Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Copper-Catalyzed Direct Amination of the Superficial Graphenic Domains of Multi-Walled Carbon Nanotubes

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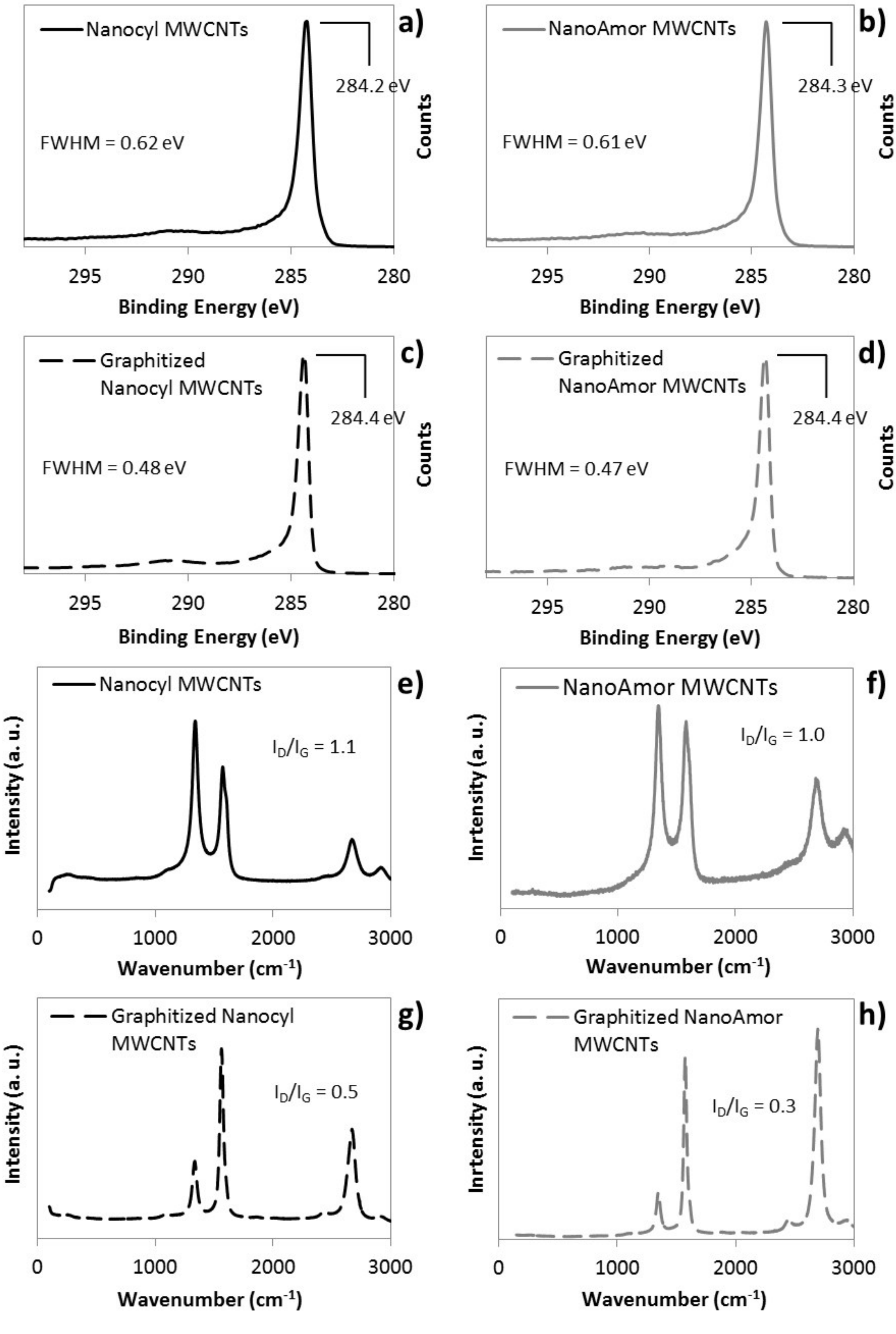

Figure S1. C1s XPS high resolution spectra of pristine nanotubes: a) MWCNTs from Nanocyl, b) MWCNTs from NanoAmor, c) graphitized Nanocyl MWCNTs and d) graphitized NanoAmor MWCNTs. (e – h) Their corresponding Raman spectra.

