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A high volume and low damage route to hydroxyl functionalization of carbon nanotubes using hard X-ray lithography

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Abstract

The efficient functionalization of large quantities of carbon nanotubes entangled in a non-woven fashion into bucky-papers has been demonstrated through exposure to hard X-rays generated by a synchrotron source. The X-ray beam solely functionalized the carbon nanotube outer walls and an optimum X-ray exposure energy between 1048 and 2096 J cm^{-2} has been found to achieve maximum hydroxyl group density. Sol-gel reaction between a commercial fluoro-silane and the hydroxyl-modified carbon nanotubes was successfully performed resulting in an even distribution of fluoride atoms on the carbon nanotube surface, opening the way for the mass production of functionalized carbon nanotubes.

The scope of potential applications for carbon nanotubes (CNTs) has dramatically expanded over the past 20 years opening highly promising opportunities in materials science. CNTs have demonstrated proof of concept application in biotechnology sensing separations, energy production and as composites with enhanced mechanical properties. However, the lack of solubility and the difficult manipulation in solvents and functionalization on large scale represent crucial barriers to the translation of CNT research into commercial products [1, 2].

The functionalization of CNTs has been demonstrated to improve the surface affinity and/or chemical reactivity; several studies have demonstrated the importance of such an approach [1]. Although the functionalization of CNTs with hydroxyl or carboxylic groups can be obtained in gaseous phase using plasma, gamma ray or ozone, the functionalization of large amounts of CNTs with more complex and reactive chemicals is typically achieved by chemical reaction in solution. Plasma and ozone treatment have been demonstrated to damage the CNTs and may induce wall collapse [3]. These physical functionalization methods can affect the original electrical or thermal conductive properties of the CNTs. In addition, the penetration depth of these plasma and ozone irradiation techniques is limited to the top 20-50 nm of the exposed surface due either to the thickness of the plasmon or to the reactivity of ozone corresponding to a penetration thickness of a few CNTs only [4]. Multiple treatments or exposure to severe conditions are therefore required to produce functionalized CNTs with high surface functionalization densities using these methods [5]. On the other hand, functionalization in solution often initially involves harsh treatments in strong acids while a number of steps are typically required to induce reactive pre-cursor groups prior to further chemical grafting or substitution [6]. Furthermore, a general issue in CNT handling resides in the preparation of homogeneous and concentrated suspensions of CNTs which is problematic due to the natural tendency for CNTs to agglomerate. Routes to suspend and disperse CNTs have been previously demonstrated to damage the CNT crystalline walls. Given the technological demand of materials with specific functional properties, the controlled functionalization of the CNT side walls is a fundamental step to promote CNTs for the preparation of new composites or the fabrication of novel devices.

Here we propose, for the first time, the use of hard X-rays for the large scale functionalization of CNTs. We used preformed self-supporting CNT structures, where the CNTs are individually entangled in a non-woven fashion, called bucky-paper (BP). BPs were exposed to “white” hard X-ray beams (photon energy range at 3-20 keV and a peak at 8 keV) allowing a single step functionalization of the entire 20 mg CNT disks (47 mm diameter and 50 μm thickness).This fast technique takes advantage of the high penetration depth of such high-energy radiation and was used to induce the formation of hydroxyl groups [7] on the CNT outer walls without significantly changing the wall crystallinity (TEM images in Figure 1~~Figure 1~~ A and B). Although the crystallinity of the CNT outer walls was reduced, major damage was prevented, as compared to the dramatic damages induced on the CNT outer walls by other treatment techniques such as ozone or sonication (Figure 1~~Figure 1~~ C, D and E).

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The formation of hydroxyl groups was confirmed by FTIR (Figure 2~~Figure 2~~) and subsequent functionalization can be easily carried out. For instance, in this work, we grafted a commercial fluoro-silane (FAS-13) widely used for the preparation of hydrophobic surfaces [8]. FAS-13 easily reacts with superficial hydroxyl groups through a mechanism typical of sol-gel precursors [9]. After functionalization, the

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broad hydroxyl group band was significantly reduced and the CH stretching modes were increased (Figure 2~~Figure 2~~) confirming the condensation reaction with FAS-13.

