CARBON 84 (2015) 130–137

Available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/carbon

Highly aligned arrays of super resilient carbon nanotubes by steam purification

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ARTICLE INFO

Article history:
Received 28 August 2014
Accepted 28 November 2014
Available online 4 December 2014

ABSTRACT

Steam treatment has been applied to our prefabricated highly aligned areas of electrospun carbon nanotube composite nano-fibres, leading to controlled and targeted removal of polymeric and amorphous carbon materials, resulting in areas of highly aligned, highly crystalline, pure nanotubes. Raman analysis shows how the I_D to I_G intensity ratio was reduced to 0.03, and the radial breathing mode peak intensity, used for nanotube diameter calculation, changes. Therefore, suggesting that some carbon nanotubes are more resistant to steam assisted oxidation, meaning that specific carbon nanotube diameters are preferentially oxidised. The remaining carbon nanotubes have displayed a significant improvement in both quality, with respect to defect density, and in crystallinity, resulting in an increased resistance to oxidation. These steam treated super resilient carbon nanotubes are shown to withstand temperatures of above 900 °C under ambient conditions. Applying this purification method to electrospun nano-fibres leads the way for the next generation of composite materials which can be used in high temperature extreme environments.

1. Introduction

Due to their remarkable mechanical, thermal and electrical properties, combined with their high aspect ratio, carbon nanotubes (CNTs) have received high levels of scientific interest [1–3]. Through previous research, we have already demonstrated how their remarkable properties can be implemented into composite materials and electronics [4–6]. However, these beneficial properties are only true for pristine CNTs. Using current growth processes, defects in the CNT structures and impurities such as amorphous carbon are unwanted by-products which limit the scope of these materials in future applications. However, steam treatment has been shown to purify CNTs, removing the unwanted by-products, which is expected to improve these beneficial properties.

In this work, previous research in to steam assisted purification of CNTs [7–9] has been advanced to also show selective oxidation of CNTs with high defect concentrations, which has shown selectivity towards certain CNT diameters, a previously unreported result. CNTs that survive this treatment are of extremely high quality/crystallinity, and as such display increased, and in some cases total resistance to oxidation under ambient conditions above 900 °C. This degree of improvement in oxidation temperatures has not been observed previously.

The customised steam treatment process has, for the first time, been applied to highly aligned electrospun CNT-polymer composite fibres and successfully removed polymer, surfactant, amorphous carbon and defective CNTs. This results in highly aligned CNT sheets of high CNT quality, over large areas suitable for technology integration.

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http://dx.doi.org/10.1016/j.carbon.2014.11.061
0008-6223/

Selectivity in the oxidation of carbon species arises from the lower energy required to break the chemical bonding, hence preferentially oxidising less ordered materials. CNTs are highly crystalline, tubular sp^2 carbon structures and are more difficult (require more energy) to oxidise than amorphous carbon and polymeric carbon contained in the composite fibres. Water molecules do not thermally dissociate into hydrogen and oxygen at temperatures below 2000 °C [10], but will oxidise carbon through two key reaction processes when elevated to temperatures of 700 °C and above, reacting with only defective or amorphous carbons [7]. Not only does this process have a large potential for upscale and commercialisation, it can be carried out at atmospheric pressure and only requires water as the reactant.

Applying this treatment process to electrospun CNT composite fibres allows for large scale production of highly aligned CNT buckypapers on a macroscopic scale [11]. This paves the way for applications in super-tough composite fibres [12], super capacitors and electronic textiles [13], to name a few. There are several successful routes to manipulate CNTs into uniform orientations, one being electrospinning in which large areas of aligned CNT fibres can be obtained at relatively high speed [14]. This process forms nano-fibres through exerting electrostatic forces on a viscoelastic solution, causing uniaxial stretching as it solidifies, before being collected [15]. Electrospinning a polymer solution or melt, loaded with CNTs, produces arrays of aligned fibres, in which the embedded CNTs are also aligned, which has been reported to improve many of the materials properties, including charge transport between CNTs [16–19]. However, embedding CNTs in a polymer could potentially have detrimental effects on the mechanical and electronic properties of the material, unless the polymer (and surfactant) is removed. In the work reported here we propose a method using steam treatment which supersedes traditional thermal evaporation, by removing more amorphous carbon and defects, to obtain aligned sheets of high quality extremely pure CNTs.

