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Recent Advances in the Covalent Functionalization of Carbon Nanotubes

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Applications of carbon nanotubes in different fields, ranging from nanomedicine to photophysics, have emerged since the discovery of this new carbon structure. Functionalization of the nanotubes enhances solubility, facilitates handling as well as provides a way to introduce new molecular entities that will generate interesting properties. This review focuses on the covalent modification of the surface of nanotubes by means of 1,3-dipolar cycloaddition of azomethine ylides and some recent examples will illustrate the applications of the final products.

Keywords: carbon nanotubes; covalent functionalization; 1,3-dipolar cycloaddition; nanomedicine

INTRODUCTION

This article summarizes the functionalization, characterization and applications of carbon nanotubes (CNTs) carried out in our group in the recent past. Especially, we will focus on a covalent approach that allows the introduction of different functional groups onto the surface of carbon nanotubes.

Carbon nanotubes are a new carbon allotropic form, such as graphite and diamond. They are composed of sp^2 carbon atoms, similar to

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graphite but arranged in a cylindrical fashion. The curvature that these graphite sheets possess gives rise to (i) an appreciable change in pyramidalization and (ii) a misalignment of the *p*-orbitals. Consequently, CNTs show an increased reactivity towards addition reactions [1]. Due to these factors, the sidewalls of CNTs are more reactive with respect to the planar sheets of graphene. However, at the same time, they are found to be less reactive than fullerenes, because the spherical geometry and the smaller diameters of the latter produces significantly higher strain.

There are two main kinds of nanotubes. These are called single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs). The main difference is that SWNTs are formed by seamless cylinders in a monolayer with a diameter between 0.8 and 2 nm, while the MWNTs are composed of a concentric arrangement of numerous cylinders on an onion shape structure with diameters of up to 100 nm.

Different methods to generate CNTs can be classified as (a) arc-discharge [2], (b) laser ablation [3], (c) chemical vapour deposition (CVD) [4], (d) catalytic gas-phase growth starting with carbon monoxide or other carbon sources (HiPco method) [5]. According to the procedure used to synthesize the CNTs, different types of materials can be obtained with a different degree of contamination of metals, other impurities and with a range of diameters and helicities. Consequently, mixtures of metallic and semiconducting CNTs coexist, due to their different electronic structures. The presence of these mixtures, limits the applications of CNTs as versatile building blocks for molecular electronics because semiconducting and metallic tubes have different function in electronic devices [6]. Semiconducting SWNTs, for example, exhibit a significant electronic response to field gating effects and chemical doping effects. These characteristics are essential for FET (field effects transistors) and chemical sensors. Metallic SWNTs, on the other hand, are needed as nanometer-sized conductors. While targeting their versatile applications in nanotechnology, many researchers have focused on the selective purification of metallic and semiconductive SWNT. Therefore, not surprisingly, the chemistry of CNTs has emerged as a powerful tool for separating metallic from semiconducting species [7].

CNTs are usually obtained as ropes or bundles of up to tens of nanometers in diameters (10–30 nm) for SWNTs. This issue affects the characterization and applications of CNTs because of their lack of solubility. Increasing the solubility by introducing different functional groups helps disperse the nanotubes and makes it possible their characterization, purification and the tuning of their intrinsic properties in the search of new applications. Depending on the origin

of the CNTs, the amount of impurities and the procedure used to purify them, different degrees of dispersion can be obtained. As far as purification is concerned, treatment with a strong acid such as hot nitric acid is one of the most common methods in order to oxidize the metallic impurities [8]. Unfortunately, this technique implies a shortening effect in the length of CNTs (average length less than 500 nm). A softer method consists on treating the raw material in a multimode microwave in the absence of solvent and under air [9]. The irradiation will cause the oxidation of the metals, while the subsequent treatment with concentrated hydrochloric acid will wash away the metal oxides. Other methodologies like flocculation and selective sedimentation [10], filtration [11], size-exclusion chromatography [12] or interaction with organic polymers [13] have been used. In any case, the slight difference in the reactivity toward oxidation between CNTs and most impurities makes the purification a very difficult task.

As seen before, the way CNTs are made causes the presence of impurities and affects the solubility of CNTs. For example, solvents that present high polarity such as *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidine (NMP) and hexamethylphosphoramide (HMPA) have been chosen for helping dispersion of laser-oven-produced SWNTs [14]. By the use of sonication, it has also been possible to obtain stable suspensions [15]. Aromatic amines have been proved to be suitable solvents for SWNTs purified by oxidation [8]. Some authors have justified this fact with the formation of charge-transfer complexes between molecules of solvent and graphene moieties. Small diameter HiPco SWNTs can be dissolved in different organic solvents according to a UV-Vis-NIR spectroscopic study, where 1,2-dichlorobenzene was the solvent that gave the best results [16].

