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Comparative study of the modification of multi-wall carbon nanotubes by gamma irradiation and sonochemically assisted acid etching

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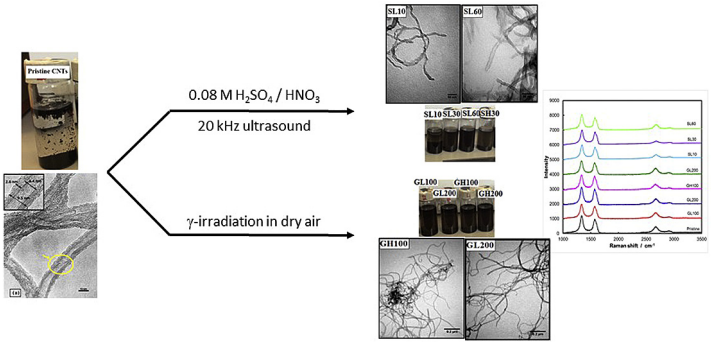
HIGHLIGHTS

- Multi-wall carbon nanotubes have been treated by ultrasound-assisted acid etching and by γ-irradiation.
- Both methods change the structure of the CNTs and oxidise their surfaces.
- Both methods allow enhanced dispersion of the nanotubes.
- Ultrasound allows oxidation at much lower acid concentrations than previously used.
- Careful control of experimental conditions is needed if optimum results are to be obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-walled carbon nanotubes (CNTs) have been treated with gamma irradiation in air or by using dilute acids (H_2SO_4/HNO_3) combined with 20 kHz ultrasound to compare their effects. The CNT microstructure has been investigated using transmission electron microscopy which revealed that both methods effectively modified the CNTs to overcome aggregation of the nanotubes, resulting in efficient dispersion in ethanol. The nature of the surface modifications was investigated using Raman and FTIR spectroscopies. The introduction of oxygenated species at the CNT surface was detected. At longer treatment times or high ultrasound intensities, the sonochemically assisted acid treatment showed the highest degree of reaction and functionalisation. Modification of the structure with γ-radiation with doses of 100 kGy or 200 kGy also resulted in a reduction of defects, attributed to an annealing and reorganisation process. The observed effects could be correlated with the time and intensity of the ultrasound used or the dose and dose rate of the γ-radiation. Both methods offer the possibility for processes with lower environmental impact than those that currently exist. Our results also illustrate the importance of careful control over these experimental parameters if optimum results are to be obtained.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention and shown enormous commercial potential in a range of

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applications [1] due to their unique mechanical, electrical and gas storage properties [2–4]. Their use as reinforcing fillers to increase mechanical strength and elastic moduli as well as other functionality has led to the development of a number of examples of nanocomposite materials containing CNTs [5,6]. However, strong van der Waals interactions between the nanotubes means that they readily aggregate together and this makes difficult their distribution in a matrix. The hydrophobic and inert nature of the CNTs surface further restricts their application [7,8]. Functionalization is therefore necessary before use. It has been widely reported that the number of defect sites, their surface properties and the degree of graphitization are important parameters for the characterization of CNTs [9,10].

Among the methods used to obtain CNTs with controlled properties are coating with surfactants, chemical etching, ultrasonic treatment, mechanical treatment and high energy irradiation [11,12]. Chemical etching of CNTs is usually carried out by treatment with strong oxidizing agents such as potassium permanganate or highly concentrated solutions of nitric or mixed nitric/sulphuric acids. Using oxidizing acids is more common than other methods due to its easier implementation in laboratory and industrial settings. Detailed observation and analysis by Zhang et al. showed that the presence of defects in CNTs plays a crucial role in the oxidation process [13]. Other studies on acid-oxidized CNTs have demonstrated that the degree of functionalization on the surface of the CNTs can be significantly increased when acid treatment is assisted by high power ultrasound [14].