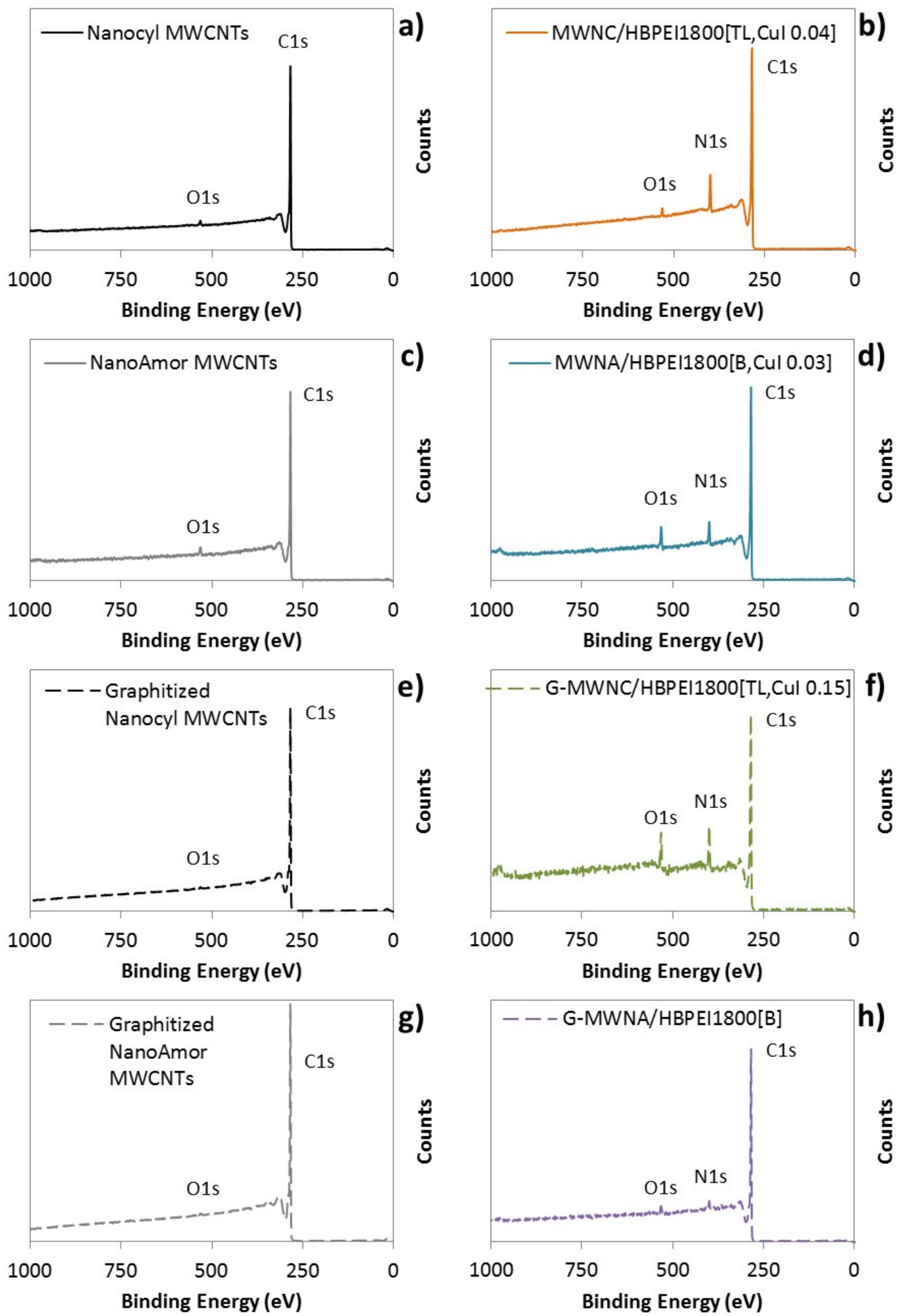

Figure S2. XPS survey spectra of pristine nanotubes (a, c, e and g) and of selected hybrids obtained from them (b, d, f and h).