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The effect of the hard X-rays on the BPs was investigated by exposing only one side to the radiation source with a dose matrix ranging from 262 up to 16760 J cm^{-2}. The treatment efficiency was first demonstrated by measuring the contact angle of water on both sides of the BPs (Figure 3~~Figure 3~~-A). The contact angle decreased on both sides of the BP from ~120^{o} for the pristine CNTs, down to ~40^{o} after 8385 J cm^{-2} exposure dose corresponding to a ~66% reduction. Although just one side of the sample was irradiated, the well-known high penetration depth of such radiation source allows the surface along the entire thickness to be modified. Further evidence of the homogeneous distribution of the hydroxyl groups was the improved stability of suspensions of irradiated CNTs in polar solvents (e.g. ethanol and 50 v/v water/ethanol mixture - Figure 4~~Figure 4~~), making this a novel technique to efficiently functionalize CNTs prior to their suspension.

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The success of the reaction of the hydroxyl-functionalized CNTs with FAS13 was further demonstrated by the increased contact angle on both sides of the BP after the grafting procedure (Figure 3~~Figure 3~~-A). The plateauing of the contact angle around 145^{o} clearly demonstrates the presence of the fluoro-silane groups on the CNT side walls while the deep penetration of the initial X-ray beam exposure was confirmed by similar contact angle behaviour on both sides of the BPs. Furthermore, from the simultaneous plateauing of both the contact angle and the relative amount of fluoride present on the surface the optimal energy input for this experiment was found to be in the 1048 to 2096 J cm^{-2} range. As determined by XPS (Figure 3~~Figure 3~~ B), the oxygen content of the X-ray exposed CNT BPs was consistently reduced by

~30 % after silanisation, corresponding to a significant fluoride surface concentration of 6.13 at%. Higher exposure doses did not further enhance the initial hydroxyl coverage suggesting that saturation was reached over this range of dose matrixes. Finally, the distribution of the hydroxyl groups across the surface of a BP is demonstrated by Energy Dispersive X-ray Spectroscopy (EDS). The distribution of the fluoride atoms after grafting is shown to be even and homogeneous across the two BP surfaces (Figure 5~~Figure 5~~). This result demonstrates the absence of site selectivity and the large scale applicability of the technique to functionalize CNTs.

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In conclusion, we have presented a novel and efficient way to functionalize CNTs with hydroxyl precursor groups with minimal damage to the CNT crystallinity. This one-step process allows for subsequent functionalization using the hydroxyl group for molecular grafting. This is the first report of the ability of hard X-rays to functionalize CNTs. Notably, medium value X-ray doses are sufficient to reach maximum hydroxyl groups surface density and this treatment is shown to be able functionalize through a thickness of 50 µm. The limitation of the proposed approach is the need of a synchrotron facility, however emerging research in the field is investigating laboratory hard X-ray sources [7]. Further studies are needed to investigate the penetration depth of hard X-rays with various CNT structures, such as forests, bucky-papers or yarns, in order to optimize the functionalization efficiency process. An interesting perspective is the possibility to localize specific functional groups in precise areas of the membrane taking full advantage of the deep X-ray lithographic technique [7].

