Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

COMPARISON OF FUNCTIONALIZED CARBON NANOFIBERS AND MULTI-WALLED CARBON NANOTUBES AS SUPPORTS FOR Fe-Co NANOPARTICLES

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Electronic Supplementary Information (ESI)

Experimental setup for pseudo in-situ XPS measurements

For pseudo in-situ XPS measurements, the spectrometer is equipped with a reaction cell fitted on the sample transfer chamber. The powder sample is pressed in a small stainless steel trough of 4mm diameter and 0.5mm depth. This trough is inserted in a stainless steel stub in which it is maintained by a small spring. The cell body is made of quartz and is heated by a boron nitride insulated heater. The temperature is controlled by a k type thermocouple incorporated in the pin in which the sample stub is inserted. The requested temperature is adjusted using a MicroMega temperature programmer, the maximum temperature being 1000 °C at 1 mbar. A hand grip assembly is used to open and close the cell door in a vertical plane. Gas in and out lines are passing through the cell door and the reaction gas (here N_2) is introduced via a precision micrometer valve in the quartz reaction cell. The base of the cell is cooled by a copper tube which, in turn, is cooled by a water cooled flange at the top of the cell housing. The door of the cell is cooled using compressed air. After reaction, the gas cell is pumped down, then it is opened and the stub holding the sample is transferred in the specimen transfer chamber and then the analysis chamber, where the XPS analyses are performed. Samples are thus never re-exposed to

air. The following experimental conditions were used for temperature programmation: increase up to 300°C with a heating ramp of 100°C/h, keeping 1h at 300°C, and then decrease to room temperature.

Table S1. O/C XPS ratios for different oxidation reaction durations of MWCNT.

XPS	Oxidation duration (refluxing HNO_3)						
	2h	4h	6h	8h	12h	16h	24h
O/C	0.055	0.060	0.065	0.054	0.054	0.059	0.085

(a) (b)

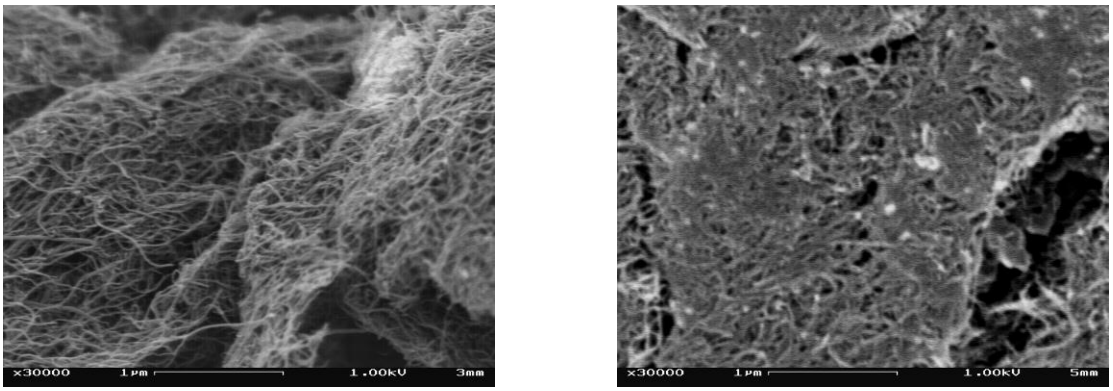


Figure S2. SEM images of MWCNT-OX : (a) after 2h and (b) after 24h of treatment with HNO_3 under refluxing conditions.