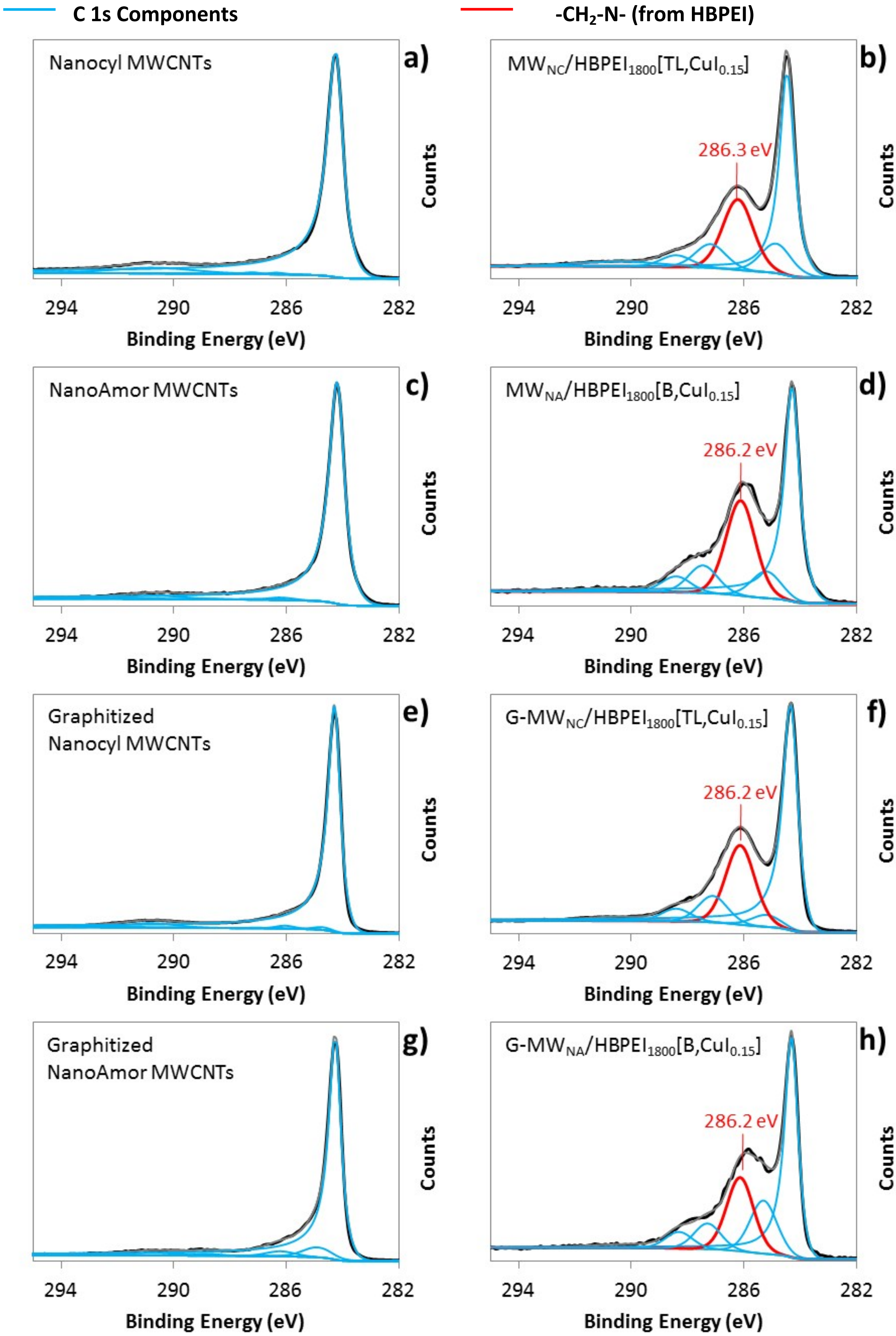

Figure S3. C1s XPS high resolution spectra of pristine nanotubes (a, c, e and g) and of selected hybrids obtained from them (b, d, f and h).

