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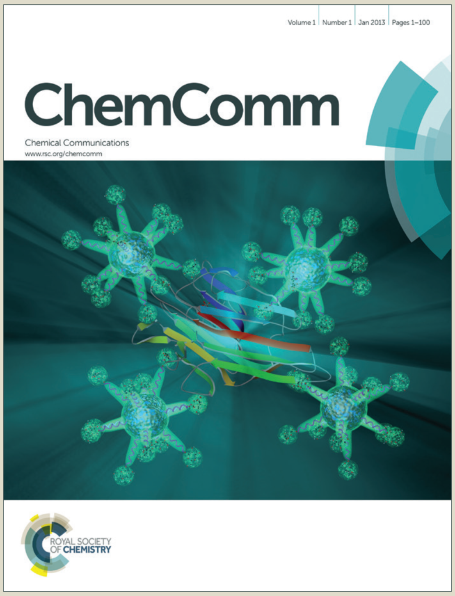

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Shear induced fabrication of intertwined single walled carbon nanotube ring

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Thin film microfluidic shearing of a mixture of toluene dispersed single walled carbon nanotubes (SWCNTs) and water in a vortex fluidic device results in SWCNT nanorings (and related structures), diameters 100 to 200 nm or 300 to 700 nm in diameter, for respectively 10 mm or 20 mm diameter rotating tubes.

Single walled carbon nanotubes (SWCNTs) continue to attract attention, having exceptional mechanical and electrical properties in high performance electronics[1] and applications in scanning probe microscopy,[2] fuel cells,[3] composites,[4] chemical,[5] biological,[6] and physical sensors.[7] They are available as long fibres, centimetres in length and beyond, and tend to aggregate into large bundles because of the relatively strong inter-SWCNT van der Waals interactions. Indeed, difficulties in generating individual strands of SWCNTs is an issue in optimizing their mechanical, thermal, and electronic properties.[9] Carbon nanotubes have in general extremely high flexural rigidity,[3,4] and permanently bending them in a controlled way into well-ordered nanorings/toroidal structures is challenging,[10] with the potential to circumvent or control the aforementioned aggregation and impart different functionality. A variety of techniques have been reported on generating such structures with control over their diameters.[12-15] However, they mostly involve long periods of high-energy sonication, chemical modifications and lengthy physical processing as well as the use of highly reactive chemicals such as concentrated sulphuric acid and hydrogen peroxide, which are potentially damaging to the SWCNTs. In this context, the development of more benign methods is warranted, as is the ability to scale up the conversion of SWCNTs in particular, into the nanorings, with control over their diameter while maintaining a high level of purity. Hydrophobic carbon nanotubes and hydrophilic palladium nanowires form coils in the presence of a water/oil mixture, and this establishes the utility of an immiscible solvent mixture and the associated interfacial surface tension as an important consideration in overcoming high flexural rigidity of these one dimensional materials.[13]

We now report a simple and novel one-step method to produce nanorings of SWCNTs in high yield, where liquid-liquid interfacial tension involving a mixture of water and toluene is amplified using mechanoenergy from a recently developed energy efficient microfluidic vortex fluidic device (VFD), Figure 1a.[16] Well-defined nanorings of SWCNTs with the average diameters depending on the diameter of the tube, being accessible down to ca 100 nm. The ability to control the diameter of such rings, and the ability to scale up, has implications for applications in electronic devices.[10]

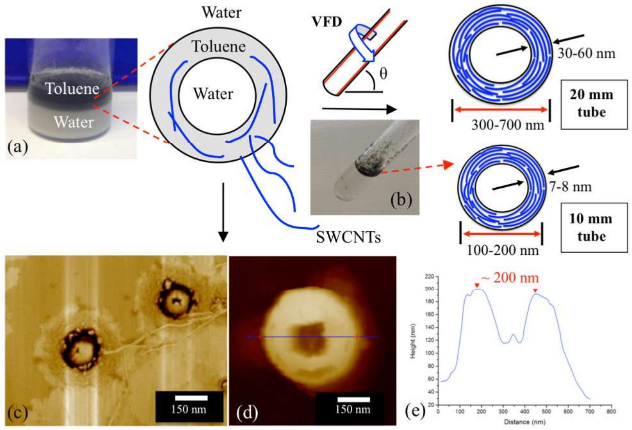

Fig 1: (a) Synthesis and proposed templated mechanism of formation of nanorings of SWCNTs from a sonicated mixture of toluene and water, (b) photograph of SWCNT/toluene/water mixture post-VFD processing, θ = 45°; and pre-VFD processing AFM phase image, (c), height image (d), and associated height profile, (e), of a toroidal structure with radiating SWCNTs, formed on drop casting the mixture from (a).

