Electronic Supplementary Material (ESI) for RSC Advances

SUPPLEMENTARY INFORMATION

1. Characterization of functionalized MWCNTs

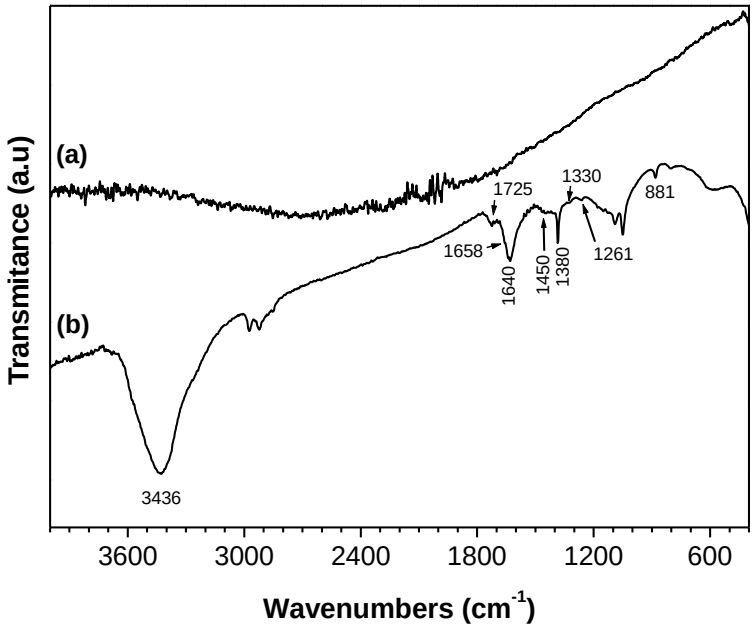

Figure S-1 FTIR-ATR spectra of (a) pristine and (b) functionalized MWCNTs.

Figure S-1 shows the FTIR spectra of the MWCNTs before and after surface functionalization. Oxygen functional groups were not detected on pristine MWCNT (Figure S-1a). In the range of 400-4000 cm^{-1} the functionalized MWCNT present a set of bands characteristics of oxygen functional groups (Figure S-1b): the bands at 1261, 1380, 1450, 1725 and 3436 cm^{-1} correspond to the vibration of the groups C-O-C, C-O, C=C, C=O and O-H, respectively [S1] and is in agreement with the introduction of carboxylic acid groups at the surface of the MWCNTs. The sharp band at 1640 cm^{-1} is assigned to carbonyl of quinone type units.

MWCNTS were further analyzed by XPS to acquire information regarding the chemical oxidation states of the resulting oxidized MWCNT comparatively with the pristine MWCNT samples. The XPS spectrum of pristine MWCNT shows only a dominant peak structure for the C 1s core level at a binding energy of 284.4 eV (peak C6 in Figure S2-b), which corresponds to the graphitic carbon of the untreated MWCNT [S2]. After oxidation of MWCNTs (Figure S-2a) the C 1s peak shape changes and the broadening to high binding energies is observed, which is attributed to the presence of oxygen functionalities on the tubes. In addition, the XPS spectrum of O1s confirms the presence of oxygen functional groups on the functionalized MWCNT. The optimum curve fitting of the O1s peak for functionalized MWCNT is shown in Figure S-3 and indicates three different oxygen functionalities. The measured binding energies along with peak assignments of XPS spectra are summarized in Table S-1 and are in agreement with the values reported in literature [S2].

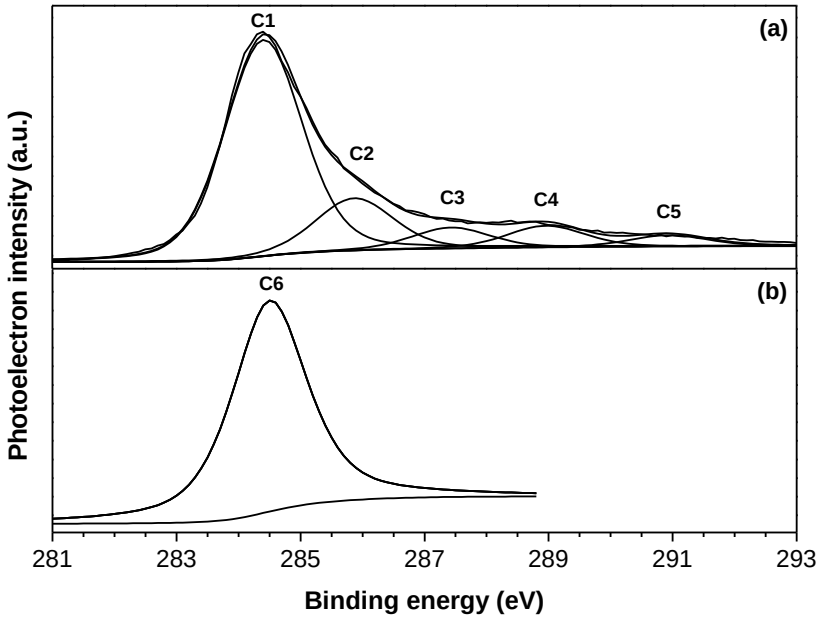

Figure S-2 XPS spectra of C 1s core levels of (a) oxidized and (b) pristine MWCNT.