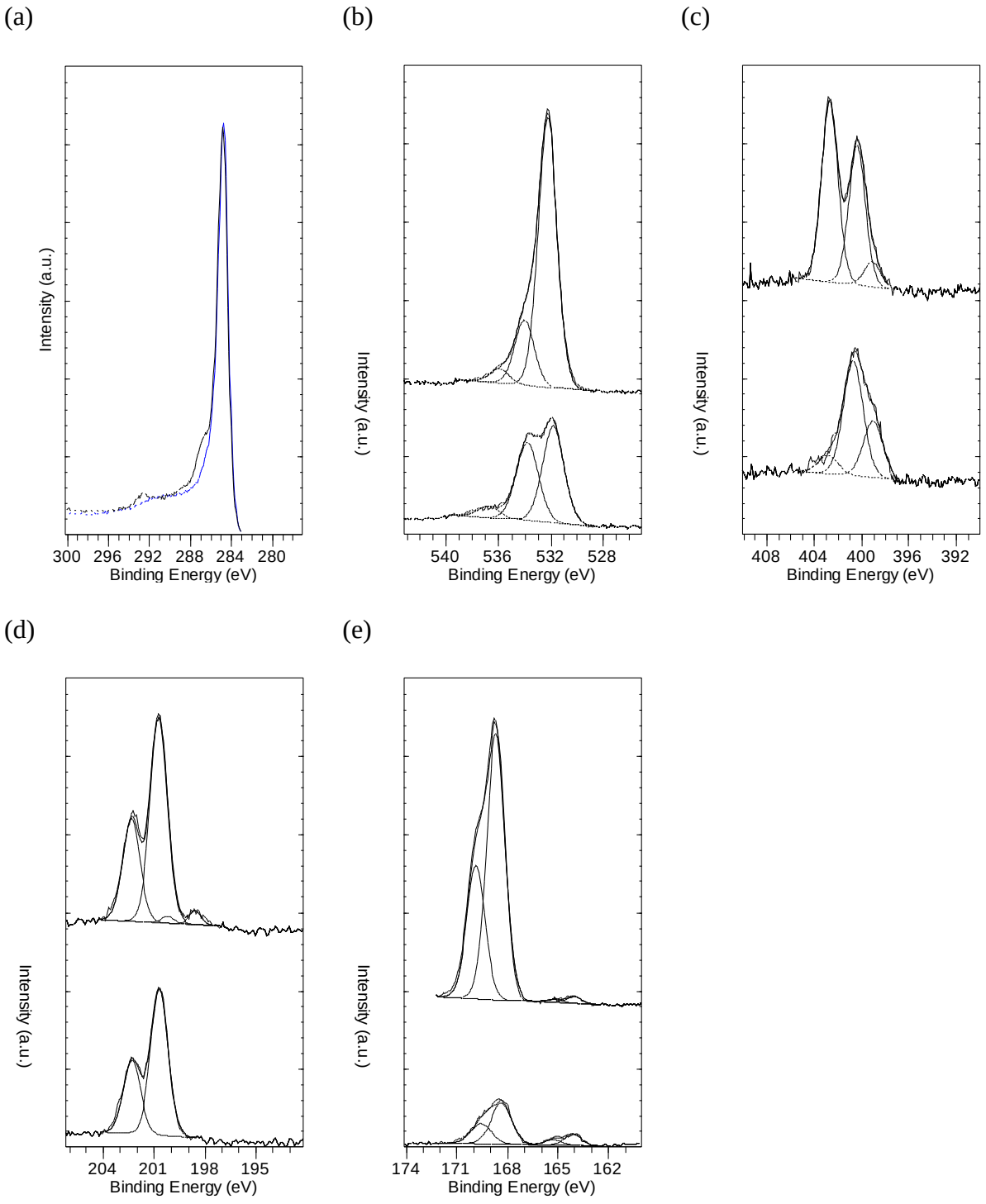


Figure S3. XPS spectra of CNF-NMe_3^+ at RT (top) and heated at 300°C (below) obtained in the tubular oven in the (a) C 1s, (b) O 1s, (c) N 1s, (d) Cl 2p, and (e) S 2p regions.

