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Fragmentation characteristics of undoped and nitrogen-doped multiwalled carbon nanotubes in aqueous dispersion in dependence on the ultrasonication parameters

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ABSTRACT

Sonication techniques are commonly used to disagglomerate carbon nanotube bundles into more or less uniformly distributed individual tubes. The present study discusses the statistical length distribution of multiwalled carbon nanotubes (MWCNTs) as affected by varied sonication time, sonication amplitude and overall energy input applied. Undoped and nitrogen-doped multiwall carbon nanotubes (N-MWCNTs) were investigated, and the influence of nitrogen in the carbon structure on the length-reduction behavior during sonication was assessed. Both kinds of MWCNTs were synthesized using the same process, an Aerosol Assisted Chemical Vapor Deposition (AACVD), utilizing cyclohexane and acetonitrile as precursors. X-ray photoelectron spectroscopy (XPS) clarified the chemical bonding in the CNTs and proved the incorporation of nitrogen in the carbon lattice. A drastically shortening of the initial length, i.e. the carpet length, after short times was shown. It was also found that such incorporation of nitrogen results in distinctly modified length reduction behavior during ultrasonication. The N-MWCNTs showed a much more pronounced length-reduction with higher ultrasonication amplitude than the undoped MWCNTs. This can be explained by the weaker chemical bond between C and N in a CNT-lattice, as compared to that among the carbon atoms only. On the other hand, sonication time has no particular effect on the fracture of N-MWCNTs when compared to the undoped MWCNTs.

1. Introduction

Undoped carbon nanotubes (CNTs) constitute a high performance material [1] known for its unique properties, such as very good electrical conductivity [2] and high mechanical performance [3,4,5]. Therefore, they are very attractive candidates as constituents for the production of composites having multifunctional properties. However, the positive effect of CNTs strongly depends both on the geometric properties of CNTs, such as their lengths and diameters and, hence, their aspect ratio, and on the uniformity of the spatial distribution of the CNTs. The aspect ratio of CNTs can be subject to strong variation due to different methods of synthesis. Certain CNT aspect ratios are essential for their functioning as a kind of reinforcement in cement-based matrices [6,7], polymers [8,9] or metals [10].

Customarily CNTs are produced in a chemical vapor deposition (CVD) process in which the MWCNTs grow as reproducible carpets. These carpets may exhibit lengths of more than one millimeter [11].

Beside the geometric features, the chemical composition of CNTs strongly determines their mechanical properties and their interaction with the matrix. With a higher thermodynamic affinity to the chosen medium, CNTs are dispersed more easily. Undoped CNTs can be considered as nonpolar structures. Only CNTs possessing a very small diameter show a modicum of polarity due to their delocalized electron cloud [12]. In contrast, nitrogen-doped, multiwalled carbon nanotubes (N-MWCNTs) possess a correspondingly small but considerable polarity, which enables their better dispersion in water [13]. Nitrogen doping of MWCNTs can be achieved by using specific precursors such as acetonitrile [6] or benzyl amine and toluene [14]. This modifies the chemical structure of the MWCNTs [15,16] and hence their electrical behavior [16,17]. Furthermore, such doping significantly influences their mechanical properties. Ganesan et al. [18] postulated a more plastic deformation behavior in direct tension experiments of N-MWCNTs in comparison with undoped MWCNTs. The authors observed that undoped MWCNTs fail via a brittle bond-breaking mechanism while nitrogen-doped MWCNTs exhibit a certain degree of plastic behavior before failure. The incorporation of different elements into the MWCNT structure changes their carbon sp^2 hybridization state; inequalities in the sp^2 structure are assumed to affect the mechanical

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performance. Nitrogen-doped carbon nanotubes (N-CNTs) are interesting within the scientific community due to their altered band structures, which result in conductive metallic behavior [19,20]. Further applications of doped CNTs, especially N-CNTs, as sensor materials have been described [16,21,22].

To utilize the intrinsic CNT properties in compounds, they usually need to be dispersed. Ultrasonification treatment is the most frequently applied method used to disperse CNTs in liquids [23–26]. Sonification studies for dispersing CNTs in water were performed for instance by Yu et al. [27]. Their focus was on the dispersion quality of different combinations of sonification parameters. Both main parameters, sonification time and power, influenced the dispersion quality. It has been proven that the sonification power, as arrayed against sonification time is the more powerful feature in dispersing CNTs. This conclusion was confirmed by Zou et al. [28], who showed that higher ultrasonification energy may effectively increase the amount of dispersed MWCNTs in aqueous solution [28].

Dispersion by ultrasonification means overcoming the strong van der Waals forces between the CNTs to disentangle the CNT agglomerates. However, the CNTs break and thus exhibit a pronounced shortening as the result of such a procedure. Hence, the native carpet lengths of approximately 1 mm could never be found after ultrasonication in suspension. Up to now, only a few experimental studies have tried to explain this effect [29], in particular for melt mixing CNTs with polymers [30–32]. In some investigations the influence of ultrasonication energy on the shortening effect was discussed, e.g. [27]. However, these studies addressed only undoped CNTs for their dispersion in liquids. The influence of nitrogen doping in MWCNTs has not yet been investigated. Furthermore, the total ultrasonication energy is mainly determined by the two parameters of time and amplitude. So far, it has not been understood how these parameters contribute individually to CNT shortening during the sonication process. With this in mind, the present work should answer three major questions which have arisen from both the literature survey and numerous individual preliminary results obtained by the authors:

- Which ultrasonication parameter, amplitude or duration, dominates the shortening effect of MWCNTs?
- Which role does ultrasonication energy input play over the treatment time regarding MWCNT shortening?
- Is there a difference between the shortening effect of undoped and nitrogen-doped MWCNTs by an ultrasonication process?

