Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Comparative study of the covalent diazotization of graphene and carbon nanotubes by spectroscopic techniques coupled to thermogravimetric analysis.

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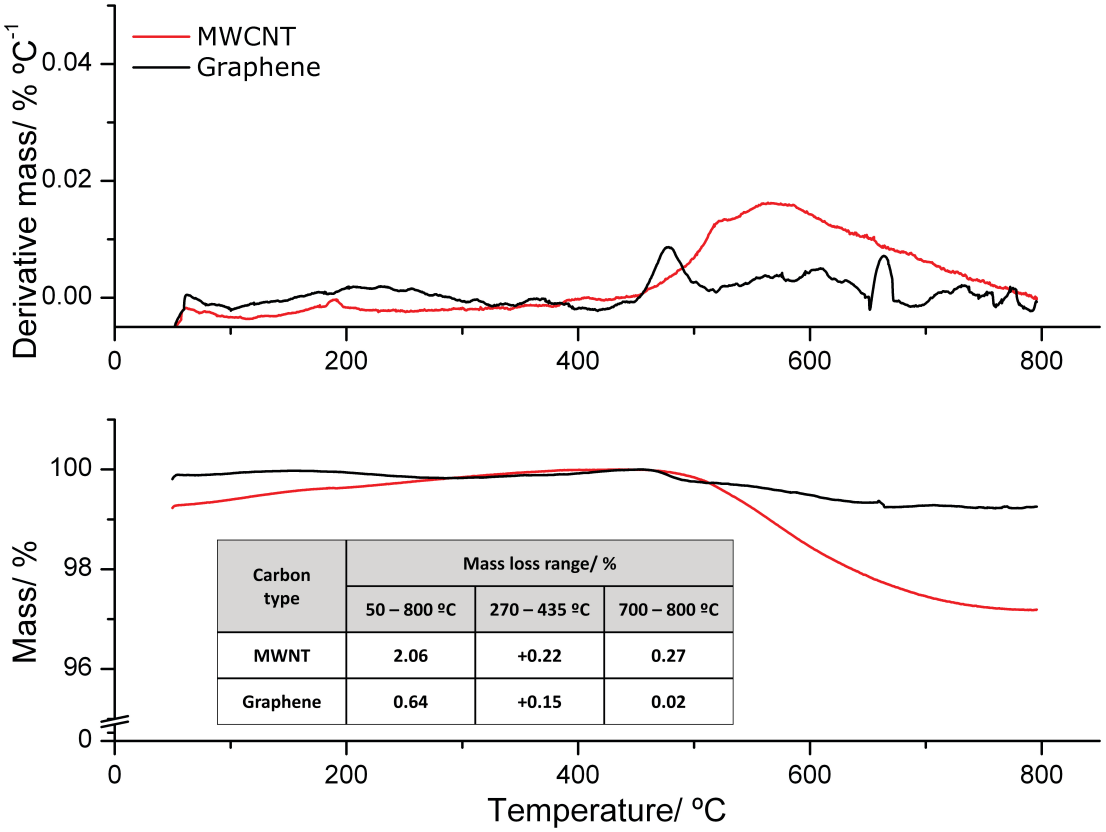


Carbon type	Mass loss range/ %		
	50 – 800 ºC	270 – 435 ºC	700 – 800 ºC
MWNT	2.06	+0.22	0.27
Graphene	0.64	+0.15	0.02

Figure S1. TGA traces of the unmodified MWNTs and Graphene samples tested at 10 ºC min^{-1}, N_2.