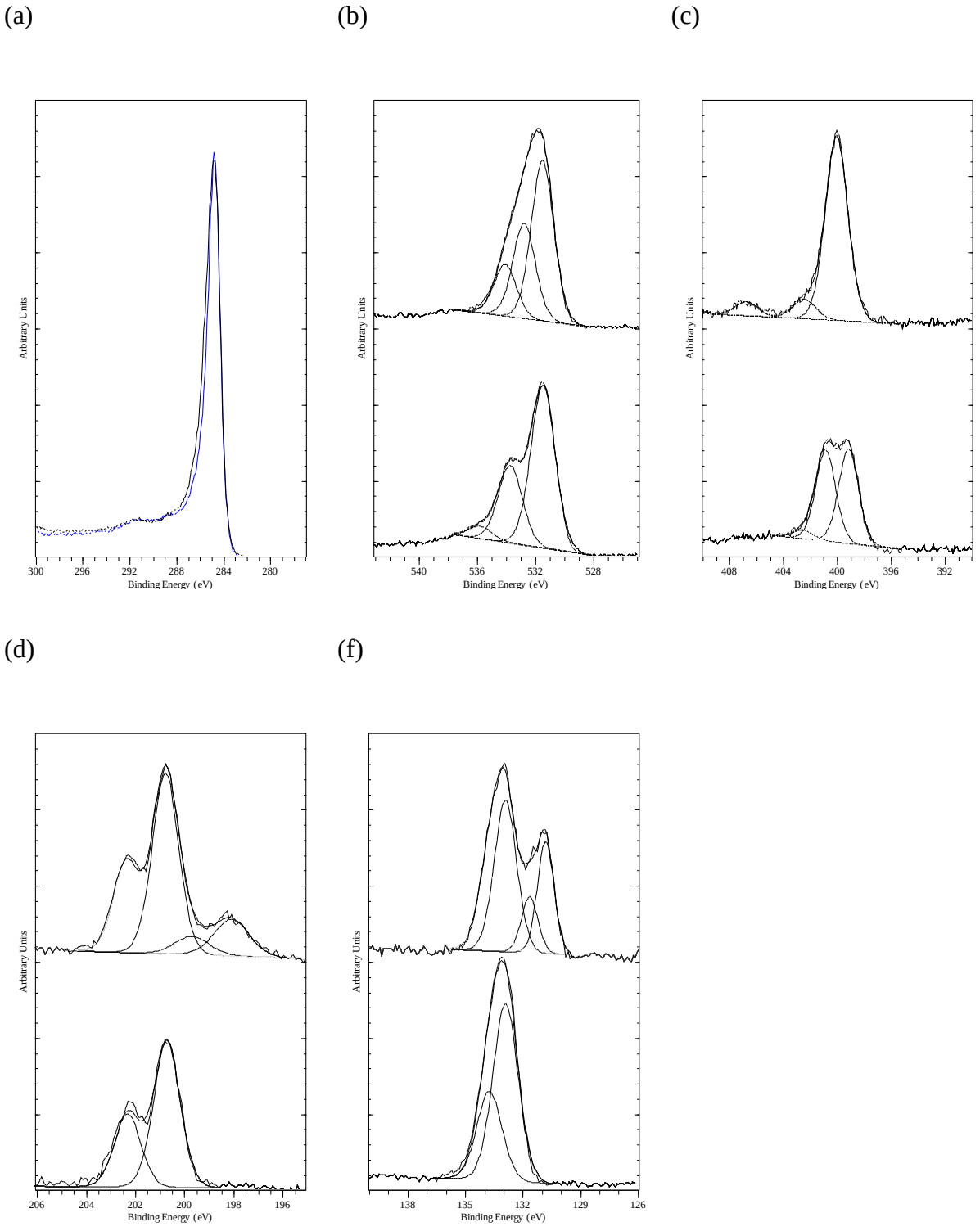


Figure S4. XPS spectra of CNF-PPh_2 at RT (top) and heated at 300°C (below) obtained in the tubular oven in the (a) C 1s, (b) O 1s, (c) N 1s, (d) Cl 2p, and (e) P 2p regions.

