A facile and ecofriendly functionalization of multiwalled carbon nanotubes by an old mesoionic compound

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Electronic Supplementary Information

Contents:

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Experimental Section

All reagents and solvents were obtained from commercial suppliers and used without further purification. Melting points were determined on a Kofler melting apparatus and are uncorrected. IR spectra were recorded in Nujol with a Nicolet Impact 410D spectrometer. ^{1}H-NMR spectra were obtained with a Bruker AMX R300. Merck Kieselgel $60F_{254}$ plates were used for TLC and Merck silica gel 60 (0.063- 0.100 mm) for column chromatography. MWCNTs were produced by catalytic chemical vapor deposition CCVD) from isobutane on Fe/Al_2O_3 catalyst and purified as reported in previously procedure, giving the CNT sample with purity >95%.[1,2] Oxazolone **1** was prepared according to literature method.[3]

Typically Solventless Functionalization Method

Method A: Oxazolone **1** (100 mg) and pristine MWCNTs (100 mg) were combined using a mortar and a pestle and the resulting powder were transferred in a sealable glass vial. The reaction mixture was heated at 100 °C for 20 h (entry 1, table 1) or 80 °C for 6 h (entry 2, table 1) . The mixture was cooled, the solid residue was washed for three times with ethanol (3 x 20 mL) and each time sonicated for 10 min and separated from the supernatant by filtration under vacuum on Millipore membrane of 0.1 μm. The solid residue was then dried under vacuum at 50 °C to give **f-MWCNT 2.**

Method B: Oxazolone **1** (500 mg) and pristine MWCNTs (500 mg) were combined using a mortar and a pestle and the resulting powder were transferred in a fixed bed down-flow U-tube glass reactor operating at atmospheric pressure equipped with an internal coaxial thermocouple connected with a PID temperature controller; the reaction mixture was heated at 80 °C for 20 h (entry 1 table 2) or 100 °C for 6 h (entry 1 table 2) under an helium flow (20 cc/min) and the exhaust gases were flowed in a flask containing a standard barium hydroxide solution. The mixture was cooled; the solid residue was washed for three-time with ethanol (3 x 50 mL) and each time sonicated for 10 min and separated from the supernatant by filtration under vacuum on Millipore membrane of 0.1 μm. The solid residue was then dried under vacuum at 50 °C to give **f-MWCNT 2.** The amount of CO_2 evolved during the reaction was evaluated by acid-base titration of the barium hydroxide solution with 0.196 M hydrochloric acid solution using phenolphthalein as indicator.

Functionalization Method in Molecular Solvent

The mixture of pristine MWCNTs (100 mg) and oxazolone **1** (100 mg) in 20 mL of dry acetonitrile was irradiated under microwave conditions at 100 W and 80 °C for one hour. The mixture was cooled and filtered on Millipore membrane of 0.1 μm and the solid residue was subject to the above reported work up procedure.

Work-Up procedure

The cooled reaction mixture was treated with ethanol (50 mL), sonicated for 10 min and filtrated under vacuum on Millipore membrane of 0.1 μm. The filtrate was evaporated under vacuum and the residue was analyzed by ^{1}H NMR. The ^{1}H NMR showed the presence of three main products, oxazolone **1**, *N*-benzoyl alanine and1,3-dibenzoyl-3,5-dimethylpyrrolidine-2,4-dione, which were separated by flash chromatography and characterized.

The solid residue was washed with ethanol for further two times and the filtrate residues were analyzed. Traces of benzoyl alanine and 1,3-dibenzoyl-3,5-dimethylpyrrolidine-2,4-dione were found in the residue of the second ethanol washing. No organic products have been detected in the third washing. **1,3-dibenzoyl-3,5-dimethylpyrrolidine-2,4-dione**: IR (Nujol): 3258 (NH), 1784 (CO), 1745 (CO);^{1}H-NMR (CDCl3): 1.55 (d,CH3,), 1.67 (s, CH3), 4.89 (q, CH), 7.49-7.8 (m, CH arom).

