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Tunable hydrophylicity/hydrophobicity of fluorinated carbon nanotubes via graft polymerization of gaseous monomers

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ABSTRACT

In order to further change the surface chemistry of fluorinated single-walled carbon nanotubes (SWCNTs), gas-phase grafting of monomers onto their surface was performed thanks to the presence of long-lived radicals resulted from the fluorination. Such a two-step process, i.e. fluorination followed by monomer vapor exposure, used here for the first time, resulted in a fast graft polymerization without any solvent using. The total treatment duration does not exceed 4–5 h, contrary to the other reported routes in solvent, and the grafted SWCNTs are ready for use without any purification step. The grafting of monomers from a gaseous phase allows to avoid the homopolymer formation on the tube surface. Grafting drastically changes the SWCNTs surface chemistry. The hydrophilicity/hydrophobicity character may be adjusted according to the monomer nature. Poly(acrylic acid) grafting is resulted in enhanced hydrophilicity, and consequently a better dispersion in water and ethanol. On the contrary, grafted polystyrene improves the dispersion in low-polarity organic solvents because of more hydrophobic nature. Once dispersed in an adequate solvent (commonly used in "wet" chemistry, low hazard and low toxic), the grafted fluorinated nanotubes can be then used for further uses, e.g. incorporation into nanocomposites.

1. Introduction

Carbon nanotubes (CNTs, multi-walled MWCNTs and single-walled SWCNTs) have unique properties and can be used in polymeric composites, electronic devices, field emission displays, hydrogen storage, etc. [1–7]. Unfortunately pristine CNTs exist in a form of bundles so their dispersion in liquids is highly restricted and further functionalization by ordinary methods of "wet" chemistry is made difficult. To improve solubility CNTs must be functionalized. One of the most promising and frequently applied methods of the functionalization of the nanotube surface is the direct fluorination which makes their surface more polar and reduces agglomeration of nanotubes in solutions. Fluorinated CNTs solubility in alcohols and water is increased as compared with pristine CNTs but nevertheless remarkable amount of CNTs is still combined in bundles [8–10]. So an additional modification of CNTs is needed to improve their solubility. There are a lot of papers devoted to functionalization of SWCNTs and MWCNTs to make ones soluble in polar (water, alcohol, etc.) and nonpolar/low polarity solvents. Below we refer to covalent functionalization only.

One of the frequently applied methods to modify SWCNTs is the direct fluorination of SWCNTs at elevated temperature firstly proposed in [8]. Fluorinated SWCNTs are dispersed (by ultrasound sonication, e.g. in DMF, and further subjected to an additional modification with 6-aminohexanoic acid and pyridine (catalyst) [10], 2-aminoethanethiol hydrochloride and pyridine [11], terminal alkylidene diamines [12], diols and glycerol in the presence of alkali, LiOH, NaOH, or KOH or with amino alcohols in the presence of pyridine [13], urea-related chemicals [14], alkyllithium reagents [15], 3-aminopropyltriethoxysilane or 3-aminopropyl-phosphonic acid and pyridine [16]. Treated by CF_4 plasma SWCNTs were dispersed in 3′-(aminopropyl)tri-ethoxysilane by an ultrasonic sonication [17] and aminosilanated SWCNTs were synthesized. Then the mixture was stirred at elevated temperature (over 70 to 170 °C range) under N_2 atmosphere during several hours to 5 days. Then the mixture was cooled, filtered or centrifuged, washed with different solvents (water, acetone, ethanol) and dried or vacuum dried at elevated temperature. Modified SWCNTs acquired better solubility in water solution between pH 4 and 11 [11], water,

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ethanol and DMF [13,14], THF and chloroform [15], and can be uniformly dispersed in silica [16].

Another method includes SWCNTs and MWCNTs surface activation by acid (HNO_3, HCl) or $SOCl_2$ treatment followed by a grafting of monoamine-terminated poly(ethylene oxide) dissolved in NaOH solution [18], glucosamine dissolved in anhydrous THF [19], poly-(propionylethylenimine-co-ethylenimine) poly(vinyl acetate-*co*-vinyl alcohol) [20], poly(acrylic acid) and poly(sodium 4-styrenesulfonate) [21], poly(propionylethylenimine-*co*-ethylenimine) [22]. Then the solution containing modified SWCNTs was filtered or centrifuged, washed with different solvents (water, acetone, ethanol) and dried at elevated temperature. The treatment procedure was rather long i.e. from 1 to 2–5 days.

Several researches were devoted to using of irradiation-initiated grafting. Grafting of poly(acrylic acid) to MWCNTs was made possible via two-step process [23]. At first MWCNTs were gamma-irradiated in ethanol. Then ethanol-MWCNTs mixture with added acrylic acid was again gamma-irradiated. In reference [24], UV irradiation of MWCNTs metastable dispersion in DMF with added acrylamide, N-isopropylacrylamide, (ethylene glycol)-methacrylate or sodium methacrylate and benzophenone was used to improve solubility.

Ref. [25] reports the method of 1,3-dipolar cycloaddition reaction to the SWCNTs and MWCNTs external surface for their derivatisation with N-protected amino acids. Total duration of the multi-step process exceeded 4 days.

