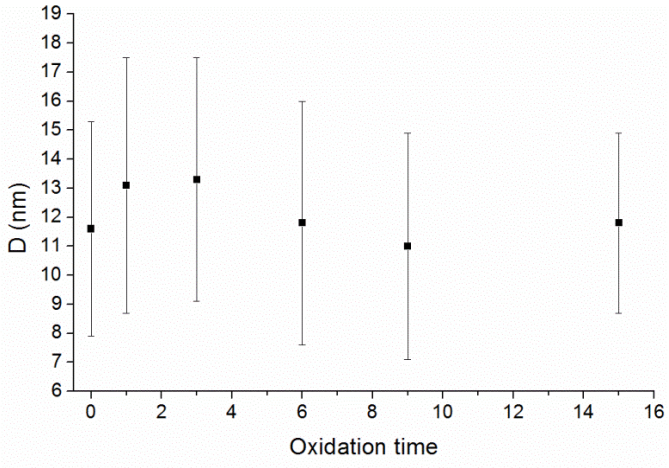


Figure S-5.3. Average diameter of CNTs and its standard deviation against the oxidation time

S-6. Effect of the oxidation time on the intensity ratios of D bands to G band.

The equations used for curve fitting and obtained best-fit parameters:

I_{D1}/I_G: y = y0 + A*exp(x/t), y0 = 1.7 A = -0.3 t = -4.1

I_{D2}/I_G: y = a + b*x + c*r^x, a = 0.33 b = 0.01 c = -0.15 r = 0.07

I_{D3}/I_G : y = y0 + A*exp(x/t), y0 = 0.07 A = -0.04 t = -1.3

I_{D4}/I_G : y = y0 + A*exp(x/t), y0 = 0.06 A = -0.05 t = -4.0

S-7. Disordered bands to G band intensity ratios in CNT12 annealed at different temperatures

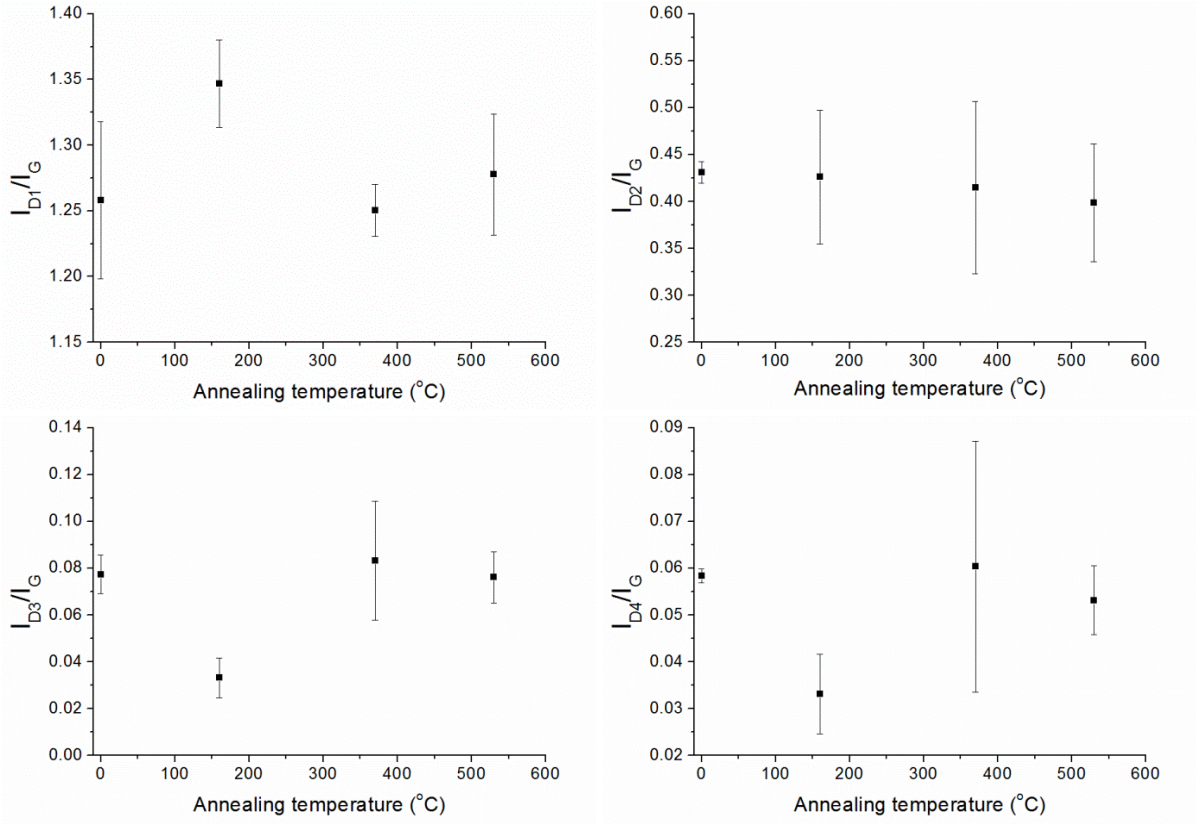


Figure S-7. Disordered bands to G band intensity ratios in CNT12 annealed at different temperatures