CO_2 titration

The reactions were performed at 100 °C for 6 h on a fixed bed down-flow U-tube glass reactor operating at atmospheric pressure equipped with an internal coaxial thermocouple connected with a

PID temperature controller under an helium flow (20 cc/min) and the exhaust gases were flowed in a flask containing a standard barium hydroxide solution. A blank reaction containing only 4-methyl-2-phenyloxazol-5(4*H*)-one was also performed. The carbon dioxide released from the reaction was transformed in barium carbonate and the amount of CO_2 was evaluated by classical quantitative acid-base titration method[4] of the filtered barium hydroxide solution with 0.196 M hydrochloric acid using phenolphthalein as indicator. The CO_2 amount produced during the reaction was calculated by Eq 1.

$$CO_{2\,evolution} = \frac{M_{HCl} \times (V_i - V_f)}{2}$$

Equation S1 $CO_{2evolution} =$ mmol of carbon dioxide delivered; M_{HCl} = concentration of hydrochloric acid; V_i = mL of HCl used for the titration of 20 mL $Ba(OH)_2$ before the reaction; V_f = mL of HCl used for the titration of 20 mL $Ba(OH)_2$ after the reaction.

In Figure 1 is reported the experimental setup used to collect the CO_2 evolved during the 1,3-dipolar cycloaddition reaction. Table 1 reports a detail of the results obtained during the titration of the $Ba(OH)_2$ solution before and after the CO_2 evolution in the 1,3-dipolar cycloaddition and in the blank reaction.

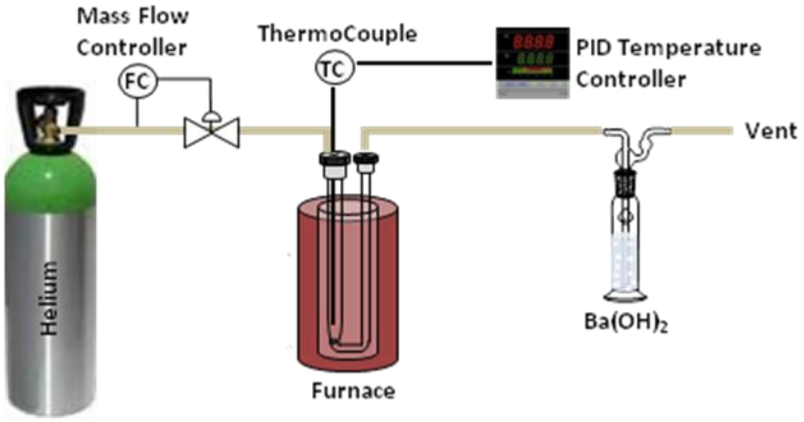

Figure S1. Laboratory scale plant used for the collection of CO_2 evolved during the reaction.

Table S1. Detailed results of titration analysis.

Reaction	$[Ba(OH)_2]$	[HCl]	$V_{ml\ Ba(OH)2}$	$V_{i\ HCl}$	$V_{f\ HCl}$	mmoles CO_2
Blank	0.140	0.196	20	28.6	28.6	0
1,3-dipolar cycloaddition	0.140	0.196	20	28.6	27.9	0.07

Carbon Nanotube Analysis

The morphology of MWCNTs was analyzed using an HRTEM JEOL JEM 2010 analytical electron microscope (LaB_6 electron gun) operating at 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging. HRTEM samples were prepared by placing a drop of the MWCNTs dispersed in isopropanol on 400 mesh holey-carbon coated copper grids. Thermogravimetric analysis (TGA) were done by using a SDTQ 600 (TA Instruments) in the temperature range 100-700 °C. About 7 mg of each sample was, firstly, placed in an alumina pan and kept at 25 °C under a 100 ml/min pure-argon flow until balance stabilization and subsequently heated with a scan rate of 20 °C/min under the same argon flux. Balance sensitivity was 0,1 µgr. A baseline recorded in the same measurement conditions with empty allumina pans was subtracted from each thermogram before data analysis. MS experiments were carried out with Pleiffer Vacuum, D35 614 Asslar, Model GSD 301 T3. Elemental analyses were performed using a Thermo FlashEA 1112 Series with an accepted tolerance of ± 0.4 units. Raman spectra were recorded with an Invia Renishaw microspectrometer (50x) and a laser source at 532 and 633 nm. XRD data were collected with an Ital Structures diffractometer (Mod. APD 2000) using nickel filtered CuKα radiation source ($\lambda = 0.15418$ nm). The patterns were recorded in step scan mode from 10° to 60° (2 theta angles) with a step of 0.02° and a counting time of 1 sec/step.

RAMAN Spectra

Raman spectra were recorded with an Invia Renishaw microspectrometer (50x) and a laser source at 633 nm.

