



# Multi-method analysis of functionalized single-walled carbon nanotubes for cesium liquid–solid extraction



Helena Kaper<sup>a,b</sup>, Jimmy Nicolle<sup>a</sup>, Julien Cambedouzou<sup>a,\*</sup>, Agnès Grandjean<sup>a</sup>

<sup>a</sup> Institut de Chimie Séparative de Marcoule, UMR 5257 CEA/CNRS/ENSCM/Université Montpellier 2, BP 17171, F-30207 Bagnols-sur-Cèze, France

<sup>b</sup> Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR 3080 Saint Gobain/CNRS, F-84306 Cavailon, France

## HIGHLIGHTS

- We functionalized single-walled carbon nanotubes by dimethyl acetylenedicarboxylate.
- We performed a complete characterization using a wide range of analytical techniques.
- We quantified grafting homogeneity using a micro-Raman mapping based procedure.
- A Cesium sorption rate of 250 mg per gram of grafted nanotubes was measured.

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## ABSTRACT

We report a detailed analysis of single-walled carbon nanotubes (SWCNTs) functionalized with Dimethyl Acetylenedicarboxylate (DMAD) using a large range of techniques, involving different spectroscopic analysis, transmission electron microscopy, thermogravimetric analysis, and X-ray diffraction. SWCNT functionalization is based on a simple protocol associating ultrasonication and moderate heating under endogenous pressure of the molecules to be grafted. The complete and careful characterization of the resulting grafted SWCNTs revealed that a grafting rate of more than 1 molecule per nanometer of tube length is achieved. Furthermore an original quantification of the grafting homogeneity is developed using the micro-Raman mapping technique. Sorption experiments of Cs<sup>+</sup> ions onto grafted SWCNTs resulted in a high loading capacity, i.e. about 250 mg of Cs<sup>+</sup> per gram of grafted carbon nanotubes, opening exciting opportunities towards the design of carbon nanotube based materials for liquid treatment applications.

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## 1. Introduction

Single-walled carbon nanotubes (SWCNTs) are fascinating nano-objects considering their unique mechanical and electronic properties, their large surface area, and their excellent chemical and thermal stability [1]. This set of properties make them highly desirable for use in various applications [2], ranging from catalysis to drug delivery, and including wastewater cleaning (see in particular the reviews in Refs. [3,4]). The latter application is of great interest today, in particular for separating heavy or toxic ions from water. Many kinds of sorbents have been developed such as silica-based materials, carbon-based materials, or ion exchange sorbents in order to achieve Solid Phase Extraction (SPE). SWCNTs represent a new kind of carbon-based sorbent, which appears very attractive compared to other carbon-based materials mainly due to

their unique electronic and mechanical properties. They may ideally be grafted with specific functions in order to increase their processability and to enable them to capture targeted ions. Many works are undertaken in order to chemically graft organic moieties on SWCNTs [5], but it remains difficult to ensure homogeneous grafting and to provide an effective characterization of the resulting materials. Furthermore, it is delicate to find a good balance between an important and homogeneous grafting rate and the preservation of the desired mechanical and electronic properties of SWCNTs. As a matter of facts, the electronic properties of SWCNTs are unevenly affected depending on the functionalization method [6–8].

Diels–Alder (DA) cycloaddition is a simple way of grafting carbonaceous surfaces. The possibility to functionalize SWCNTs by DA reaction was predicted theoretically in 2002 [9], and since then it was successfully used to functionalize SWCNTs with o-quinodimethane under microwave irradiation [10]. A few years later,

\* Corresponding author. Tel.: +33 4 6679 5803.

E-mail address: [julien.cambedouzou@enscm.fr](mailto:julien.cambedouzou@enscm.fr) (J. Cambedouzou).

SWCNT reactivity towards dienes was shown to be enhanced using high pressure and metal catalysts [11]. It was also shown that fluorinated SWCNTs could be functionalized with improved efficiency [12]. Recently, a variety of diene functionalities were grafted on SWCNTs, multi-wall carbon nanotubes [13–15], and mesoporous carbonaceous materials [16]. The use of dienophils for the functionalization of carbon nanotubes is less reported in the literature. One example is the functionalization of carbon nanotubes using *N*-(4-hydroxyphenyl)maleimide [14]. Another example is described by Zhang and Swager, who used a zwitterionic approach with dimethyl acetylenedicarboxylate (DMAD) and dimethylaminopyridine [17,18].

In this work, we present a new route to functionalize SWCNTs with DMAD by DA cycloadditions directly and with an excellent grafting homogeneity. This original protocol involves a preliminary ultrasonication (US) of SWCNTs dispersed in pure DMAD, and the subsequent heating of the mixture under endogenous pressure. The US step aims at partially debundling the SWCNT aggregates, and therefore increases the grafting homogeneity. Such a treatment was successfully carried out in a recent study by Kitamura et al. [19] in order to functionalize SWCNTs with nitric acid. In the present work, we managed to functionalize a larger organic molecule by a DA reaction with a simple and economic protocol [20], which can be applied to the grafting of other molecules possessing carbon–carbon double bonds.