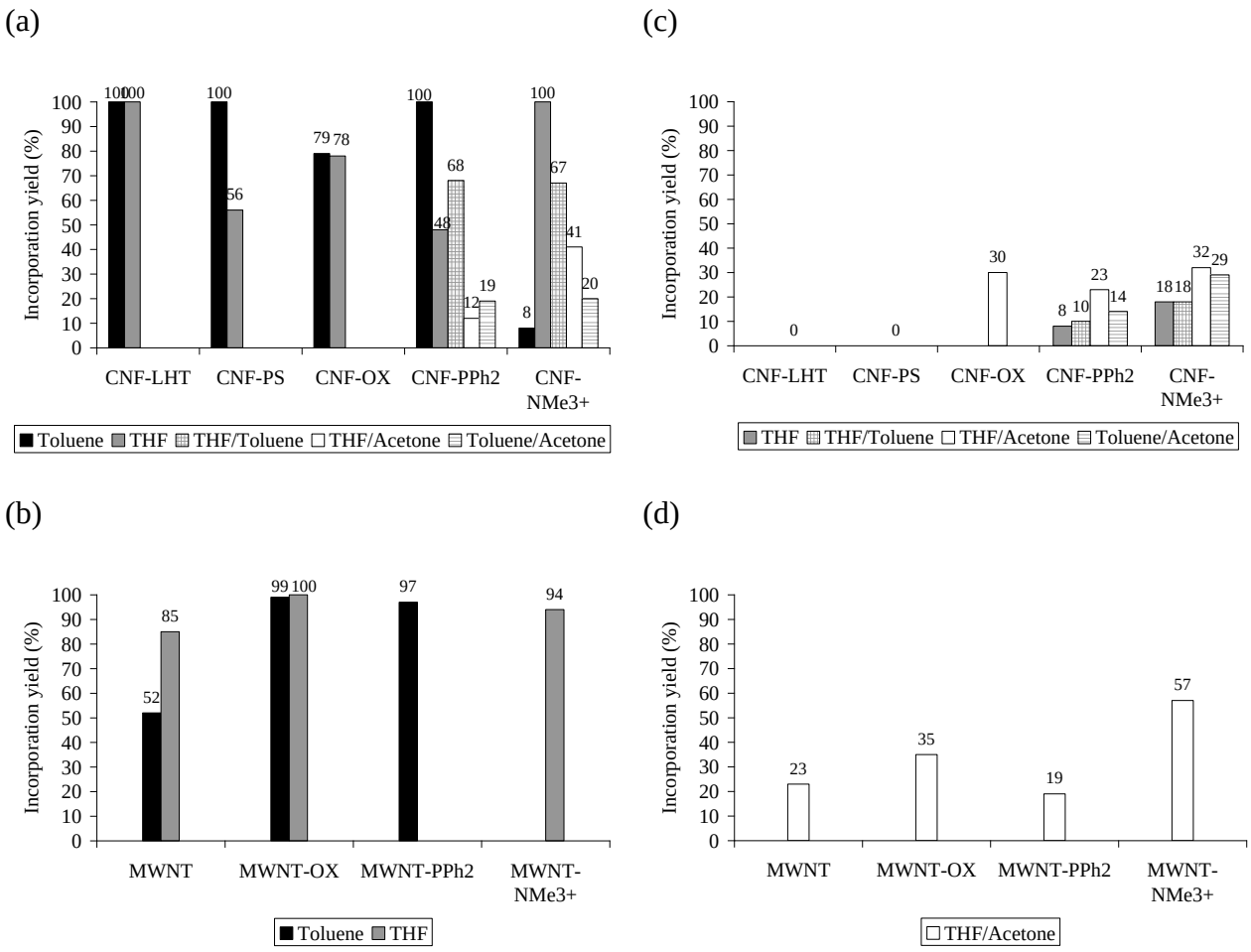


Fig. S5. Incorporation yield (%) of $[HFeCo_3(CO)_{12}]$ (a) on CNF and (b) on MWCNT and of $(NEt_4)[FeCo_3(CO)_{12}]$ (c) on CNF and (d) on MWCNT.

Table S6. Carbonyl stretching frequencies of $[H_nFeCo_3(CO)_{12}]^{n-1}$ (n = 0, 1) in different solvents.