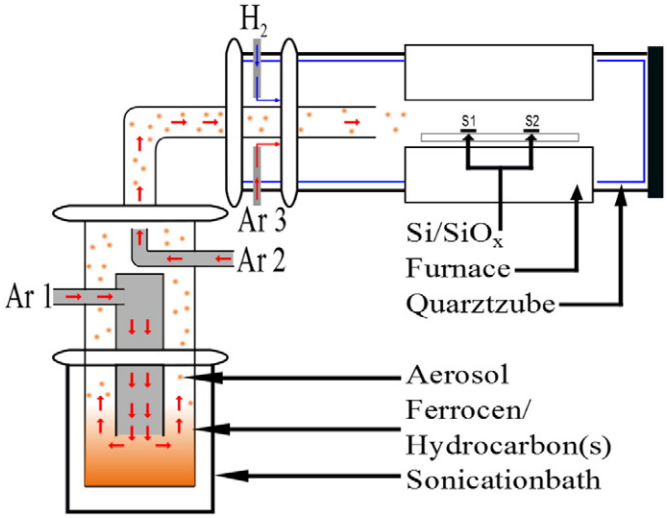

Fig. 1. Scheme of the AACVD reactor.

2. Experimental details

2.1. CNT synthesis

All MWCNTs were synthesized in an Aerosol Assisted Chemical Vapor Deposition System (AACVD), schematically shown in Fig. 1. The aerosol was produced in an ultrasonication bath at 817 kHz (Ultraschalltechnik Meinhardt Function Generator HM8030-6, Leipzig/Germany). Two gas streams of argon, Ar1 (400 sccm) and Ar2 (600 sccm), transported the aerosol into a quartz tube having an inner diameter of 29 mm. Ar3 (200 sccm) and a H_2 gas stream (200 sccm; intercalated at 400 °C) transported the aerosol into the heating zone furnace (length: 600 mm). Inside the furnace two silicon wafers (10 mm ∗ 10 mm) with an oxidized surface (layer thickness: 500 nm) were placed on an extra quartz glass on which the MWCNTs could grow. Before the process the wafers had been cleaned with ethanol (synthetic grade, Merck, Darmstadt/Germany) and acetone (synthetic grade, Merck, Darmstadt/Germany) and the furnace temperature profile was measured under additional consideration of the wafer location. At this particular wafer position the reaction temperature was set at 800 °C. The carbon precursor cyclohexane (used as obtained, 60 mL, synthetic grade, Merck, Darmstadt/Germany) was chosen for undoped MWCNTs and acetonitrile (used as obtained, 60 mL, synthetic grade, Merck, Darmstadt/Germany) for the nitrogen-doped MWCNTs. For both kinds of synthesis 20 mg/mL ferrocene (synthetic grade, Sigma Aldrich, Seelze/Germany) was used as catalyst precursor. The reaction time was 20 minutes.

2.2. Process of MWCNT dispersion

All dispersions were produced in an ultrasonication generator (Sonopuls 3100, Bandelin, Berlin/Germany) equipped with an ultrasonic probe (Sonotrode VS70T, Bandelin, Berlin/Germany). This system allows monitoring the applied ultrasonication energy during the entire process; these measurements delivered the crucial data for the discussion. 17.5 g MWCNT-in-water-dispersions were produced with 0.005 wt.% MWCNT, without any dispersant. Different sonication times (30 s, 180 s, 300 s) and amplitudes, 30% and 70% relative to the maximum of the apparatus, were applied. As overall energy inputs, these combinations impose 1.2 k*J*, 6 k*J* and 10 k*J* at the 30% and 2.1 k*J*, 10 k*J* and 17 k*J* at the 70% settings. During the ultrasonication process the vessels were cooled in ice water and fixed in the ultrasonication box. Immediately after each ultrasonication interval, 0.5 mg to 1.0 mg of the dispersion were taken out with a pipette and dropped onto the copper grids (S162, Plano GmbH, Wetzlar/Germany), which are placed on a tissue to remove the water instantly to fix the state of dispersion and to prevent re-agglomeration.

2.3. Characterization methods

Scanning electron microscope (SEM) images were realized by an FEI NanoSem 200 (FEI, Eindhoven/The Netherlands) at an operational voltage of 10 kV. From these SEM images the lengths and the morphology of the MWCNT carpets were determined. Dispersed, individual MWCNTs were prepared by dropping 0.5 mL–1 mL MWCNT dispersion onto a TEM grid. Their lengths were recorded on these grids and analyzed using the software iTEM (software version 5.2, Olympus Soft Solution, Hamburg/Germany). The as discussed CNT lengths are derived from the arithmetic mean of the each 100 measured CNT individuals. For a better visualization of the CNT length distribution a log — normal fit was applied. It is important to note that for the analysis of the MWCNT length the contour length was measured. To ensure meaningful statistics expressing length distribution, 100 individual MWCNTs were considered. The length distributions were fitted with a "log-normal" distribution [24] using software Origin version 8.6 (OriginLab, Northampton/USA).