



Regular Article

Towards highly stable aqueous dispersions of multi-walled carbon nanotubes: the effect of oxygen plasma functionalization



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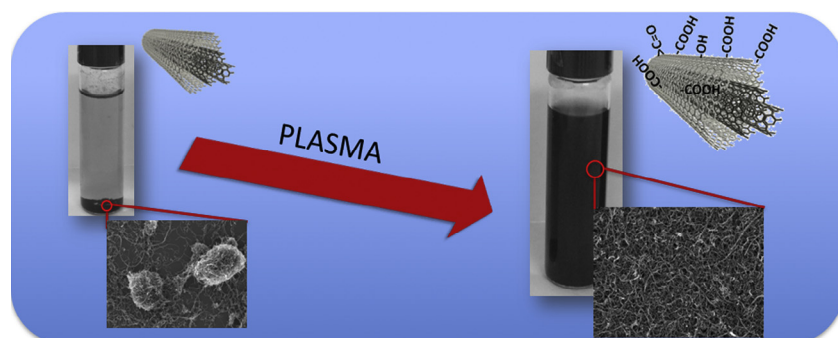
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GRAPHICAL ABSTRACT



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ABSTRACT

In order to improve the dispersion of multi-walled carbon nanotubes (MWCNTs) in aqueous media, their surface functionalization was carried out in O₂-fed low-pressure plasmas. Differently from what can be found in the literature of this field, homogeneous functionalization was achieved by generating the plasma inside vials containing the nanotube powders properly stirred. Experimental parameters, such as input power, treatment time and pressure, were varied to investigate their influence on the process efficiency. A detailed characterization of the plasma treated nanotubes, dry and in aqueous suspension, was carried out with a multi-diagnostic analytical approach, to evaluate their surface chemical properties, morphology, structural integrity and stability in the colloidal state. The plasma grafting of polar ionizable (e.g. acid) groups has been proved to successfully limit the agglomeration of MWCNTs and to produce nanotubes suspensions that are stable for one month and more in water.

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1. Introduction

Carbon nanotubes (CNTs) are an interesting molecular form of carbon belonging to the fullerene family, usually described as hollow tubular channels of one or more layers of graphene, denoted

respectively as single wall (SWCNT) or multiwall (MWCNT) [1–3]. Due to their unique mechanical, thermal and electronic properties, they are a promising material for a variety of potential applications [2,4–6]. In particular, because of their size (one to tens nm in diameter) and high aspect (length-to-diameter) ratio, CNTs can be finely dispersed in ceramic, polymer and cement matrices as filling and reinforcing nanoparticles, for producing high-performance composite materials with superior mechanical, electrical, thermal and multifunctional properties with respect to traditional reinforcing materials [5,7–13]. The desired properties improvement, however, can only be achieved if CNTs are, at the same time, finely dispersed within the matrix and strongly bond to it. CNTs, instead, due their large surface area, intertubular Van der Waals interactions and high chemical inertness, usually generate inhomogeneous dispersions and large aggregates in those matrices, with no effect on the expected performances of the nanocomposite [14,15]. Therefore, a proper and durable functionalization of CNTs is a prerequisite for their successful application in composites. Moreover, despite the peculiarities of CNTs, their low solubility in most solvents together with their weak affinity with most polymer matrices, mainly due to their hydrophobic and inert nature, greatly hinder their practical use in several fields of applications [16]. For these reasons, the chemical functionalization of nanotubes is extensively studied. The most common functionalization approach is the harsh wet chemical oxidation with inorganic acids that often results in structural damage and properties degradation [17]. On the other hand, plasma treatments proved to be an appropriate technique for producing functionalized CNTs with minimal structural damage, mainly due to the mild conditions applied, in terms of treatment time and temperature [18]. Plasmas, ionized gases with equal density of positive and negative particles, can be ignited at very high (thermal plasmas, 10^3 – 10^4 K) or at room (cold, non equilibrium plasmas) temperature. Cold plasmas permeate today several industrial fields [19] for their ability to modify the surface composition and properties of materials with no alteration of the bulk with fast and flexible processes, for their limited use of reagents and no use of solvents (dry technology), for their easy integration in industrial processes and intrinsic sterility [20–24].

It is well known that the excited molecules and radicals generated in the plasma discharge attack the sp^2 -hybridized graphite-like C=C bond, creating open ends and defect sites that act as prime sites for functionalization with chemical groups. Various functional groups can be grafted onto CNTs under a glow discharge, depending on the feed and on the experimental conditions [23].