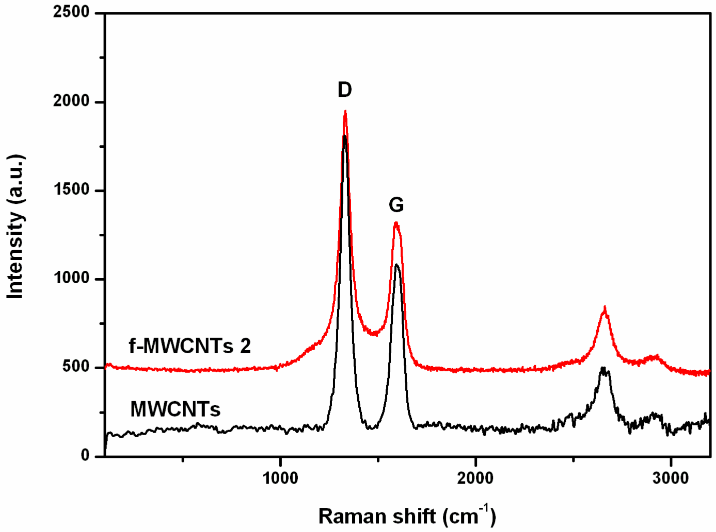

Figure S2. Overlapped Raman spectra (633 nm excitation) of pristine MWCNTs (black line) and *f*-MWCNTs **2** (red line).

MS Analysis

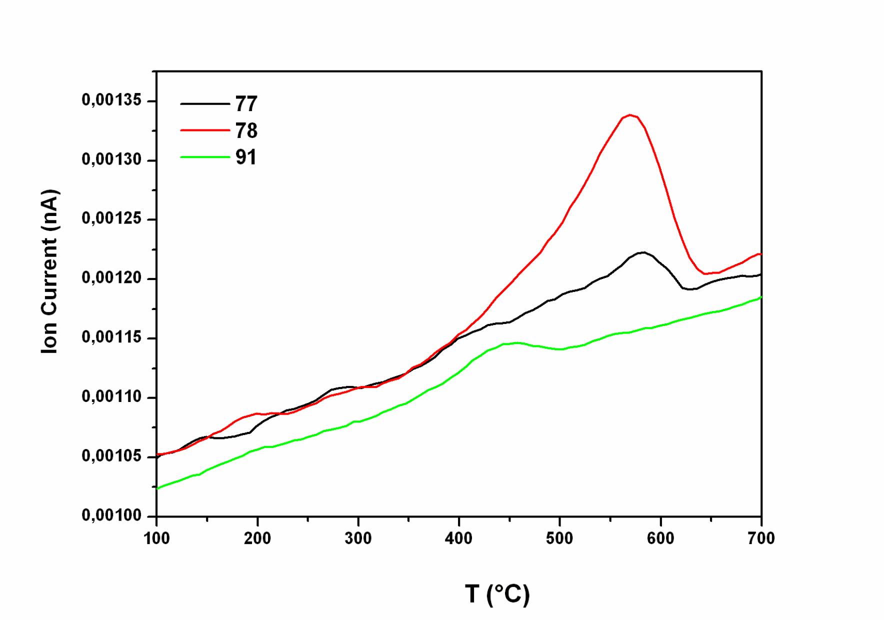

Figure S3. Temperature programmed MS analysis of *f*-MWCNTs **2**.

XRD Analysis

The XRD patterns of pristine and functionalized MWCNTs indicate that the crystalline and the morphology of the MWCNTs are essentially preserved during the organic functionalization. The main diffraction peaks of graphitic structures at 2θ = 25.3°, 42.1°, 43.6° and 49.1° (JCPDS card 41-1487) correspond to reflections of (002) crystallographic planes (interlayer spacing between adjacent graphite layers) and to the in-plane orderings of (100), (101) and (102) crystallographic planes respectively. Diffraction peaks at 2θ = 38° and 44.8° correspond to iron based catalyst (JCPDS card 06-0696) encapsulated into MWCNTs used for their synthesis. The (002) peak appears broaden because of the finite number of layers and of the curvature of each tube. The broaden (10) bands indicate the curved sheet of the materials. The average coherence length or mean crystalline size along the *c*-axis (L_c) of MWCNTs can be deduced from the width of the (002) Bragg peaks using Debye–Scherrer's equation (Eq. 3).[5]

$$L_c = \frac{0.9\,\lambda}{\beta\ \cos 2\theta}$$

Equation S2: L_c value represents an average stacking height of graphitic planes; β is the peak width at the half maximum of the (002) peak; λ is the wavelength of the X ray radiation (Cu Kα radiation, λ = 0.15418 nm) and 2θ is the angular position of the (002) peak.