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Figures

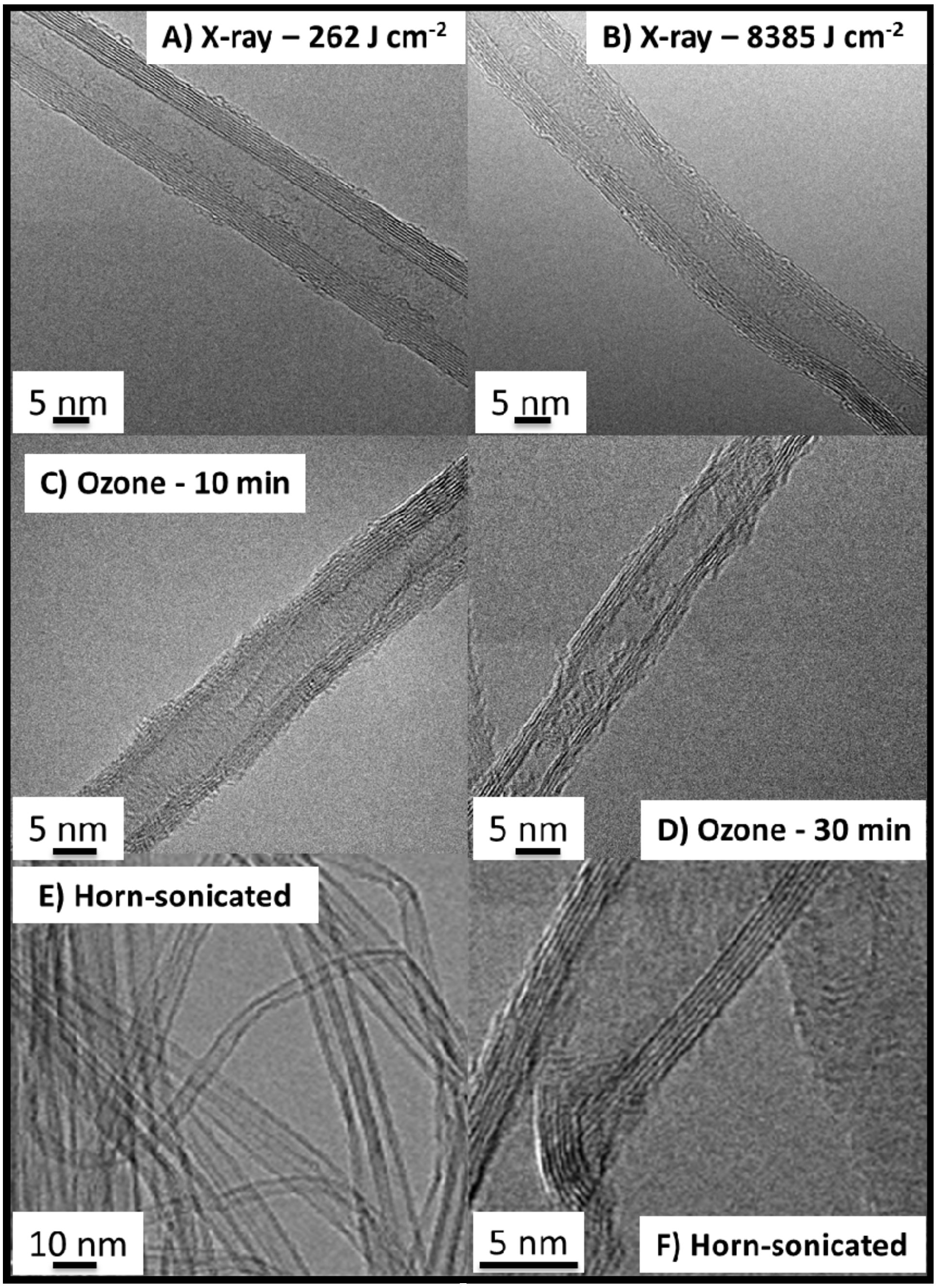
A) X-ray – 262 J cm^{-2}
B) X-ray – 8385 J cm^{-2}
5 nm
5 nm
C) Ozone - 10 min
5 nm
5 nm
D) Ozone - 30 min
E) Horn-sonicated
10 nm
5 nm
F) Horn-sonicated

Figure 1 Representative Transmission Electron Micrographs (TEMs) of CNTs after various treatments (200 keV, lacey formvar carbon TEM grids); A and B: CNTs after exposure to hard X-ray doses of 262 and 8385 J cm^{-2}. Even after the 8385 J cm^{-2}, only minor damage has occurred to the CNT outer walls. This is compared to severe damage for CNTs treated by a 10 and 30 minute ozone treatment (C and D) or horn sonication (E). Images C, D and E (left and right) were made as part of previous studies within our group [9]. Plasma performed with oxygen for 5 min in a Harrick Plasma cleaner (PDC-002) at 200 W.