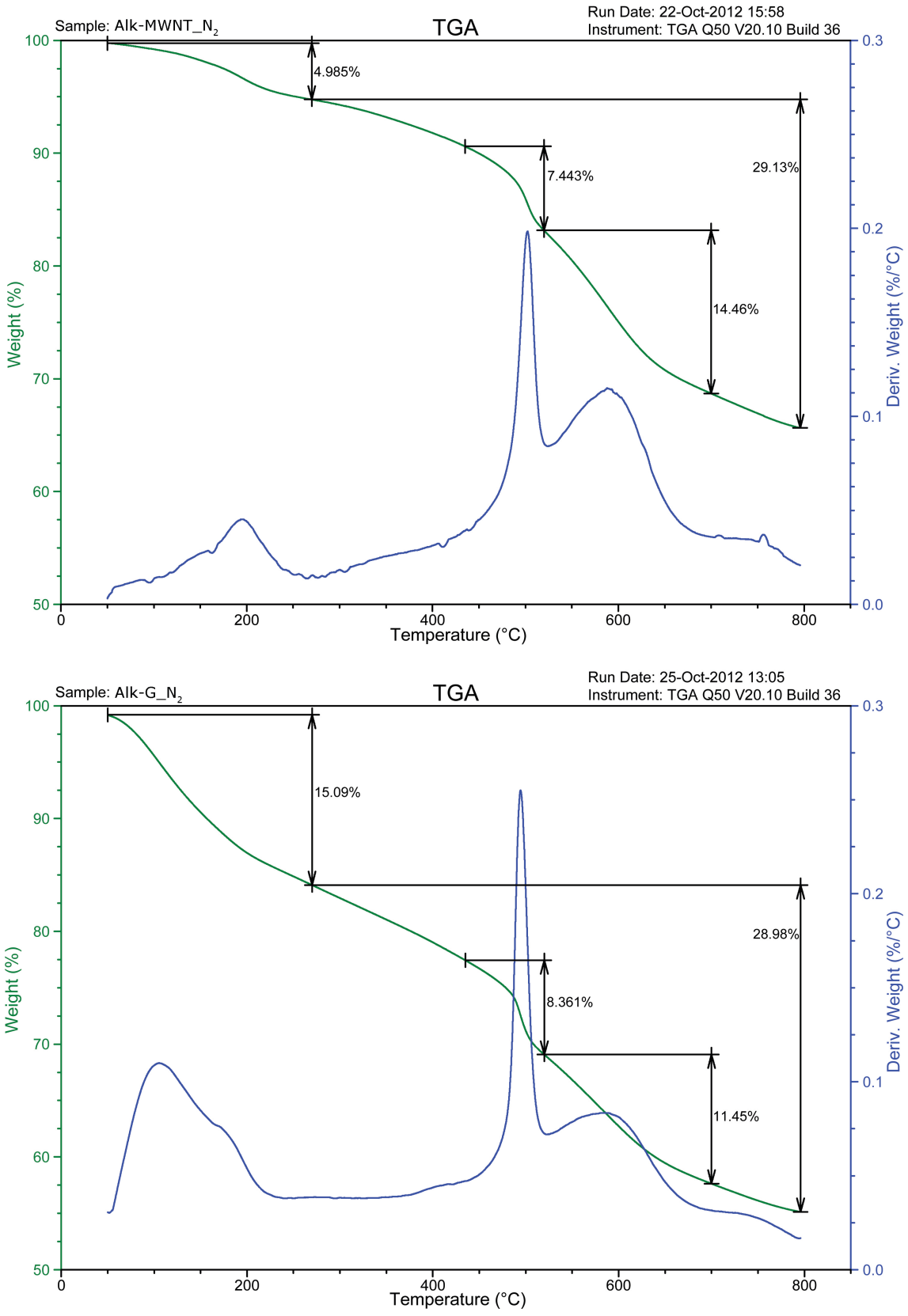


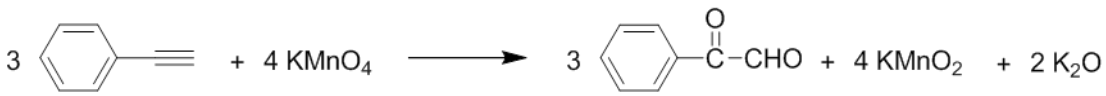
Figure S2. TGA and dTGA traces for the MWNTs and Graphene alkyne derivatives tested at 10 ºC min^{-1}, N_2

Table S1. TGA mass loss data for the MWNT and Graphene alkyne derivatives tested at 10 ºC min^{-1}, N_2.

Temp. range/ ºC	Mass loss/ %	
	ALK-MWNT	ALK-G
50 – 270	5.0	15.1
435 – 520	7.4	8.4
520 – 700	14.5	11.5
270 - 800	29.1	29.0
50 - 800	34.1	44.1
270 - 435	4.2	6.7
435 – 700	21.9	19.9
700 - 800	3.1	2.5

Baeyer test

One of the simplest tests to determine instauration is Baeyer's test. It consists in a mild oxidation of the double or triple bonds with a diluted solution of potassium permanganate ($KMnO_4$). Here we use the same principle to roughly determine the amounts of alkynes by following the changes in the absorption spectrum of $KMnO_4$. Under the conditions employed the reaction can be described as follow:



Briefly, permanganate solutions were prepared for each sample. Then two aliquots of 3 ml were taken. One aliquot was maintained, while the other was added to a precisely weighed amount of

solid alkyne-modified carbon nanostructure. Both solutions were stirred in the dark for 10 minutes and the solid-containing solution filtered. The absorption spectra of both aliquots were collected in a short period of time to avoid any changes produced by the photodecomposition of permanganate. The Figure S1 shows the changes in the absorption spectrum of $KMnO_4$ after the addition of Alk-MWNT and ALK-G. In both cases the baseline of the spectra were corrected for the displacements caused by the dispersion of the nanoparticles.