L_c of pristine and functionalized MWCNTs are close to 5 nm. The very similar values indicate that the crystalline organization remains almost the same after the reaction with the mesoionic compound which install a Δ-1-pyrroline moiety on MWCNT surface. The mean number of graphitic wall (*N*) calculated by the equation S3,[6, 7] are estimated to be 15 layers.

$$N = \frac{L_c}{d_{(002)}}$$

Equation S3: $d_{(002)}$ is the interlayer spacing between adjacent graphite layers (nm).

The results confirm that the reaction treatment does not damage the graphene layer organization. The intensity of (002) peak of pristine MWCNTs is much larger than functionalized MWCNTs; this evidence might be caused by the much lower packing density in the latter sample as a result of debundling induced by the Δ-1-pyrroline group insertion.

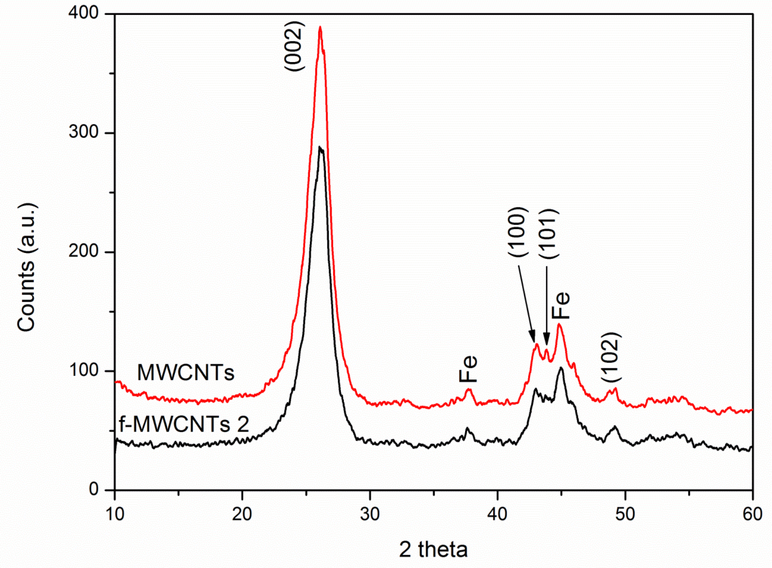

Figure S4. XRD spectra of pristine MWCNT and *f*-MWCNTs **2**.

From XRD data (an average walls thickness of 5 nm and an average diameter of 20 nm and an average number layer of 15-17) we have calculated the functionalization density of the other layer; in fact, considering that the number of carbon atoms in each layer is proportional to the layer area it is possible to calculate the percentage of carbon atoms on the outer layer as a ratio between the area is of the outer layer and the total area of all layers by the following equation :