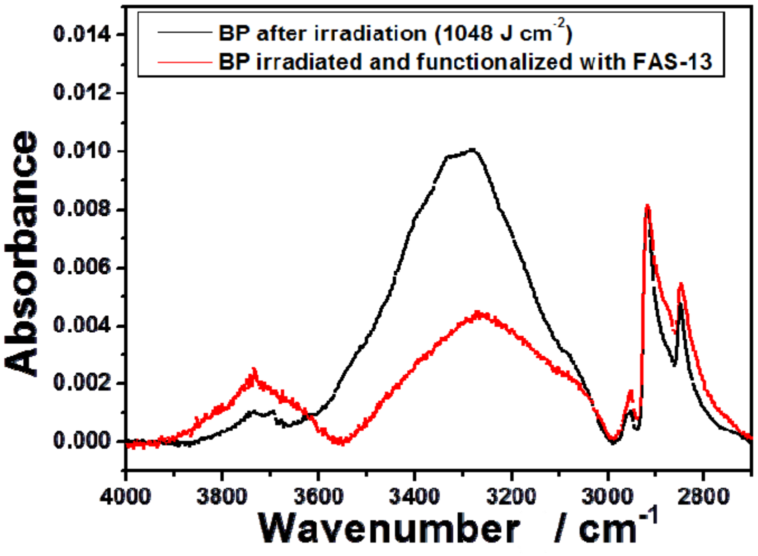

Figure 2 FTIR spectra of both irradiated and fluorinated BPs (1048 J cm^{-2} exposed sample). The irradiated sample (thin black line) presents a significant amount of OH group (broad band in the 3900-3000 cm^{-1} region). The 3000-2700 cm^{-1} region presents the C-H stretching. After functionalization (thick red line) the intensity of the main band is decreased while the intensity of the isolated OH is slightly increased [10]. The CH modes are weakly increased due to the CH groups in the fluoro-silane molecule. The samples were stored in analytical grade ethanol directly after X-ray beam exposure and dried in a vacuum oven overnight prior to any characterization.