Enhancement of solubility will facilitate the purification, dispersion and will improve the properties of CNTs [17, 1c, 1j]. Different approaches have been envisaged such as non-covalent approach where van der Waals and π–π stacking interactions are responsible for the solubilization, while changes that involve a chemical modification in the structure of the CNTs will result in a covalent approach. Inside this group, one of our main contributions to the CNTs field consists in the development of the 1,3-dipolar cycloaddition to CNTs.

One of the most challenging problems in this field consists in proving unequivocally that a new covalent bond has been created on the CNTs and, therefore, that the structure of the nanotube has changed. In general, there is not a general and simple technique to solve this issue but a combination of techniques is needed. Diverse characteristics

of the CNTs before and after modification are keys to figure out the new structure.

Proton and carbon NMR, although used, usually reveal the presence of multiple isomeric forms. In addition, the lack of solubility and the anisotropy of the π bonds in the CNT make it difficult to discern the new materials due to broadened signals. Qualitatively, a broad band close to 250 nm in functionalized nanotubes in UV-Vis-NIR spectra indicates a change in the electronic properties due to a high degree of functionalization [18]. Nevertheless, increase in the size of functionalized CNTs gives rise to a linear scattering that affects negatively the resolution of the spectra. Other important features in this technique consist in the presence of typical transitions identified as van Hove bands in the NIR region for HiPco-SWNTs that are partly [19] or totally [20] lost after the functionalization. One of the most useful techniques is Raman Spectroscopy [21], with the presence of three characteristic bands for functionalized and non-functionalized CNTs: at 250–350 cm^{-1} (Radial Breathing Mode, RBM), at 1550–1600 cm^{-1} (G-Band) and at 1250–1450 cm^{-1} (D-Band) [22]. Addition reactions to carbon-carbon double bonds cause a transformation of sp^2-hybridized into sp^3-hybridized carbon atoms [1f]. Such dramatic changes are associated with the modification of the predominantly trigonal-planar local bonding geometry into a tetrahedral geometry. For this reason, when the nanotubes are functionalizated, an increase of this characteristic Raman D-band is observed.

Thermal gravimetric analysis (TGA) [19] is a valuable technique to discern the functionalization of CNTs as well as their degree of purity [23]. Functional groups covalently attached to the surface of the nanotube are lost before the temperature reaches the decomposition of the CNT structure. This methodology has been used to remove functional groups and recuperate non-functionalized cleaner CNTs in a useful procedure [20].

Qualitatively, microscopy techniques such as TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) will give structural details, like aggregation, purity, size of CNTs, although in order to observe structural details of CNTs, high resolution methods are required.

The main goal of our group in this field is the functionalization of carbon nanotubes [1j] in the search of new biological [24,25] and electronic photovoltaic applications [26]. Therefore, we employed two strategies: covalent functionalization [27, 1b, 1c] or non-covalent sidewall functionalization [28]. Here we will focus mainly on the covalent approach.

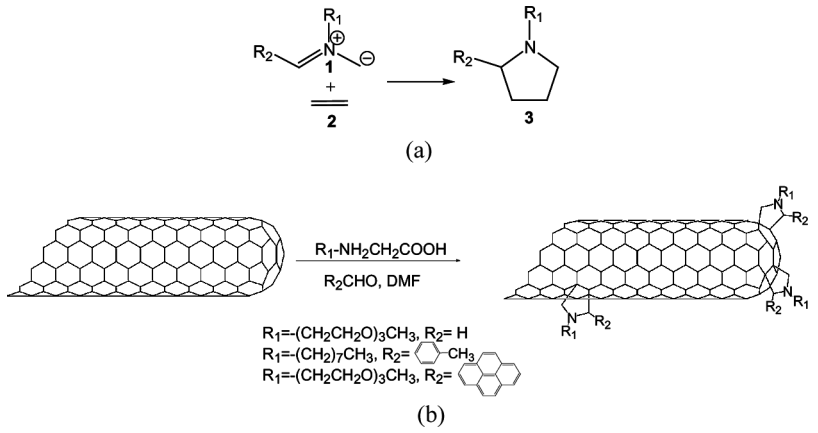
COVALENT FUNCTIONALIZATION OF CARBON NANOTUBES BY THE USE OF 1,3-DIPOLAR CYCLOADDITION

In a similar way to the known 1,3-dipolar cycloaddition of azomethine ylides to fullerenes [29], we have developed a strategy for functionalizing and solubilizing CNTs [30]. The azomethine ylides are generated *in situ* by the condensation of α-amino-acids and aldehydes (Scheme 1a). In our first application, the triethylene glycol group was used as *N*-sustituent group of the α-amino acid (Scheme 1b).