In the last few years several plasma sources have been utilized in different configurations and experimental conditions for the surface functionalization of supported carbon materials, including vertically-aligned CNT arrays and CNT films obtained by drop casting of powder/solvent suspensions [25–29]. Coulombe et al. [30] developed a different method to obtain stable aqueous nanofluids, which consists in low pressure (LP) plasma treating CNTs grown directly on a stainless steel mesh, followed by their removal from the mesh via ultrasonication in deionized water (DI).

The direct treatment of CNT powders is less studied, primarily because of the difficulty in handling them and in obtaining homogeneous modifications on a large scale. Most studies deal with the use of plasma reactors without a suitable system for stirring the nanoparticles [31–35]. Recently, for instance, MWCNTs have been functionalized with amine or carboxyl functional groups, by exposing them to He/NH₃ or humid air feeds, respectively, in a dielectric barrier discharge reactor, in order to form compatible interfaces for enzyme immobilization [31,32]. Chen et al. [33] reported that amine-functionalized MWCNTs can be obtained either by means of N₂/H₂ plasma treatments or with plasma deposition processes fed with heptylamine, improving their dispersion and interfacial

bonding with an epoxy resin. Enhanced dispersion of MWCNTs in water was found after grafting of O-containing groups with LP plasmas fed with Ar/H₂O [34] or with O₂/N₂ mixtures [35].

There are few papers describing plasma processing of CNTs in reactors equipped with adequate stirring systems. As an example, plasma pre-treatment in N₂ was used to activate stirred MWCNTs toward the polymerization of acrylic acid or the grafting of chitosan molecules, for enhancing their pre-concentration and immobilization capacity of heavy metal ions for the abatement of the environmental pollution [36,37]. Shi et al. [38], instead, reported the plasma polymerization of styrene in radio frequency (RF) LP plasma, under vigorous stirring of carbon nanotubes. Kim et al. [39] reported that LP plasma treatments in a fluidized bed reactor, using glow discharges of argon, oxygen and methane/oxygen mixtures, led to very hydrophilic CNTs and to stable CNT dispersions in water; surface structure changes and defects were noticed, though.

O₂ plasma treated CNTs have proved to be a promising material for a wide range of applications. Recently, they have been also used to develop a selective sensor for nitrogen dioxide [40], as supports to disperse platinum–ruthenium nanoparticles catalysts [41] and as reinforcing fillers in polymers [42].

Despite the above-cited studies, though, a full comprehension of the impact of plasma treatment on the dispersion stability of CNTs in water is still lacking.

In the present research, MWCNTs were LP plasma processed to impart them hydrophilic character and facilitate their dispersion in water, the common solvent used in the manufacturing of MWCNT containing composites. In order to graft oxygen-containing groups, O₂ was selected as gas feed and different experimental parameters were tuned to study their influence and to optimize the process. MWCNT powders were stirred during the plasma treatments to enhance the homogeneity of the functionalization and to reduce the anisotropic modification of the nanopowders, hence preventing the inhomogeneity issues generally occurring when plasma treatments are performed on CNTs deposited or grown directly on a substrate.

The aim of this work was to thoroughly evaluate the physical-chemical properties and the colloidal stability of the plasma treated MWCNTs, correlating them with the different plasma parameters investigated. The integrity of plasma treated MWCNTs was confirmed by means of TEM and Raman analyses. A deep characterization of the powders and of the suspensions in water of untreated (U-CNTs) and O₂ plasma treated (PT-CNTs) samples was performed. The behavior of MWCNTs dispersed in water was evaluated in terms of bundles disentanglement and stability of the suspensions.

2. Materials and methods

2.1. Substrate

Commercially available MWCNTs (8–15 nm in diameter, 10–50 μ m long, Cheap Tubes Inc., Cambridge, USA) were used without further purification. Such low cost MWCNTs were chosen as suitable candidates in large-scale industrial applications, such as cementitious composites.

2.2. Reactor set-up and experimental plasma treatment conditions

The plasma functionalization of MWCNTs was carried out in a borosilicate glass tubular LP plasma reactor (3 cm in diameter, 118 cm long), shown schematically in Fig. 1 and described in detail in [43]. The discharge was ignited by three external copper ring electrodes, two grounded and one connected to a 13.56 MHz RF power generator (RFX600, Advanced Energy). The CNT samples were placed in the reactor in Pyrex vials (2.2 cm in diameter,

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