In paper [26] MWCNTs thermal treatment at 1000 °C was followed by a grafting of various monomers from the liquid and gas phase. Total treatment duration exceeded 14 h. Modified CNTs maximum solubility 0.052 mg/ml in DMF was obtained. Necessary to mention that reported solubility is extremely small as compared with a set of papers [8–25] where authors obtained solubility of modified CNTs close to 1 mg/ml. When ethanol and toluene were used as solvent the maximum solubility of 0.021 mg/ml and 0.0008 mg/ml were obtained, respectively. Dependence of dispersion stability with time was not investigated.

Many above-mentioned methods can be successfully applied to improve solubility of SWCNTs and MWCNTs in polar and nonpolar solvents, but majority of the described methods include multi-step procedures, need too long time (sometimes – up to several days) and protocols are not always clear. All the proposed functionalization methods were used at elevated temperature and also highly toxic and volatile liquid chemicals like DMF, THF, HNO_3, HCl, etc. (plasma treatment is an exception of the rule) were used. In the present work, we propose "dry" chemistry method: CNTs are at first fluorinated using undiluted F_2 gas. Such treatment allows both tubes debundling of the tubes and long-lived radicals formation,

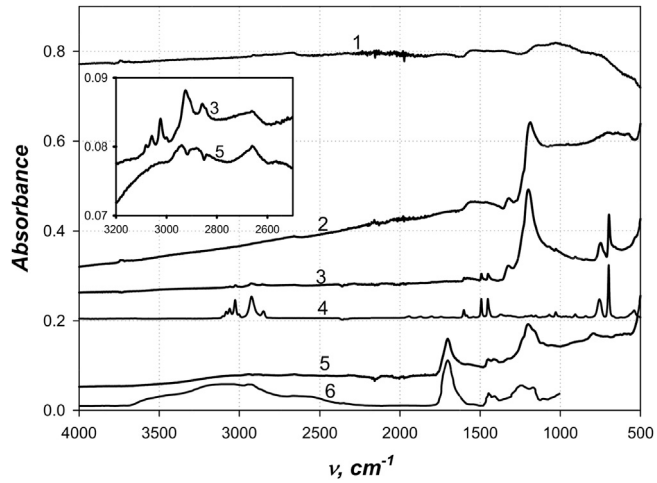

Fig. 1. ATR FTIR spectra of virgin SWCNTs (1), fluorinated only SWCNTs (2), fluorinated and styrene grafted SWCNTs (3), absorbance spectrum of polystyrene measured by the current paper authors (4), fluorinated and acrylic acid grafted SWCNTs (5) and absorbance spectrum of poly(acrylic acid) (6) [28].

i.e. dangling bonds (DB). Such radicals may both act as traps for monomer from the vapor state (acrylic acid or styrene) at room temperature and initiate their graft polymerization.

The grafting mechanism is as follows (similar to both styrene and acrylic acid). As it was mentioned above direct fluorination results in a formation of long-lived radicals $R^{\bullet}$ inside fluorinated layer. Half-termination time of those radicals is around several hours so it is enough time to provide graft polymerization of monomers having double bond (styrene $CH_2{=}CH{-}Ph$ or acrylic acid $CH_2{=}CH{-}COOH$) to those radicals. Such a two-step process, fluorination/monomer vapor exposure, used here for the first time, resulted in a fast graft polymerization (grafting) without any solvent using. The total treatment duration did not exceed 4–5 h and the grafted CNTs were ready for use without any purification step. Moreover, grafting drastically changed the SWCNTs surface chemistry. The hydrophilicity/hydrophobicity character may be adjusted. Our strategy is as follows: grafting of poly(acrylic acid) may result in enhanced hydrophilicity, and consequently a better dispersion in polar solvents (water, alcohol, etc.). On the contrary, grafted polystyrene may improve the dispersion in low polarity/nonpolar organic solvents because of more hydrophobic nature. The first part of the paper is focused on the presence of radicals after fluorination and their termination in air measured by electron

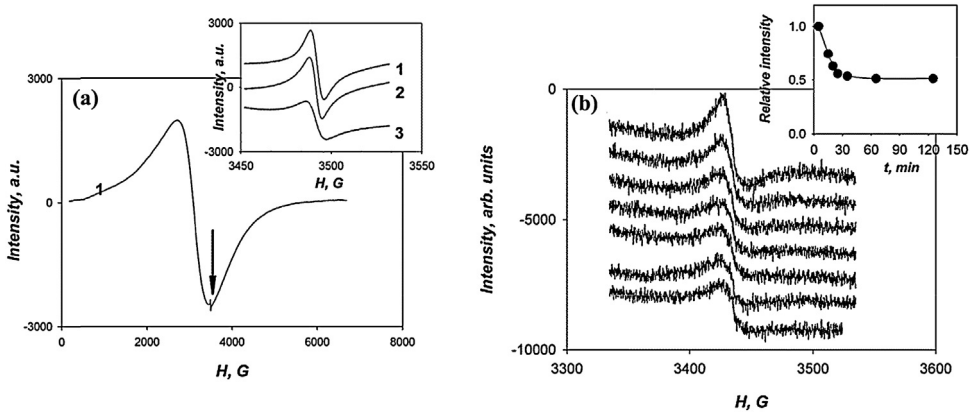

Fig. 2. (a) EPR spectra (X band) of fluorinated (1) and grafted with styrene and acrylic acid SWCNTs (2, 3), (b) kinetic of recombination of radicals in air taking into account the changes of the lines with time after exposure to air (from 10 to 130 min from top to bottom).