Ultrasound-assisted acid-treatment is therefore potentially an ideal alternative for creating defects and increasing the rate of oxidation reactions while operating under less forcing conditions. The main effects of using ultrasound arise from cavitation; the collapse of micrometer-sized bubbles which are generated during the rarefaction phase when ultrasonic waves pass through a liquid. As the bubbles collapse, strong shock waves and high speed liquid jets are generated [15]. These are strong enough to overcome the van der Waals interactions and disperse the CNT agglomerates. Some C-C bonds within the CNTs may be ruptured, generating active sites at which subsequent chemical reactions can take place [16]. A further advantage is that reactive species such as, in aqueous systems, hydroxyl radicals are produced during cavitation. To illustrate its potential, some years ago Yang et al. suggested that ultrasound-assisted functionalization methods might replace conventional acid treatments opening up the possibility of more efficient and cleaner treatment methods [17]. Tian and co-workers also showed that sonication could speed up permanganate oxidation and increase the number of oxygen-containing functional groups at the surface [18]. In further studies, Ng and Manickam demonstrated [19] that the extent of surface reaction could be controlled by varying the sonication time and Huang et al. indicated that ultrasound could be used to vary the mean length of the CNTs as well as to prepare the surface for further reaction with a polymer [20]. Other oxidizing agents and organic modifiers have been used in conjunction with ultrasound, albeit at high concentrations and under forcing conditions [21,22]. Ultrasound has also been applied to CNT modifications in solvents other than water [23,24].

Gamma-ray irradiation is an alternative method for modifying the physical and chemical properties of CNTs [25,26]. It allows ready control over the extent of reaction at low temperatures with lower levels of pollution. Irradiation of CNTs with energetic particles has been demonstrated to create defect sites and molecular junctions [27,28]. A linear relationship between the amount of γ-irradiation and the introduction of functional groups and defects on CNTs has been reported [28]. Xu et al. suggested that the surface functionality and interlayer spacing can be enhanced by γ-ray treatment with consequent changes to the structural order of CNTs and decrease of their inner-wall distance [29]. Danilchenko et al. also reported the introduction of defects into CNTs by irradiation [30] while other groups have exploited these effects to functionalize the surfaces of CNTs [31]. In work directly related to this paper, we established that gamma irradiation under similar conditions to those reported here is a useful pre-treatment for the functionalization of CNTs with silanes [32]. An irradiation dose of 100 kGy was shown to increase graphitization in CNTs while changing the radiation dose or dose rate affected other structural modifications [33].

Despite the large number of publications dealing with modification of CNTs, there have been few systematic studies comparing the various modification methods on identical CNT samples and exploring the implications for particular application such as a nanocomposite filler. In this work, we have performed such a study comparing the effects that the conditions of sonochemical or γ-irradiation have on CNTs and on their use in chitosan nanocomposites. Specifically, this paper describes the modification and characterisation of a batch of multi-walled CNTs (MW-CNTs), allowing us to directly compare and contrast the effect of various experimental parameters. We have compared in detail the effect of ultrasound assisted acid treatment at much lower concentrations than conventionally used. The effect of different reaction conditions (e.g., time and ultrasound intensity) on the CNT structure has been measured along with the effects of various doses and dose rates of γ-irradiation in dry air. Changes in the surface chemistry and structure have been elucidated using high resolution TEM together with FTIR and Raman spectroscopies.

2. Experimental

2.1. Chemicals and materials

The multi-walled carbon nanotubes used were from the NANOCYL™(Korea) NC700 series, produced by catalytic carbon vapour deposition. They were in powder form having 90+ % purity, 9.5 nm diameter and 1.5 μm average length. All other chemicals were purchased from Aldrich (UK) and used as received.

2.2. Chemical modification of CNTs with sonochemical treatment

Raw CNTs (20 mg) were suspended by gentle shaking in 36 cm^3 of a mixture of H_2SO_4 and HNO_3 with the concentration of both acids at 0.08 mol dm^{-3} and sonicated with an ultrasonic horn (Sonic Systems L500-2 Processor with a 1 cm dia. horn). The temperature was maintained at 60 °C and sonication conducted for varying times at fixed intensity (measured calorimetrically [34]) or with varying intensity for a fixed time of 30 min. The results below use the following sample codes SL10, SL30, SL60 were used to represent 10, 30, 60 min sonication at the lower intensity of 12 W cm^{-2} (L = lower intensity) and SH30 indicates sonication for 30 min at the higher intensity (H = higher intensity) of 18 W cm^{-2} respectively.

2.3. Chemical modification of CNTs with gamma treatment

Irradiation was performed at Pakistan Radiation Services using a ^{60}Co gamma irradiator (Model JS-7900, IR-148, and ATCOP) in dry air at a dose rate of 1.02 kGy h^{-1}, varying the dose from 100 kGy to 200 kGy. Further experiments were carried out using a higher dose rate of 6.18 kGy h^{-1} to deliver the same overall doses. The sample codes here are assigned as GL100 (100 kGy, lower dose rate), GL200 (200 kGy, lower dose rate), GH100 (100 kGy, higher dose rate) and GH200 (200 kGy, higher dose rate).