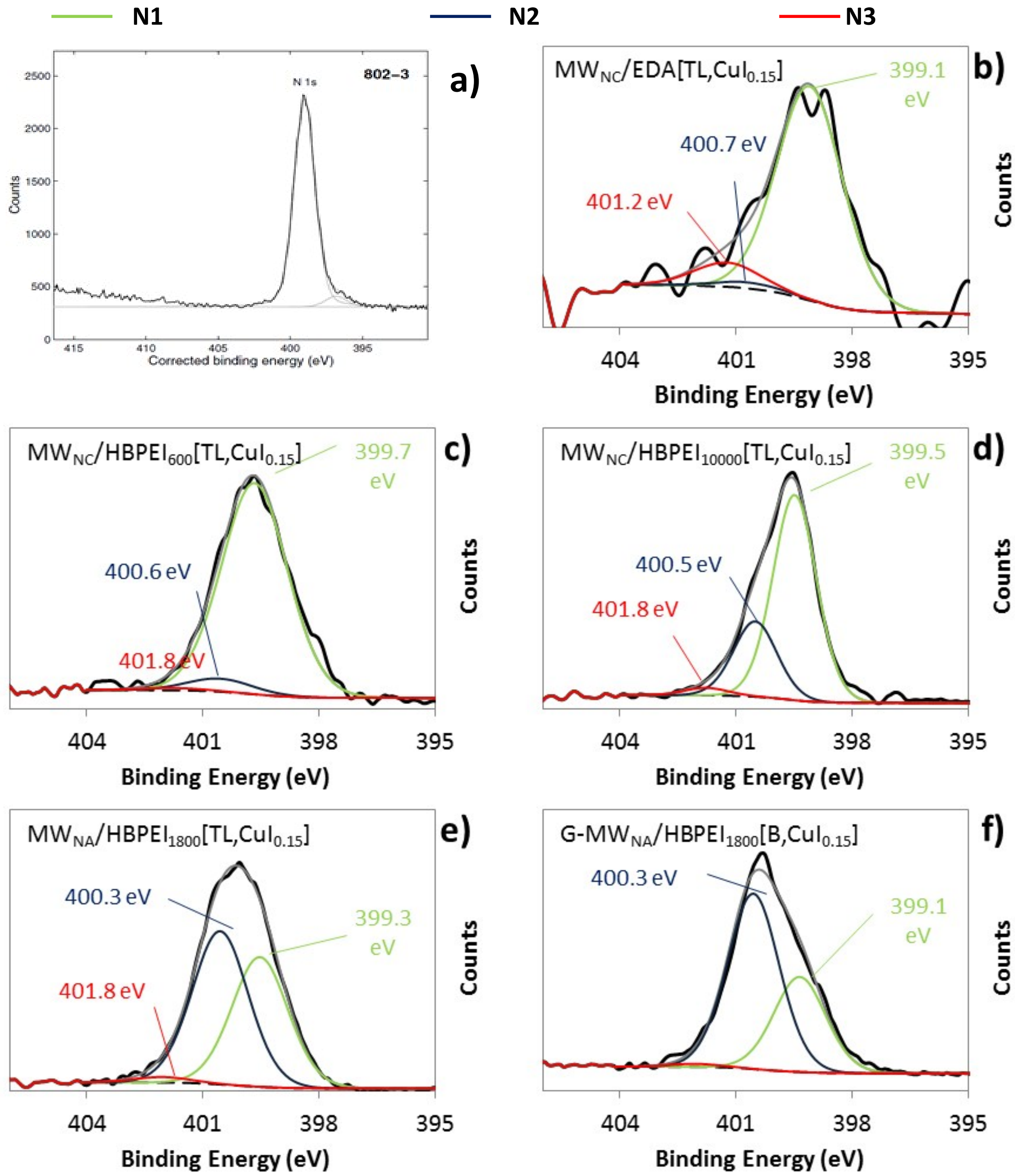

Figure S4. N1s XPS high resolution spectra of 'free' $HBPEI_{1800}$[1] and of some selected hybrid materials with different amines or polyamines.