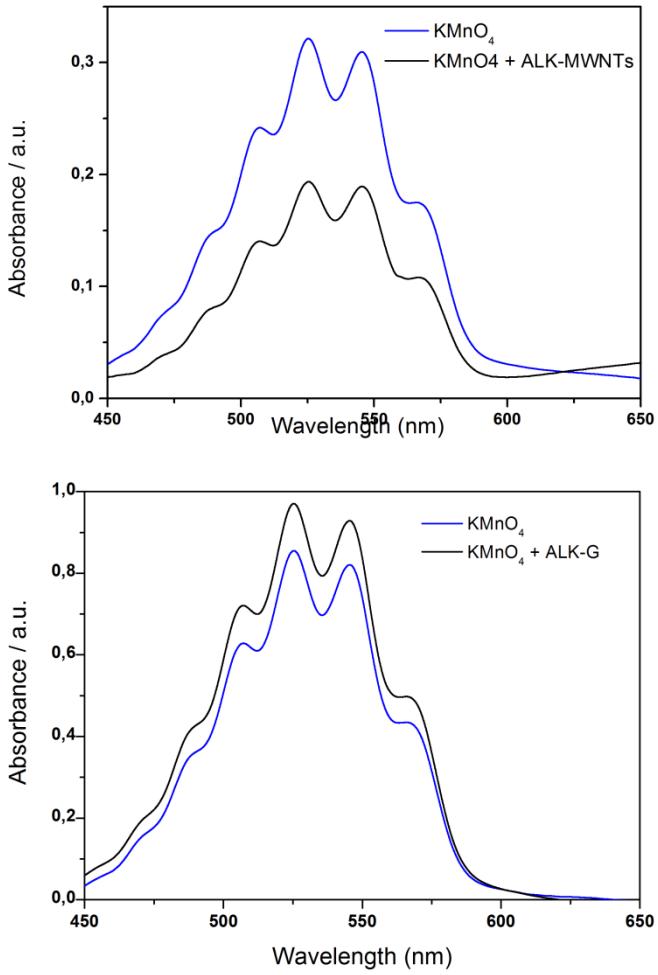


Figure S3. UV absorption spectra of $KMnO_4$ before and after mixing with ALK-MWNT (top) and ALK-G (bottom).

The loss in absorbance of the band at 525 nm can be related to the amount of permanganate consumed through the Lambert-Beer equation, using the molar absorptivity of $KMnO_4$ at this wavelength of 2.24 x 10^3 $M^{-1}.m^{-1}$. Then the concentration of the alkyne modifier in both cases was

obtained from the stoichiometry of eq. 1, giving values of 38 and 29 % w/w of ALK-MWNT and ALK-G, respectively.

The Figure S4 shows the TGA and dTGA curves for the modifying reagent, 4-ethynylaniline. It can be seen that the peak perfectly matches those observed in the modified CNS (Figure 1).