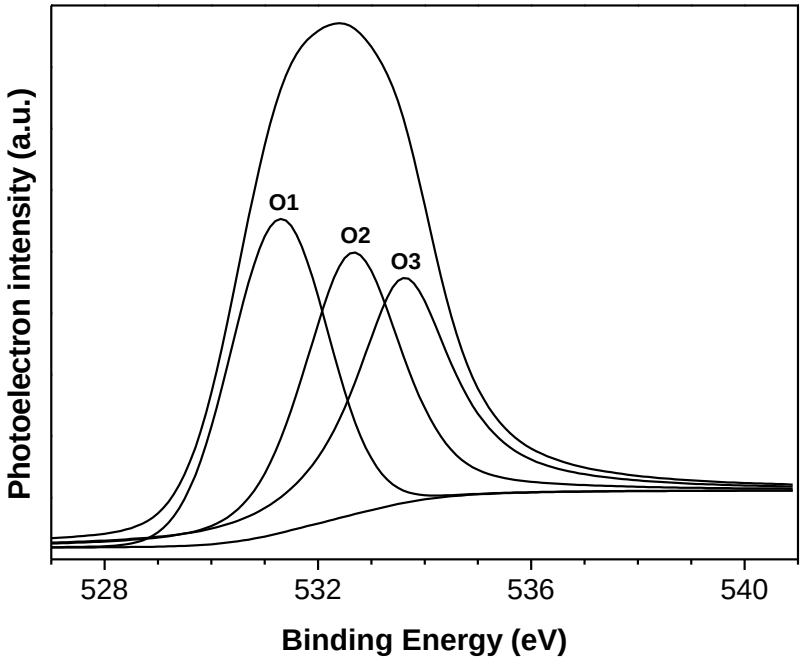

Figure S-3 XPS spectra of O 1s core levels of oxidized MWCNT.

Table S-1 XPS peak assignments of the chemical oxidation states of MWCNT of the C 1s and O 1s core levels* (Figures S3 and S4).

Sample	Peak	Binding energy (eV)	FWHM (eV)	Assignment
f-MWCNT	C1	284.4	1.47	C-C (sp^2)
	C2	285.9	1.47	-OH
	C3	287.4	1.47	C=O
	C4	288.9	1.47	-COOH
	C5	290	1.47	$\pi \leftrightarrow \pi^*$
	O1	531.3	2.13	C=O (O_{G1})
	O2	532.6	2.13	-OH (O_{G2})
	O3	533.6	2.13	-COOH (O_{G4})
MWCNT	C6	284.5	1.31	C-C (sp^2)

* Peak centers and full widths at half-maxima (FWHM) based on curve-fitting.

2. MB release upon NIR light irradiation – effect of the temperature of the release medium

The temperature of the shaker was kept at 37ºC during all the release experiments. For the experiments performed upon exposure to NIR light the temperature of the release medium was monitored. Figure S-4 shows the evolution of the temperature of the medium during the experiments performed with the composite MWCNT 0.025wt%. It was found that the temperature increased up to 42ºC in the first 3h and was constant until the end of the trial (Figure S-4 - black circles). In order to evaluate the impact of this temperature increment on the MB release, an experiment of MB release was carried out following the temperature profile above described, without exposure to NIR light. The resulting release pattern (Figure S-4 – squares) was very similar to that obtained at 37ºC without exposure to NIR light (Figure S-4 – triangles) in the first 6 hours. Conversely, the MB release carried out under irradiation of NIR light was much faster (Figure S-4 – red circles). Thus, the acceleration of the MB release from composites when exposed to NIR light cannot simply be explained by the increase of the temperature of the release medium due to the irradiation of NIR light.

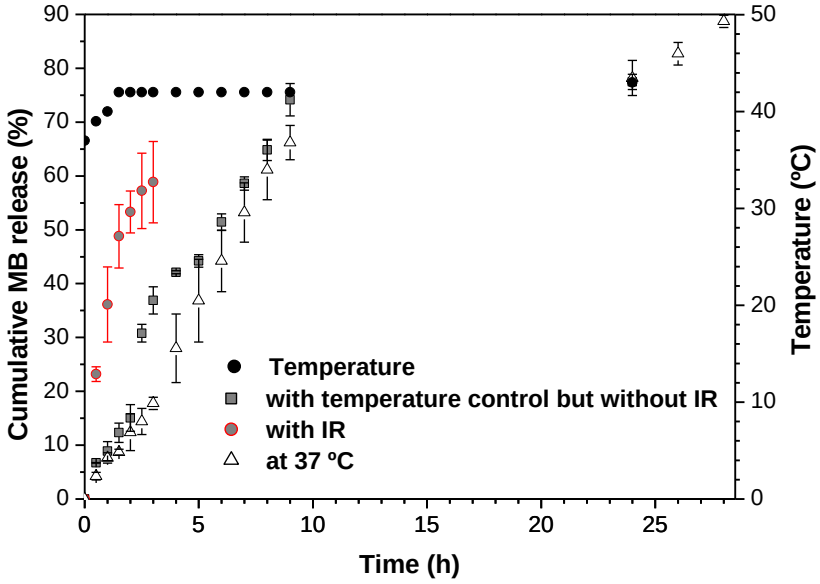

Figure S-4 *In vitro* MB release profiles from the composite MWCNT 0.025wt% performed in different conditions.

REFERENCES

S1. (a) Grujicic M, Cao G, Rao AM, Tritt TM, Nayak S. UV-light enhanced oxidation of carbon nanotubes. Appl Surf Sci 2003; 214:289-303. (b) Coates J. In: Meyers RA. Editor Encyclopedia of analytical chemistry, Chichester; John Wiley & Sons Ltd; 2000 p. 10815-10837.

S2. Chiang Y-C, Lin W-H, Chang Y-C. The influence of treatment duration on multi walled carbon nanotubes functionalized by H_2SO_4/HNO_3 oxidation. Appl Surf Sci 2011; 257:2401-10.