Cluster species	Solvent(s)	Solution color	ν_{CO} (cm^{-1})	Interpretation
$[HFeCo_3(CO)_{12}]$	toluene	purple	2103w 2060s 2051s 2028m 1986m 1881m	Protonated, neutral
	THF	brown	2061w 2002s 1965w 1932m 1822m	Deprotonated, charged
	acetone	brown	2106w 2063m 2051m 2005s 1971m 1933m	Protonated and deprotonated
	toluene/THF	brown	2062w 2002s 1969w 1932m 1822m	Deprotonated, charged
	toluene/acetone	brown	2106w 2063m 2051m 2003s 1976m 1930m 1878m 1826m	Protonated and deprotonated
	THF/acetone	brown	2062w 2003s 1968w 1932m 1820m	Deprotonated, charged
	CCl_4	purple	2098w 2058s 2051s 2030m 1988m 1889s [a]	Protonated, neutral
$(NEt_4)[FeCo_3(CO)_{12}]$	toluene	-	Not soluble	-
	THF	brown	2061w 2001s 1967w 1932m 1822m	Unchanged, charged
	acetone	brown	2063w 2005s 1969w 1932m 1826m [a]	Unchanged, charged

[a] taken from: Armstrong RS, Bell T, Masters AF, Williams MA. Fischer-Tropsch catalysts derived from surface confined $[H_nFeCo_3(CO)_{12}]^{n-1}$ (n = 0, 1). Polyhedron 1990; 9: 2815-22.

Table S7. Thermogravimetric analyses of pure clusters.

Cluster	Weight loss (%)	Final decomposition temperature (°C)	Calculated weight loss (%)
$[HFeCo_3(CO)_{12}]$ (**1**)	56	200	59 (= 12 CO +H)
$(NEt_4)[FeCo_3(CO)_{12}]$ (**2**)	61	300	67 (= 12 CO + NEt_4)

Table S8. Loading and XPS results for the incorporation of $[HFeCo_3(CO)_{12}]$ (**1**) on different types of CNF.

Sample	Support	Solvent[a]	Metal loading (wt.%)[b]	XPS				
				Before activation			After activation	
				Co/C_{calc}[c]	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$
CNF1	CNF-LHT	Tol	5.0	0.008	0.015	1.9	0.017	2.1
CNF2		THF	5.1	0.008	0.013	1.7	0.024	3.0
CNF3	CNF-PS	Tol	5.2	0.008	0.024	3.0	0.029	3.7
CNF4		THF	2.8	0.004	0.011	2.9	0.011	2.7
CNF5	CNF-OX	Tol	4.1	0.006	0.059	9.8	0.080	13.3
CNF6		THF	4.0	0.006	0.065	10.8	0.055	9.1
CNF7	$CNF\text{-}NMe_3^+$	Tol	0.4	0.001	0.037	37.4	0.043	42.9
CNF8		THF	5.0	0.008	0.061	7.7	0.065	8.1
CNF9		THF/Tol	3.4	0.005	0.038	7.6	0.032	6.4
CNF10		THF/Acet	2.1	0.003	0.017	5.8	0.018	5.9
CNF11		Tol/Acet	1.0	0.002	0.015	7.6	0.016	8.1
CNF12	$CNF\text{-}PPh_2$	Tol	5.2	0.008	0.078	9.7	0.096	12.0
CNF13		THF	2.5	0.004	0.032	8.0	0.031	7.8
CNF14		THF/Tol	3.4	0.005	0.033	6.7	0.038	7.7
CNF15		THF/Acet	0.6	0.001	0.012	11.3	0.011	11.4
CNF16		Tol/Acet	1.0	0.002	0.013	6.3	0.013	6.3

[a] Tol = toluene and Acet = acetone.
[b] Metal loading has been calculated from the incorporation yield determined by atomic absorption of cobalt in the synthesis filtrates.
[c] Calculated values are bulk molar ratios based on the experimental metal loadings measured. The amount of metal taken into consideration for the calculations corresponds to the amount incorporated on the support. The amount of C taken into consideration corresponds to the amount of support used by considering that it is only constituted of carbon.

Table S9. Loading and XPS results for the incorporation of $[HFeCo_3(CO)_{12}]$ (**1**) on different types of MWCNT.