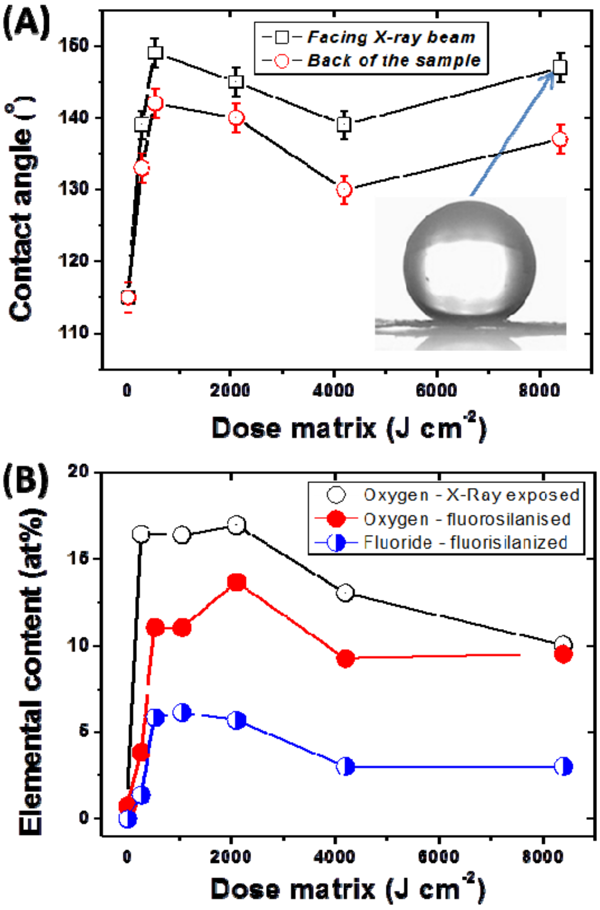

Figure 3 (A: top) Contact angle on the fluorinated samples; black squares and red disks respectively correspond to the face of the bucky-paper exposed to the X-ray beam and to the opposite side; obtained with 4 µL Milli-Q water drops with a PG3 PocketGoniometer; (B: bottom) XPS atomic composition (at%) of the surface of the BP after X-ray exposure and fluoro-silanisation. Data was acquired using a VG ESCALAB220i-XL X-ray Photoelectron Spectrometer incorporating a hemispherical analyser. The incident radiation was Monochromatic Al Kα X-rays (1486.6eV) at 220W (22 mA and 10kV). Base pressure in the analysis chamber was 8.0x10^{-9} mbar.

A low energy flood gun (~6 eV) was used to compensate the charging effect. The energy calibration was referenced to the C *1s* binding energy at 285.0 eV.

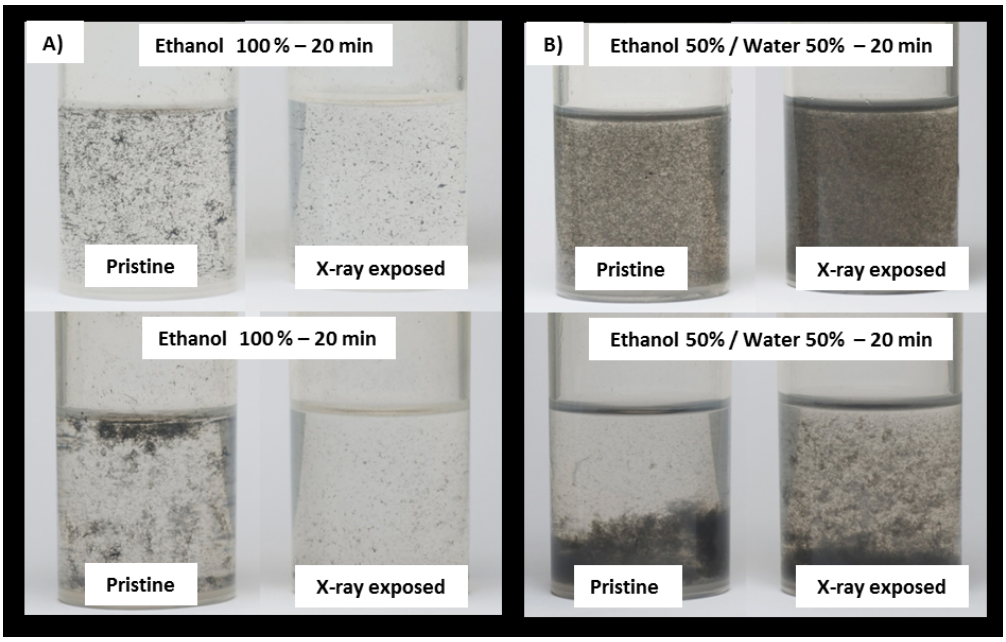

Figure 4 Suspension of pristine and X-ray exposed CNTs (at 16760 J cm^{-2}) immediately after re-dispersion and 20 minutes later: impact of the hard x-ray treatment A) in pure ethanol and B) in 50/50 v/v ethanol/water. The X-ray exposed BPs were grinded and then redispersed into solution by sonication for 10 min at $25^{o}C$ in a bath sonicator. The pristine CNTs were provided as a powder and were similar to those initially used for X-ray exposure. They were directly dispersed following the same protocol.