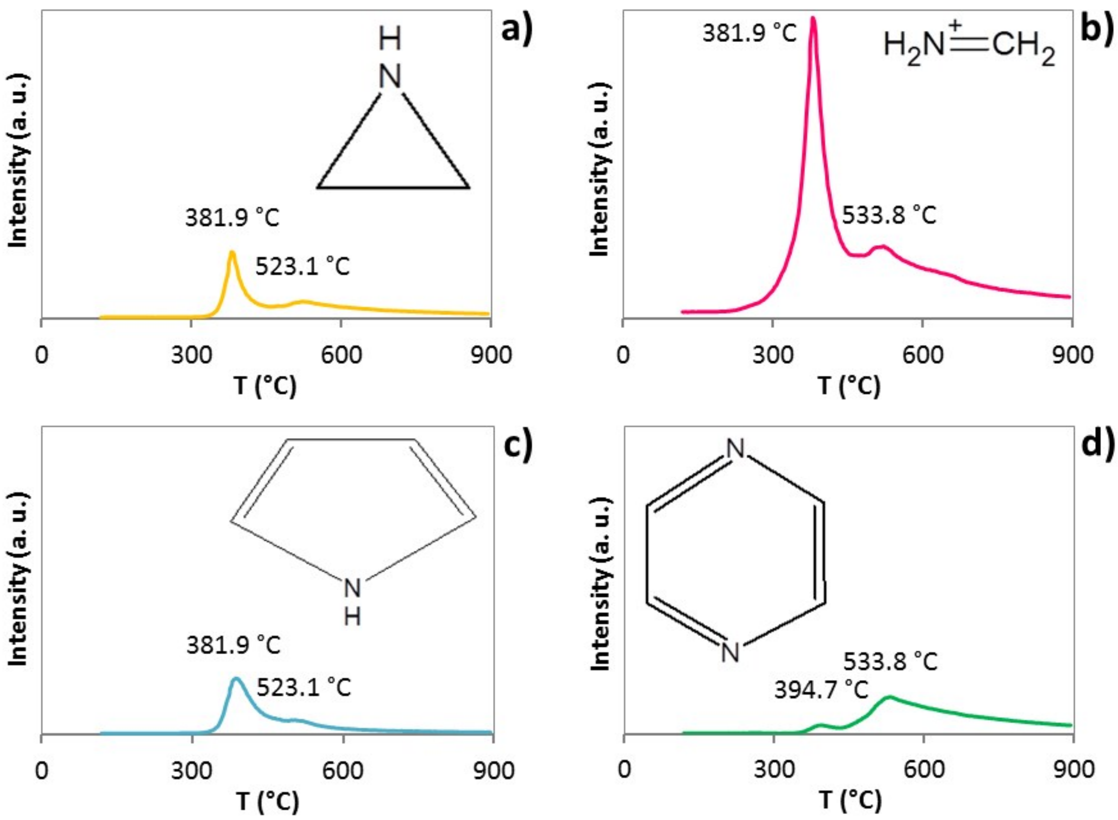

Figure S5. TPD curves of some selected ionic fragments produced by thermal decomposition of the pure $HBPEI_{1800}$ with the following mass/charge (m/z) ratios: a) m/z = 43, b) m/z = 30, c) m/z = 67, and d) m/z = 80.