Sample	Support	Solvent[a]	Metal loading (wt.%)[b]	XPS				
				Before activation			After activation	
				Co/C_{calc}[c]	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$
MWCNT1	MWCNT	Tol	2.6	0.004	0.004	1.0	0.004	1.1
MWCNT2		THF	4.6	0.007	0.012	1.7	0.012	1.7
MWCNT3	MWCNT-OX	Tol	5.3	0.008	0.024	3.0	0.022	2.7
MWCNT4		THF	5.3	0.008	0.016	2.0	0.017	2.1
MWCNT5	MWCNT-NMe_3^+	THF	4.9	0.008	0.012	1.4	0.013	1.6
MWCNT6	MWCNT-PPh_2	Tol	4.7	0.007	0.015	2.2	0.013	1.9

[a] Tol = toluene and Acet = acetone.
[b] Metal loading has been calculated from the incorporation yield determined by atomic absorption of cobalt in the synthesis filtrates.
[c] Calculated values are bulk molar ratios based on the experimental metal loadings measured. The amount of metal taken into consideration for the calculations corresponds to the amount incorporated on the support. The amount of C taken into consideration corresponds to the amount of support used by considering that it is only constituted of carbon.

Table S10. Loading and XPS results for the incorporation of $(NEt_4)[FeCo_3(CO)_{12}]$ (**2**) on different types of CNF.

Sample	Support	Solvent[a]	Metal loading (wt.%)[b]	XPS				
					Before activation		After activation	
				Co/C_{calc}[c]	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$
CNF17	CNF-LHT	THF/Acet	0	No incorporation				
CNF18	CNF-PS	THF/Acet	0	No incorporation				
CNF19	CNF-OX	THF/Acet	1.6	0.002	0.026	13.1	0.017	8.3
CNF20	$CNF\text{-}NMe_3^+$	THF	0.9	0.001	0.008	8.2	0.011	10.7
CNF21		THF/Tol	0.9	0.001	0.017	16.9	0.017	17.5
CNF22		THF/Acet	1.6	0.003	0.030	10.1	0.028	9.4
CNF24		Tol/Acet	1.5	0.002	0.016	7.9	0.020	9.9
CNF25	$CNF\text{-}PPh_2$	THF	0.4	0.001	0.006	5.9	0.007	7.6
CNF26		THF/Tol	0.5	0.001	0.006	6.4	0.007	6.9
CNF27		THF/Acet	1.2	0.002	0.015	7.8	0.019	9.6
CNF28		Tol/Acet	0.8	0.001	0.006	6.1	0.010	9.9

[a] Tol = toluene and Acet = acetone.
[b] Metal loading has been calculated from the incorporation yield determined by atomic absorption of cobalt in the synthesis filtrates.
[c] Calculated values are bulk molar ratios based on the experimental metal loadings measured. The amount of metal taken into consideration for the calculations corresponds to the amount incorporated on the support. The amount of C taken into consideration corresponds to the amount of support used by considering that it is only constituted of carbon.

Table S11. Loading and XPS results for the incorporation of $(NEt_4)[FeCo_3(CO)_{12}]$ (**2**) on different types of MWCNT.

Sample	Support	Solvent[a]	Metal loading (wt.%)[b]	XPS				
					Before activation		After activation	
				Co/C_{calc}[c]	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$	Co/C_{exp}	$(Co/C)_{exp}/(Co/C)_{calc}$
MWCNT7	MWCNT	THF/Acet	1.2	0.002	-	-	0.002	1.0
MWCNT8	MWCNT-OX	THF/Acet	1.8	0.003	0.006	2.0	0.006	2.0
MWCNT9	MWCNT-NMe_3^+	THF/Acet	2.8	0.004	0.007	1.9	0.007	1.9
MWCNT10	MWCNT-PPh_2	THF/Acet	1.0	0.002	0.002	1.3	0.001	0.9

[a] Tol = toluene and Acet = acetone.
[b] Metal loading has been calculated from the incorporation yield determined by atomic absorption of cobalt in the synthesis filtrates.
[c] Calculated values are bulk molar ratios based on the experimental metal loadings measured. The amount of metal taken into consideration for the calculations corresponds to the amount incorporated on the support. The amount of C taken into consideration corresponds to the amount of support used by considering that it is only constituted of carbon.