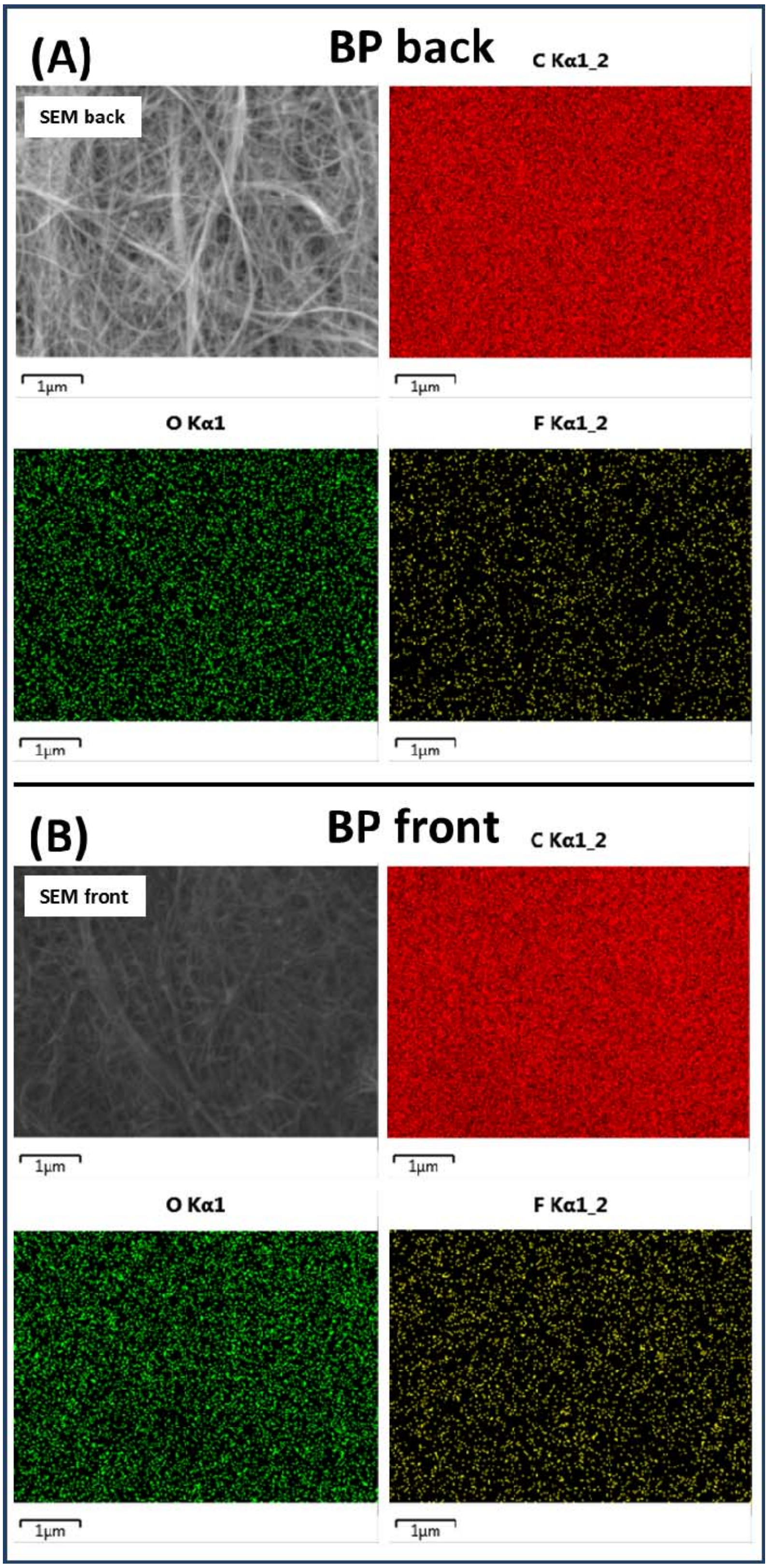
(A)
BP back
SEM back
C Kα1_2
O Kα1
F Kα1_2
1μm
(B)
BP front
SEM front
C Kα1_2
O Kα1
F Kα1_2
1μm

Figure 5 EDS spectra taken at 5keV of the front and back of the BP exposed to 8583 J cm^{-2} and functionalized using FAS-13. The spectra show the distribution of fluoride (F), carbon (C) and oxygen (O). Bright dots correspond to the presence of each respective element. A 25 keV was also performed (not shown) to ensure that iron had not been mistaken for fluorine.