$$C\,(\%) = \frac{r_{outer}}{\sum_{inner}^{outer}(r_i)}\ x\ 100$$

TEM Analysis

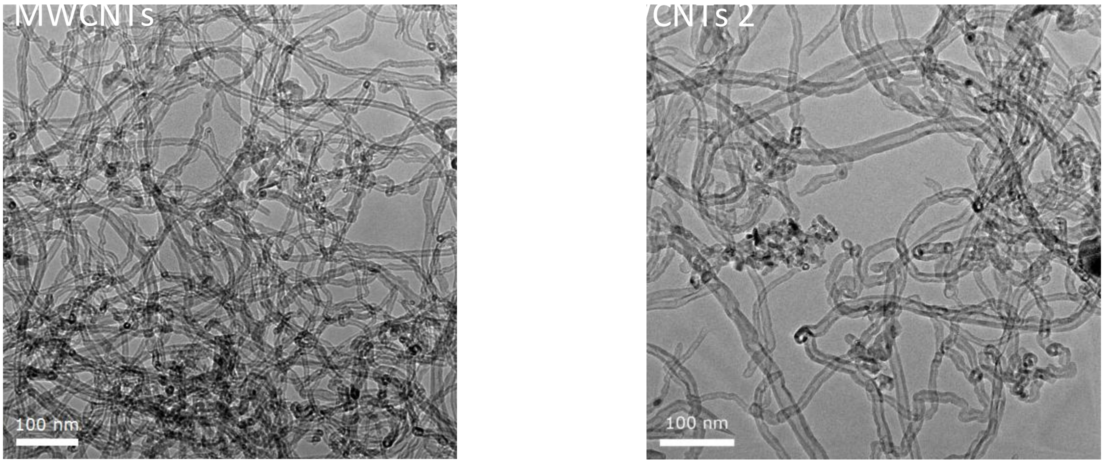

Figure S5. TEM images of raw and functionalized MWCNT

UV-Vis Spectrum

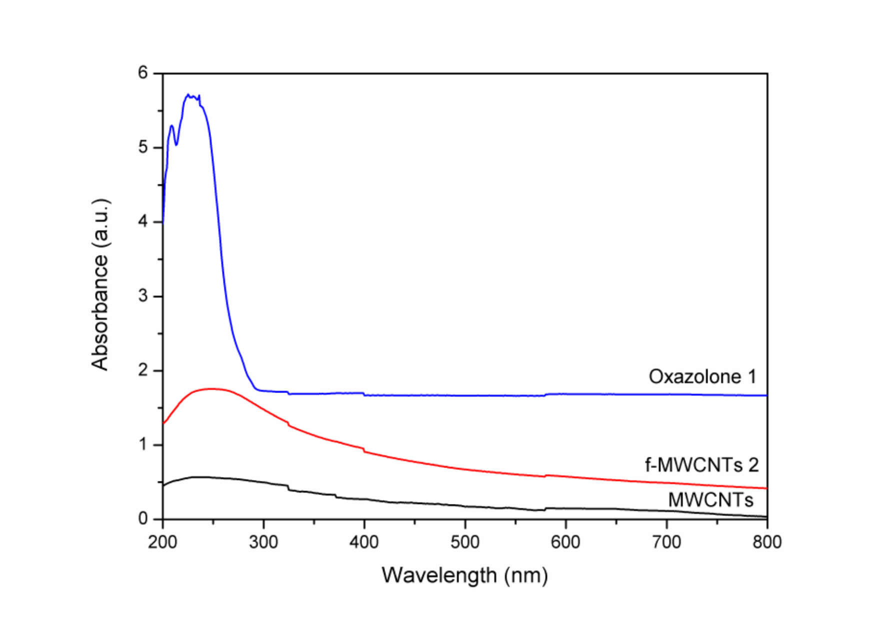

Figure S6. UV-vis analysis of pristine MWCNTs (black), functionalized MWCNTs (red) and Oxazolone **1** (blue).

UV-vis absorption spectra were obtained in ethanol using quartz cuvettes on a Thermo Nicolet mod. Evolution 500 double beam spectrophotometer. The UV-vis spectrum of *f*-MWCNT **2** sample shows that the main electronic features of pristine MWCNTs which monotonically decrease in intensity at higher wavelengths. In particular, the *f*-MWCNTs **2** exhibits in its UV-vis spectrum a broad absorption band around 250 nm more intense with respect to untreated MWCNT; this absorption band is also characteristic of the oxazolone **1** precursor. Furthermore, the band at 209 nm of oxazolone **1** due to the lactone group disappeared in the *f*-MWCNTs **2** sample while the band at

229 nm of oxazolone is shifted at higher wavelength (250 nm) in the *f*-MWCNTs **2** sample confirming the successful chemical transformation of oxazolone precursor.

XPS Analyses

The XPS analysis were carried out by means of a Physical Electronics 5800-01spectrometer. A monochromatic Al Ka X-ray source was used at a power of 300 W. In figure S7 XPS wide-scan spectra of an pristine MWCNTs and functionalized MWCNT **2** were compared. The pristine MWCNT showed an intense C 1s peak at a binding energy *ca.* 284 eV. The *f*-MWCNTs **2** sample showed a N 1s peak at *ca* 400 eV.

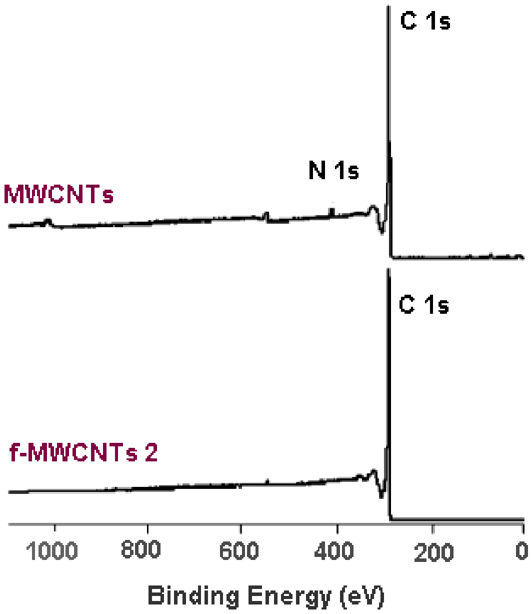

Figure S7. Wide-scan C 1s and N 1s XPS spectra of pristine MWCNTs and f-MWCNTs **2**

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