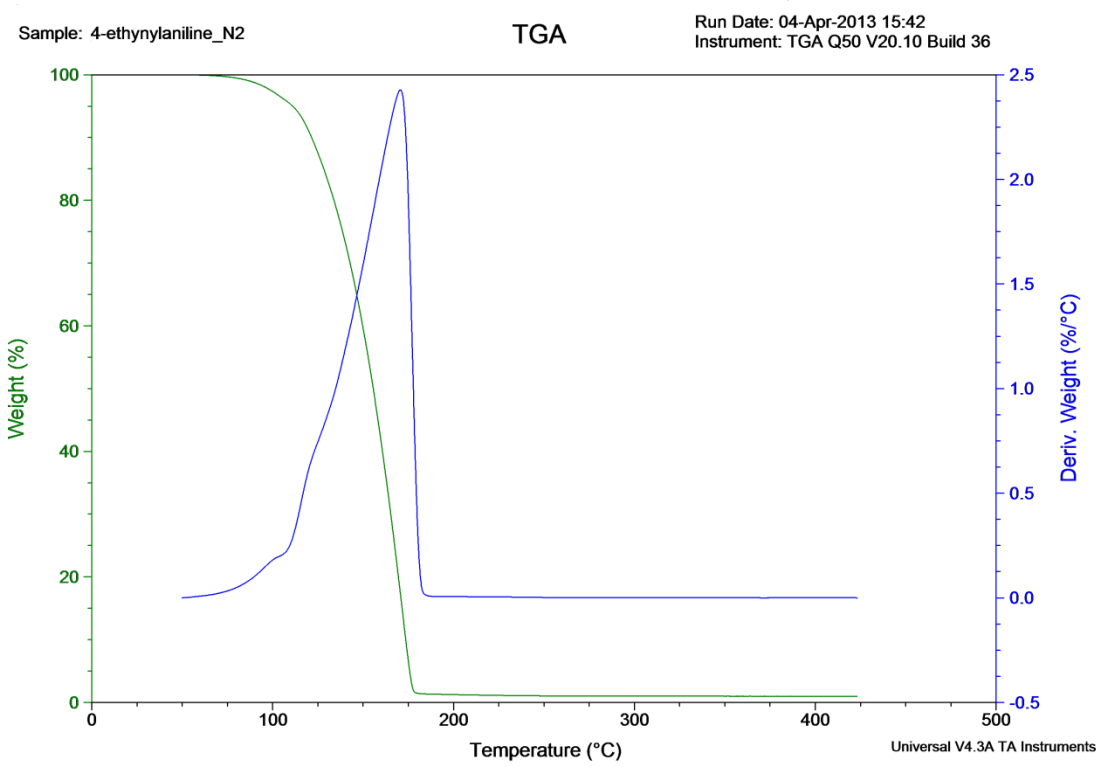


Figure S4. TGA and dTGA traces for 4-ethynylaniline tested at 10 ºC min^{-1}, N_2

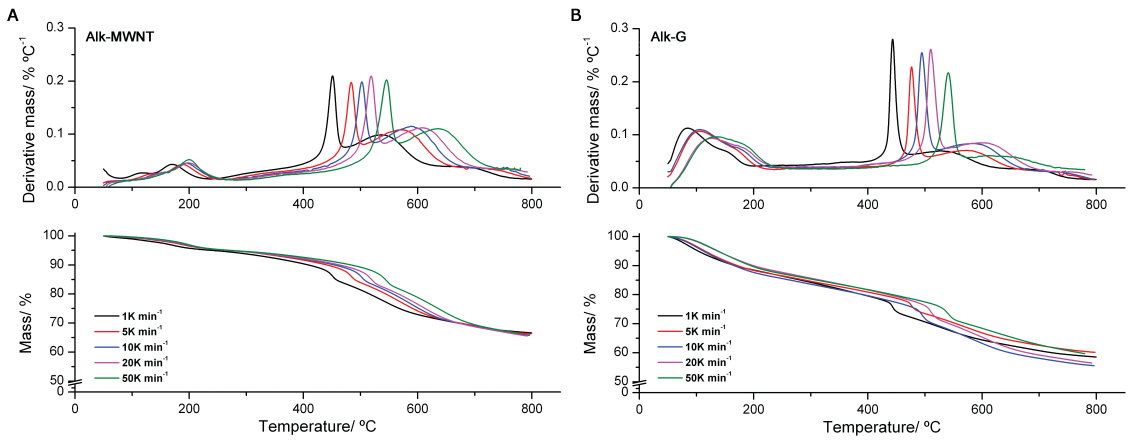


Figure S5. TG and dTG traces for the MWNT and Graphene alkyne derivatives tested at 1, 5, 10, 20 and 50 K min^{-1} under a N_2 atmosphere

The Figure S6 shows the vibrational spectrum of the modifying group 4-ethynylaniline.