2. Experimental

The single-walled CNTs (SWCNTs) used in this study were manufactured by Thomas Swan & Co. Ltd., and were supplied in a 'wet-cake' form (3.7% weight CNT in an aqueous solution, forming a jelly-like consistency). The CNTs were dispersed at 0.1% weight using an ultrasonic tip probe (30 min at 300 W, 20 kHz) while in solution with sodium dodecylbenzene sulphonate (SDBS) at a ratio of 1:10, CNT to SDBS respectively, as it has been previously reported as the ideal ratio of surfactant to CNT [20,21]. Once sonicated, the solution was centrifuged at 5000*g* for 30 min, removing any remaining agglomerated material from the dispersion. Dispersions were blended with poly (ethylene oxide) (PEO) (supplied by Sigma Aldrich, with an average molecular weight of ~2,000,000 M_v), after the CNTs were dispersed; this was in order to prevent the ultra-sonic irradiation cleaving the polymer chains, which would reduce viscoelasticity, rendering the solution unsuitable for electrospinning [22]. Once electrospun, this solution effectively produces PEO nano-fibres embedded with CNTs at 3.9% weight, assuming all of the solvent is evaporated; this was confirmed by thermogravimetric analysis (TGA).

The solutions were electrospun at +12 kV from a single needle spinneret at a distance of 20 cm from a high speed (10 m/s surface velocity), electrically ground, rotating drum. The drum itself was wrapped in a silicone coated paper, to allow easy removal of the produced fibres. The resultant electrospun fibres were folded several times (much like a sheet of paper), in a manner which maintains the fibre alignment, in order to produce a thicker sample (enabling easier handling and analysis after baking). In order to quantify the CNT alignment after electrospinning, a polarised Raman spectroscopy method, as outlined by Hwang et al. [23] was employed in this work. We found that circa 94 ± 2% of the CNTs to be aligned over large areas as described in the experimental details.

TGA was used to both confirm CNT content but also to confirm how and at what temperatures the different materials used in this investigation thermally breakdown. Fig. 1 shows individual TGA curves of the three chemicals that constitute the CNT loaded nano-fibres produced during electrospinning and then a fourth curve for the final nano-fibres themselves. For each material, the analysis was conducted in both air and nitrogen, from room temperature to 900 °C, at a heating rate of 10 °C/min.

The percentage mass losses of each of the TGA curves were assigned by calculating the relative atomic weight with respect to the total molecular weight of the sample. Detailed analysis of some of the TGA curves can be found in the Supplementary information item S1. Results confirm that, in both air and nitrogen, the majority of PEO is removed before 450 °C, with the PEO thermally degrading at a significantly lower temperature in air through an oxidation process. The thermal decomposition of SDBS takes very different routes depending on whether this is performed in nitrogen or in air. In nitrogen, the alkyl chain of the molecule is removed by 480 °C (48.5% of the total weight). The benzene ring is subsequently lost by 800 °C, leaving the head of the surfactant, now present in the form of sodium hydrogen sulphite ($NaHSO_3$). In air, the compound follows a different decomposition route due to the presence of oxygen, the head of the surfactant is still not removed but has been oxidised and as such the residue left above 800 °C is attributed to $NaHSO_4$. With regards to the wetcake material, CNTs were oxidised in air at around 590 °C and only the metal catalyst remains, whereas in nitrogen, the lack of oxygen prevents CNT oxidation and therefore the sample is unaffected. As previously mentioned, in order to align the CNTs into a sheet, all three of these materials need to be combined and electrospun. The final TGA curve in Fig. 1D is of the electrospun CNT loaded nano-fibres. This result is effectively the combination of all three of the other TGA curves, and provides an indication of what species are expected to be present after thermal treatment, with and without steam over a range of temperatures.

In preparation for the steam treatment process, the thick, aligned, CNT loaded fibre mats were mounted on a silicon wafer and loaded into the centre of a Carbolite quartz tube furnace (as shown in Fig. 2A). The quartz tube is purged with nitrogen at ambient pressure before elevating the temperature, minimising the risk of residual oxygen oxidising the