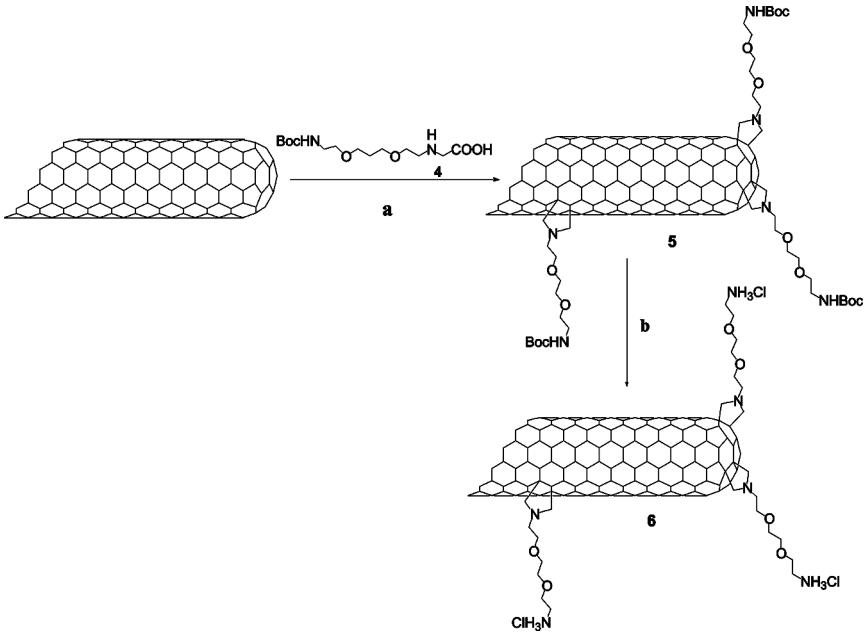
The reaction is very versatile and useful, not only for the easy attachment of pyrrolidine rings substituted with chemical functions to the sidewalls of the CNTs, but also for the possibility of the construction of novel materials with diverse applications. This reaction has been performed satisfactorily with different types of nanotubes, such as pristine HiPco-SWNTs, purified and oxidated SWNTs and MWNTs.

As previously described, a variety of techniques helps us calculate the degree of functionalization: the change in the solubility, the decrease of the van Hove transitions (NIR bands), the amount of material lost during TGA and the increase of the D-band in Raman spectroscopy. TEM and AFM give us important information about the purity and morphology of the CNTs.

SWNTs and MWNTs have been functionalized using *N*-substituted α-aminoacid **4** characterized by the presence of a terminal *tert*-butoxycarbonyl (Boc) protected amino group [31] and paraformaldehyde, leading to **5** (Scheme 2). The ammonium salt **6** was obtained



SCHEME 1 1, 3-dipolar cycloaddition of azomethine ylides to carbon nanotubes.



SCHEME 2 (**a**) HCHO/DMF and (**b**) HCl/DMF/RT.