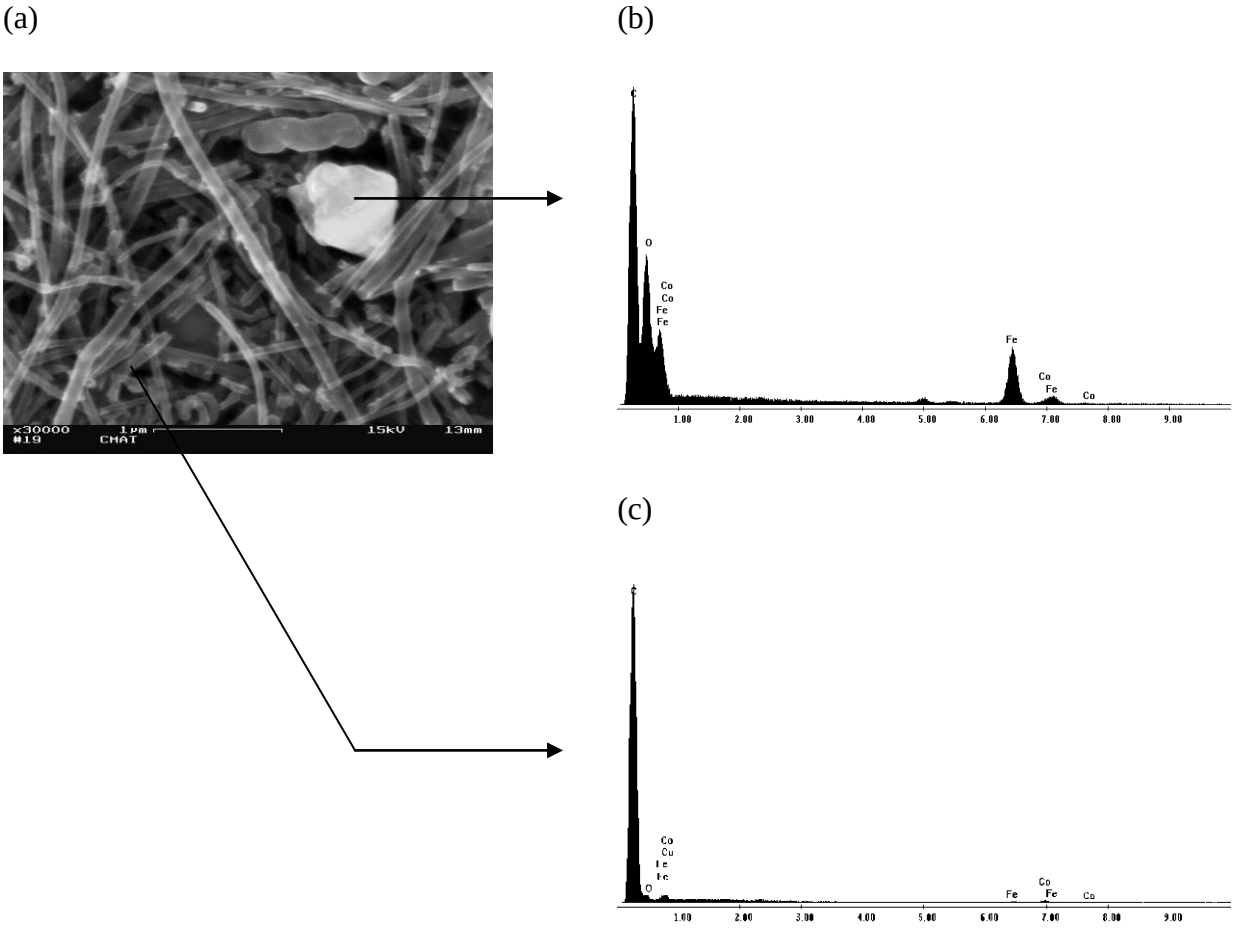
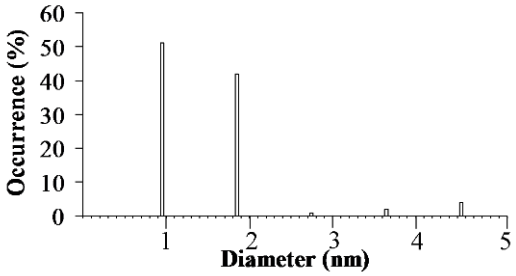