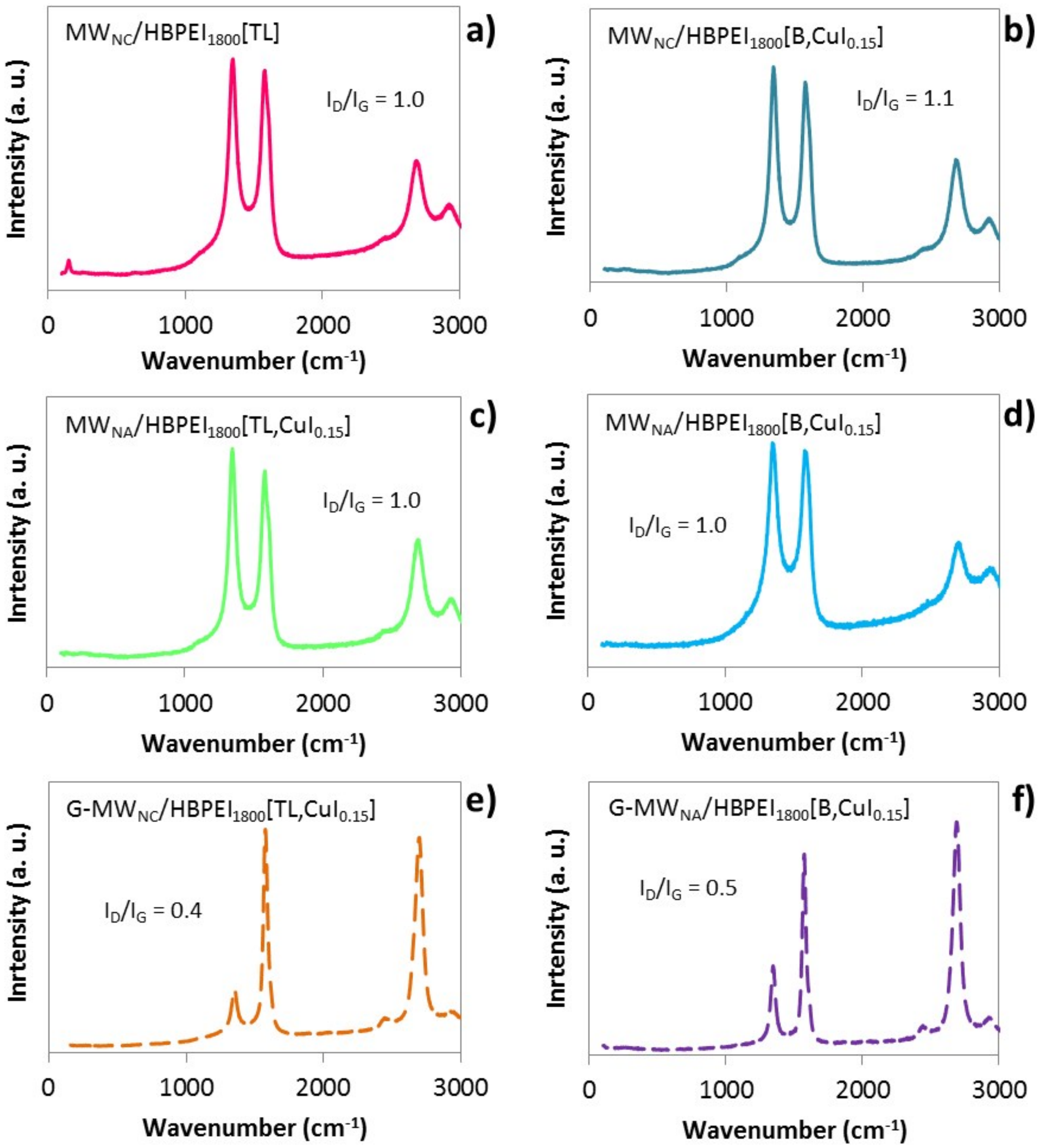

Figure S6. Raman spectra of some selected hybrid materials. Raman spectra of pristine MWCNTs are shown in Figure S1.