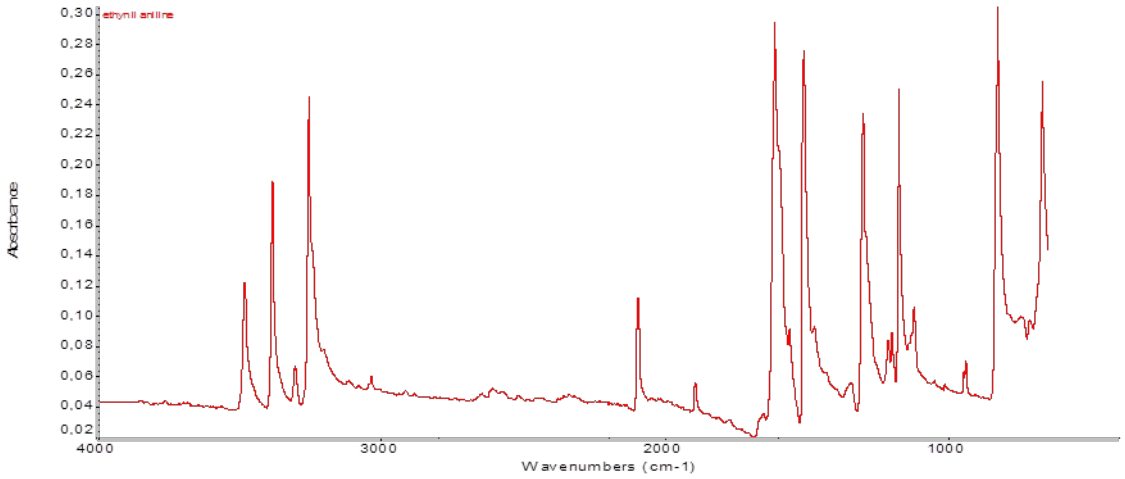


Figure S6. FTIR spectrum of 4-ethynilaniline.

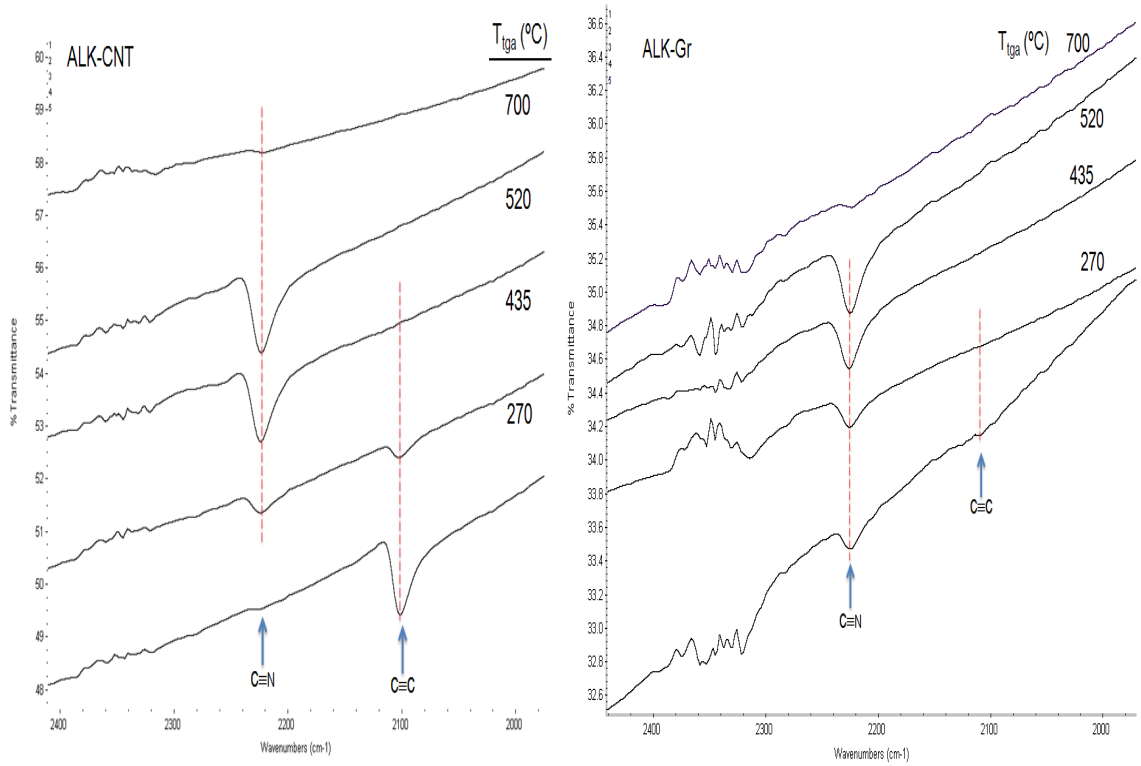


Figure S7. FTIR spectra corresponding to amplified region of the spectra in Fig 3 for ALK-G and ALK-MWNT as a function of thermal treatment under nitrogen in the thermobalance.