Figure S12. (a) SEM image of cluster $[HFeCo_3(CO)_{12}]$ (**1**) after thermal treatment on CNF-LHT, (b) EDXS analysis of the white particle in image (a) and (c) EDXS analysis of the zone on the bottom left-hand side in image (a).

(a)



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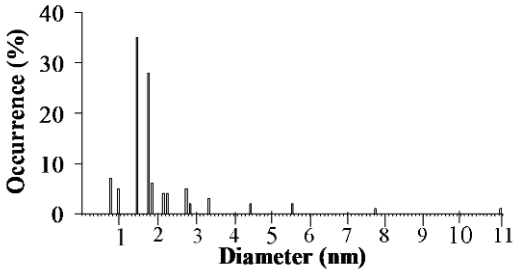
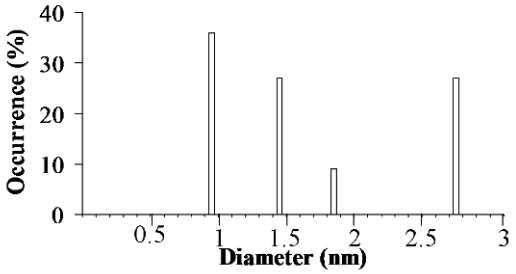
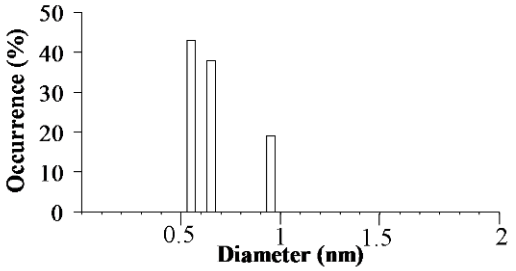


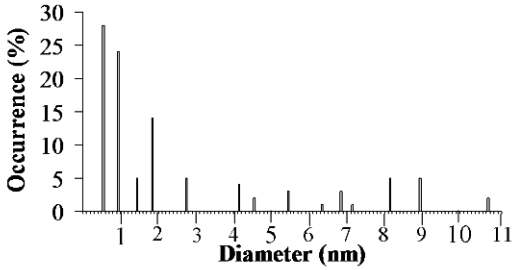
(c)



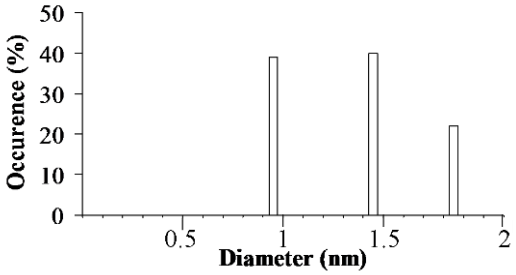
(d)



(e)



(f)



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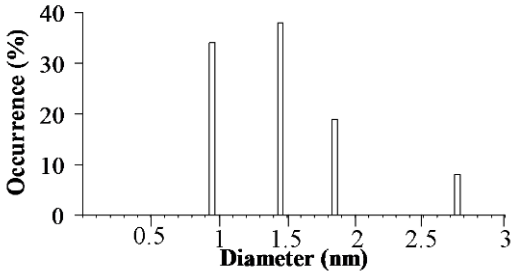

Figure S13. Histograms of particles sizes distributions (from TEM images) for cluster $[HFeCo_3(CO)_{12}]$ (**1**): (a) on CNF-LHT, (b) on CNF-OX, (c) on CNF-NMe_3^+, (d) on CNF-PPh_2 from THF and (e) on CNF-PPh_2 from toluene and for cluster $(NEt_4)[FeCo_3(CO)_{12}]$ (**2**): (f) on CNF-OX and (g) on CNF-NMe_3^+.