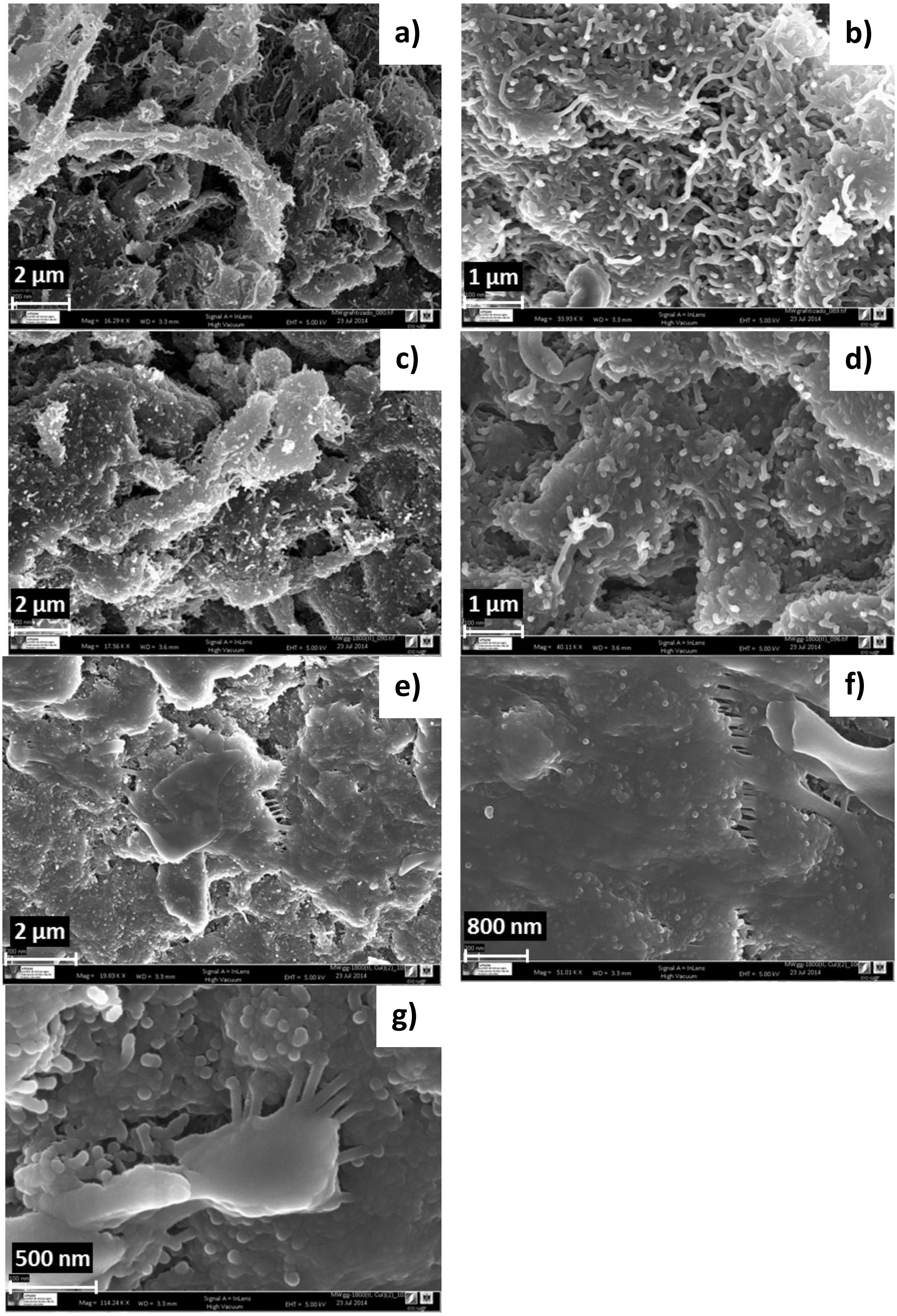

Figure S7. SEM images of a,b) Graphitized Nanocyl MWCNTs (G-MW_{NC}), c,d) G-MW_{NC}/$HBPEI_{1800}$[TL] hybrid and (e-g) G-MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$] hybrid.

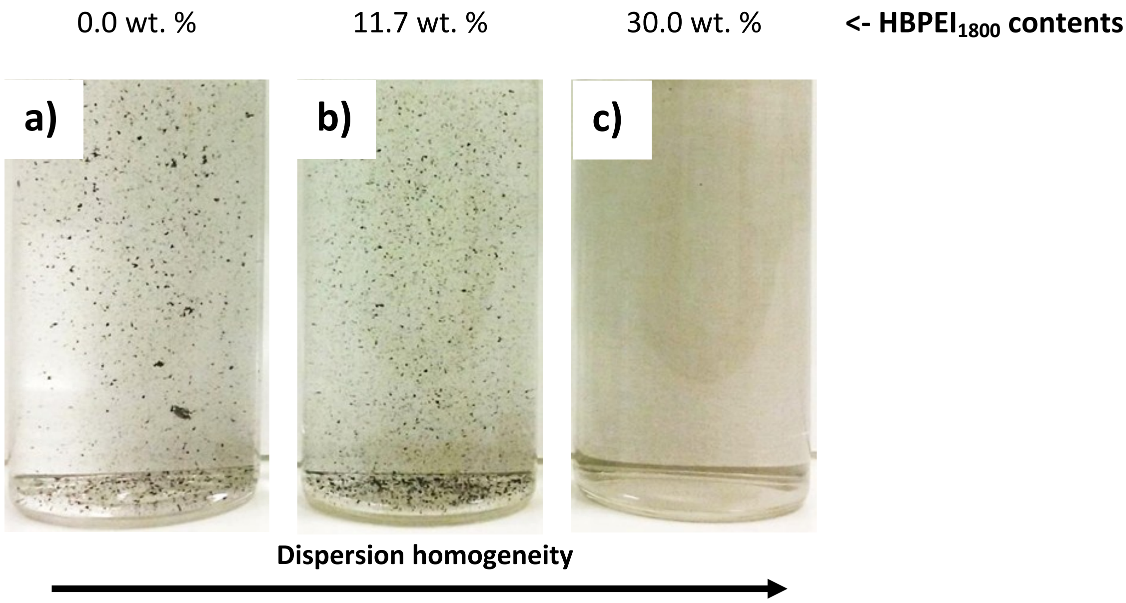

Figure S8. Aspect of aqueous dispersions (after 24 hours of sonication) of a) Nanocyl MWCNTs (MW_{NC}) and the hybrids b) MW_{NC}/$HBPEI_{1800}$[TL, $CuI_{0.01}$] and c) MW_{NC}/$HBPEI_{1800}$[TL, $CuI_{0.75}$]. Concentration of the dispersions: 5 mg/L.

Table S1. Surface atomic concentrations obtained from the XPS survey spectra of the pristine MWCNTs and of the hybrid materials.