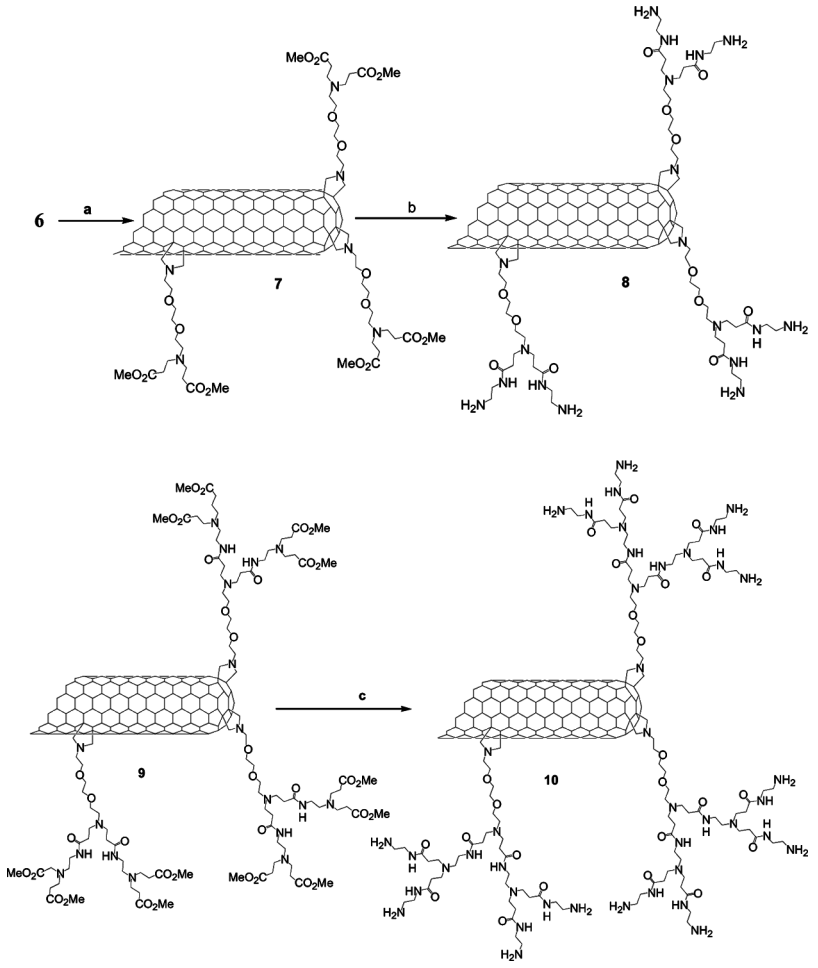
using gaseous hydrochloric acid. The Kaiser test gives us a measure of the number of free amino groups per weight of material.

SYNTHETIC STRATEGY AND APPLICATIONS OF DIFFERENT FUNCTIONALIZED CARBON NANOTUBES

The possibility of the attachment of amino terminal moieties as pendant groups makes this methodology very interesting and useful (vide infra).

In the field of supramolecular chemistry, dendrimers are very interesting macromolecules which posses a globular structure with a high density of functional groups on the periphery [32–34]. We decided to build polyamidoamine (PAMAM) dendrimer following a divergent methodology onto a CNT as a support. In the divergent route, growth starts from the core building layers around it [35]. PAMAM dendrimers, first synthesized by Tomalia and collaborators [36] consist of an iterative synthesis starting with ethylenediamine as a core reacting group, using methyl acrylate in a Michael-type addition reaction.

In our case, a sample of amino-functionalized HiPco SWNTs **6** was allowed to react with methyl acrylate to give adduct **7**. Subsequent



SCHEME 3 (**a**) methyl acrylate, N-ethyldiisopropylamine, MeOH, 80°C, 3 days; (**b**) ethylenediamine, MeOH, 80°C, 3 days; (**c**) methyl acrylate, MeOH, 80°C, 3 days.

reaction with ethylene diamine produced amino-dendrimer **8**. Repetition of this route generated the 2nd generation dendrimer-CNT adduct **10** (Scheme 3). The solubility and high dispersibility of these compounds allowed a full characterization with Raman spectroscopy, UV-Vis-NIR spectroscopy, thermogravimetric analysis (TGA) and microscopy techniques such as TEM (transmission electron microscopy) (Figure 1) and AFM (atomic force microscopy). Importantly,

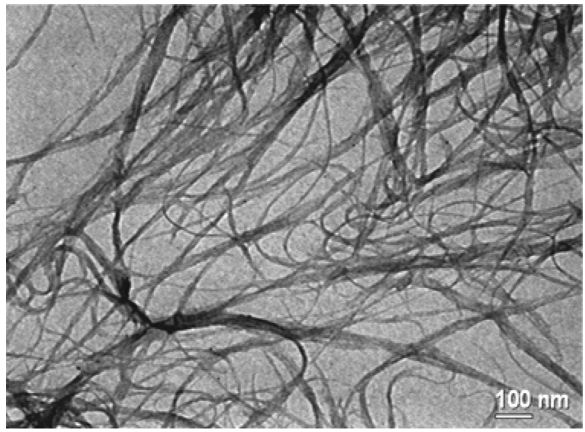


FIGURE 1 TEM images of the SWNT nanoconjugates 8 from a DMF solution.

the Kaiser test allowed us to calculate the amount of free primary amines in the periphery of the dendrimer. These amino groups play a crucial role because they were the anchor point for linking a porphyrin-acid derivative. The condensation reaction between the amino groups and the porphyrin derivative was performed in the presence of EDC (*N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide) and HOBt (1-hydroxybenzotriazole), leading to poly-porphyrin adduct **11** (Scheme 4).