Characterizing the efficiency of the grafting of small organic compounds at the surface of carbon nanotubes has always been a challenging task. In particular, it is delicate to determine whether the grafted molecules are covalently bound to nanotubes or if they are only adsorbed at the surface. In order to address this ambiguity, we performed a full set of spectroscopic analyses, involving X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared spectroscopy (FT-IR), ultraviolet–visible–near infrared (UV–Vis–NIR) and Raman spectroscopy, probing either the grafted molecules or the nanotube surface. These spectroscopic analyses were completed by thermo-gravimetric analysis (TGA), and X-ray diffraction. Next to that, we put special emphasis on the use of an original approach based on micro-Raman mapping of the intensity ratio between selected SWCNT bands over a  $1200 \mu\text{m}^2$  area in order to give an estimate of the homogeneity of the DMAD grafting on the SWCNT surface. Such an estimation of the grafting homogeneity is scarcely reported in the literature, although it is of high importance when considering further applications of grafted carbon nanotubes. Taken altogether, our results show that a homogeneous grafting of the sample is achieved, and a quantification of the grafting is determined.

Finally, we focused on the cationic sorption capacity of our functionalized SWCNTs. In particular, the sorption of  $\text{Cs}^+$  ions from aqueous effluents is a major issue in the dramatic context of nuclear accidents, after which large quantities of radioactive Cs are released in the environment. We performed  $\text{Cs}^+$  ion sorption experiments on both ungrafted and DMAD-grafted SWCNT samples. While no significant sorption was observed in ungrafted samples, a sorption capacity of about 250 mg of Cs per gram of grafted SWCNTs was measured from our isotherm of  $\text{Cs}^+$  sorption. This high loading capacity is very encouraging for the development of liquid cleaning devices involving carbon nanotubes able to remove  $\text{Cs}^+$  from liquids, and which could be adapted to remove other undesirable ions from contaminated liquid effluents.

## 2. Experimental

### 2.1. Materials

SWCNTs were purchased from a commercially available source (ref. “P2-SWNT” from Carbon Solutions, Inc.). They are fully

characterized by the supplier, whose TGA experiments indicate a metal catalyst yield between 4 and 7 wt. %. The carbonaceous purity is found to be higher than 90 wt. % using the near-IR characterization method [21]. DMAD was purchased from Sigma–Aldrich (99%) and used without further purification.

### 2.2. Functionalisation of the SWCNTs

In a typical synthesis, 10 mg of SWCNTs were dispersed in 10 mL of DMAD. The mixture was cooled to  $10^\circ\text{C}$  and then sonicated for 15 min using an ultrasonic horn delivering a frequency of 20 kHz. The US power was measured by calorimetry and was 18 W. Two distinct samples were studied in this work. The first one was only exposed to the US treatment as described above, and will be referred to as the SWCNT-US sample. The second one also endured the US treatment, but afterwards the homogenized mixture was transferred into a teflon-lined steel autoclave and heated to  $100^\circ\text{C}$  for 24 h. It is referred to as the SWCNT-US-T sample in the following. Both treated SWCNT samples were obtained by filtration and thorough washing with acetone, in order to completely remove all DMAD molecules that did not covalently bound to SWCNTs. Fig. 1 shows the scheme of the DA cycloaddition of a DMAD molecule on an SWCNT.

In order to assess the role of the US treatment, a reference sample only heated in DMAD at  $100^\circ\text{C}$  for 24 h in a teflon-lined steel autoclave was prepared (further denoted SWCNT-T) and analyzed by Raman spectroscopy. Another reference sample involved SWCNTs sonicated in water under the same conditions than the other samples.

### 2.3. Characterization

Transmission electron microscopy (TEM) was performed on a JEOL 200CX operating at 200 kV. Samples were deposited on 400-mesh holey carbon-coated copper grids.

XPS measurements were performed with a Kratos HSi spectrometer with a hemispherical analyzer. The monochromatized Al  $K\alpha$  X-ray source ( $E = 1486.6 \text{ eV}$ ) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure during the experiment in the analysis chamber was  $4 \times 10^{-7} \text{ Pa}$ . To account for charging effects, all spectra have been referred to C 1s at 284.5 eV.

FT-IR spectra were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer equipped with the Universal ATR (attenuated total reflection) Sampling Accessory. The spectra of the functionalized carbon nanotubes were recorded using the pristine carbon nanotubes as background.

Ultraviolet–Visible–Near-Infrared (UV–Vis–NIR) spectroscopy measurements were performed using a Shimadzu UV-3600 spectrophotometer equipped with an integration sphere and three detectors (namely a photomultiplier tube, a InGaAs detector and a PbS detector) covering the 400–1400 nm range. All nanotube samples were suspended in a 1 wt.% aqueous solution of Sodium Dodecyl Sulfate (SDS), were then centrifugated at 18,000 g for 20 min and the supernatant was finally analyzed.

TGA was performed on a Setaram SETSYS Evolution TGA/TDA 16 under nitrogen atmosphere with a heating rate of  $10^\circ\text{C min}^{-1}$ .

Raman spectroscopic characterization was carried out, in back-scattering geometry configuration, on a Horiba Jobin Yvon LabRAM Aramis confocal Raman microscope, using an excitation wavelength of  $\lambda = 633 \text{ nm}$  with a laser spot size of  $\sim 1 \mu\text{m}$  with an objective of X50 long working distance. The incident laser power was kept lower than 0.8 mW in order to avoid any heating or

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