Sample	C (at. %)*	O (at. %)*	N (at. %)*	Cu (at. %)*
MW_{NC}	**98.8**	**1.2**	-	-
MW_{NC}/$HBPEI_{1800}$[B]	94.4	2.7	2.9	-
MW_{NC}/$HBPEI_{1800}$[B,$CuI_{0.15}$]	84.7	5.1	9.6	0.2
MW_{NC}/$HBPEI_{1800}$[TL]	91.3	2.5	6.2	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.01}$]	92.6	1.8	5.6	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.04}$]	91.3	1.0	7.7	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$]	85.8	3.3	10.6	0.1
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.35}$]	86.2	2.9	10.4	0.2
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.75}$]	85.6	3.4	10.2	0.2
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.04}$,95°C]	96.0	0.7	3.3	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.04}$,80°C]	96.2	1.0	2.8	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$,1h]	96.6	1.2	2.2	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$,4h]	94.4	2.1	3.4	-
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$,8h]	94.3	2.0	3.4	0.1
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$,16h]	87.0	3.9	8.7	0.2
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$,48h]	93.7	2.7	3.5	0.1
MW_{NC}/$HBPEI_{600}$[TL,$CuI_{0.15}$]	90.8	2.1	7.0	0.1
MW_{NC}/$HBPEI_{10000}$[TL,$CuI_{0.15}$]	87.1	2.2	10.4	0.1
MW_{NA}	**98.2**	**1.8**	-	-
MW_{NA}/$HBPEI_{1800}$[TL]	81.4	5.4	13.2	-
MW_{NA}/$HBPEI_{1800}$[TL,$CuI_{0.15}$]	81.6	5.3	13.1	0.1
MW_{NA}/$HBPEI_{1800}$[B]	94.1	2.2	3.7	-
MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.03}$]	90.7	3.8	5.5	-
MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.05}$]	84.8	6.1	8.9	0.2
MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.10}$]	82.8	5.9	10.9	0.1
MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.15}$]	77.1	7.0	14.8	0.3
MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.25}$]	76.9	7.1	14.5	0.4
MW_{NA}/$HBPEI_{1800}$[B,Bu_4NI]	93.9	3.1	2.9	-
MW_{NA}/$HBPEI_{1800}$[B,$CuCl_2$ + Bu_4NI]	86.2	5.7	7.8	0.2
MW_{NA}/$HBPEI_{1800}$[B,Cu(0)]	88.6	4.4	6.9	0.1
MW_{NA}/$HBPEI_{1800}$[B,$NiCl_2$]	89.7	3.7	6.4	-
MW_{NA}/$HBPEI_{1800}$[B,CuOAc]	81.6	7.1	10.9	0.4
MW_{NA}/$HBPEI_{1800}$[B,CuOAc + Bu_4NI]	77.7	8.3	13.3	0.4
G-MW_{NC}	**99.8**	**0.2**	-	-
G-MW_{NC}/$HBPEI_{1800}$[TL]	98.8	0.4	0.8	-
G-MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$]	83.4	5.4	11.0	0.1
G-MW_{NA}	99.9	0.1	-	-
G-MW_{NA}/$HBPEI_{1800}$[B]	96.7	1.4	1.9	-
G-MW_{NA}/$HBPEI_{1800}$[B,$CuI_{0.15}$]	**78.2**	**7.8**	**13.2**	**0.3**

* Calculated from C1s, O1s, N1s and Cu2p peaks, respectively, in XPS survey spectra by using CASAXPS software.

Table S2. From left to right columns (starting in the second): amounts of catalyst, polyamine, adsorbed CO2, nitrogen and adsorbed CO2 per nitrogen (efficiency of the adsorption) of some selected hybrids.

Sample	Ratio CuI:MWCNT (wt./wt.)	HBPEI in hybrid (wt.-%)	n_{ads}0.03 (mmol g^{-1})	mmol N per g hybrid	mmol CO_2 per mmol N
MW_{NC}/$HBPEI_{1800}$[TL]	0.00	19.04	0.77	4.42	0.17
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.01}$]	0.01	17.32	1.36	4.02	0.34
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.04}$]	0.04	23.57	2.21	5.47	0.40
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.15}$]	0.15	32.76	1.56	7.61	0.21
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.35}$]	0.35	31.87	0.62	7.40	0.08
MW_{NC}/$HBPEI_{1800}$[TL,$CuI_{0.75}$]	0.75	31.32	0.56	7.27	0.08

REFERENCES

1. P. Louette, F. Bodino and J.-J. Pireaux, *Surface Science Spectra*, 2005, **12**, 4.