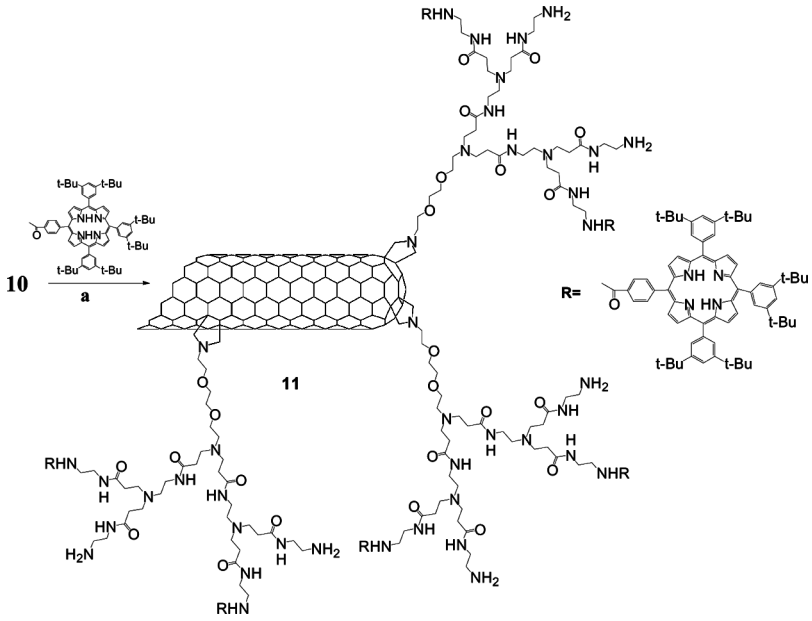
Photophysical studies were carried out on conjugate **11**. Fluorescence kinetics showed transient decays similar to the free porphyrin derivative. For this reason, no interaction between the CNTs and the porphyrin rings could be detected. Photoinduced electron transfer was observed from the porphyrin unit to the carbon nanotubes. The lifetime of the charge-separated species was in the range of microseconds. This makes compound **11** an interesting candidate for photovoltaic applications.

Other important features of CNTs can be exploited in biology or medicinal chemistry. Amine-functionalized CNT **6** are water-soluble and can be used for biological investigations in vitro and in vivo.

As easily seen from Figure 2, MWNT **6** are not wrapped in bundles but are present as individual entities, well dispersed in the aqueous medium.

Many biologically relevant moieties can be covalently attached to the amine functions of **6**, such as active peptides [37], and the antibiotic amphotericin B [38] or the anticancer drug methotrexate [39].

The presence of the positive charges on the outside of the nanotubes can be used for gene delivery purposes [40]. These charges will



SCHEME 4 **(a)** EDC, HOBt, DMF, room temperature, 5 days.

interact electrostatically with the phosphate groups present in plasmid DNA. The association DNA-CNTs was observed by TEM techniques. The gene expression of cells treated with the CNTs was found

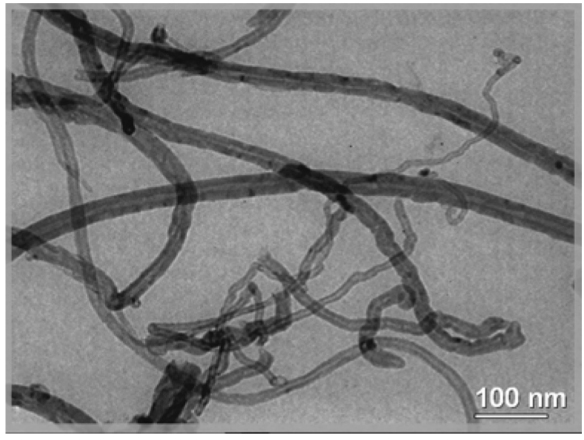


FIGURE 2 TEM images of the MWNTs from a water solution.

to be 10 times higher with respect to naked DNA. Besides, the modified CNTs display a low toxicity, while the mechanism does not seem to follow an endocytotic pathway [41].

CONCLUSIONS AND PERSPECTIVES

We have briefly summarized some applications in diverse fields where the CNTs can be used. These technologies could not be performed without the modification of the surface of the nanotubes. Although there is already an established methodology for tuning the properties of the nanotubes, more efforts should be devoted in many aspects, from purification of the nanotubes to characterization of the final products. Nanomedicine is one of the emerging fields where these materials seems to be promising as support for different molecules with biological activity, due to their lack of toxicity and inertness. CNTs are a striking example of a multidisciplinary material that can generate many expectations and where contributions of numerous groups with broad expertise are needed.

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