The VFD has a rapidly rotating tube, within which liquids form dynamic thin films for finite sub-millilitre volumes of liquid, as the so-called confined mode of operation of the device.[16] The shear intensity in the films depends on a number of parameters, including inclination angle relative to the horizontal position, θ, and the rotational speed,[16] which collectively define the interplay between centrifugal and gravitational forces within the films.[17] The confined mode of operation of the VFD results in the formation of a thin film for a defined volume of liquid (herein 1 mL) within the tube, at least above a threshold speed such that a vortex is maintained to the bottom of the tube, otherwise there are different regimes of shear within the liquid.[16]

The VFD can also operate under continuous flow where jet feeds deliver solutions to the bottom of the tube which results in intense micro mixing, and collectively with the confined mode of operation, a number of applications of the device have been established. These include controlling chemical reactivity and selectivity in organic synthesis,[14] exfoliation of graphene and boron nitride,[15] controlling the decoration of palladium nanoparticles on carbon nano-onions and graphene sheets,[16] generating graphene algae hybrid material for nitrate removal,[17] generating mesoporous silica at room temperature with control of pore size and wall thickness,[18] and more.

SWCNTs produced by a catalytic chemical deposition synthesis method with > 90% purity were purchased from Thomas Swan and Co. (UK), and used as received. Toluene was purchased from Sigma Aldrich and also used as received. SWCNTs (1.0 mg) were dispersed in toluene (3 mL) and added to MilliQ water (3 mL). Sonication for 10 minutes afforded a stable two-phase dispersion with the top phase black and the bottom phase milky (Figure 1(a)). A 1 mL portion of the mixture under sonication was collected to ensure that it was a uniform mixture of the three components, and was placed in a 20 mm (I.D = 16.000 ± 0.013 mm) or 10 mm (I.D= 7.100 ± 0.013 mm) diameter VFD tube, as standard borosilicate glass NMR tubes.

A systematic evaluation of the operating parameters of the VFD was carried out to ascertain the optimal parameters for the formation of the nanorings. These were established as an inclination angle of 45° with the 20 mm VFD tube rotating at 7500 rpm, for a reaction time of 20 minutes. At other rotational speeds and inclination angles, ie. higher or lower than the optimized conditions, the formation of the nanorings was either in low yield or not evident (See ESI for details †). The diameters of the rings produced were within the range of 300 to 700 nm, as established using atomic force microscopy (AFM) and transmission electron microscopy (TEM). Optimisation of the operating parameters were also established for a 10 mm diameter tube, which resulted in the formation of nanorings with a significantly smaller diameter range, 100 to 200 nm.

Overall the nanorings formation (Fig. 2 and 3) is at a high conversion. There was no evidence of non-coiled SWCNTs, with some different morphologies generated, namely nanorings, figure of "8" shaped rings and crossed lattice rings.[9b] Processing in the smaller internal diameter tube afforded smaller rings, 100 to 200 nm in diameter, Figure 3, for a reaction time of an hour under the same VFD operating parameters (namely 45 degree inclination angle, 7500 rpm rotational speed). Small amounts of toroidal structures based on a single SWCNT are also present (Fig. 3f), where it appears that SWCNTs 'bite' their tail, with the diameter of the toroid at approximately 100 nm. This corresponds to a length of 314 nm for a straight SWCNT, from which the toroid presumably originates, Figure 3f, and this has implications on the nature of processes involved in the dynamic thin films in the VFD. It is noted that the initial lengths of these as-received SWCNTs were approximately 1-2 µm in length, and thus in forming these structures based on a single SWCNT there has been some lateral slicing in generating shorter lengths.

Shear forces in the VFD are effective under both confined mode and continuous flow modes of operation in controlling the fabrication of nanomaterials,[14-18] including exfoliation of carbon nanomaterials such as graphite.[17] In the confined mode at $\theta > 0^o$, centrifugal forces accelerate the emulsion droplets and nanotubes to the bottom of the tube. The ensuing shear forces can overcome the large van der Waals forces between the bundles of SWCNTs and thus facilitate exfoliation of individual SWCNTs, with the shear forces then also responsible for their lateral slicing.

Drop casting the interfacial SWCNT laden material in Figure 1(a) affords toroids with radiating SWCNTs, as established using AFM, Figure 1(c) – (e). This suggests that toroids of toluene containing hydrophobically matched SWCNTs are present pre-VFD processing, and the subsequent shear forces result in compacting and intertwining he SWCNTs at their van der Walls limit, also drawing in the radiating SWCNTs into the nanorings. These nanorings were characterised using AFM and TEM, Fig. 2 and 3. They have smaller wall thickness (differences between the internal and external diameter) relative to the toroids formed from drop casting pre-VFD processing mixture. For 10 mm diameter VFD tubes, the external diameter of the nanorings dramatically reduces relative to the size of the toluene toroids, resulting is greater curvature in the SWCNTs.

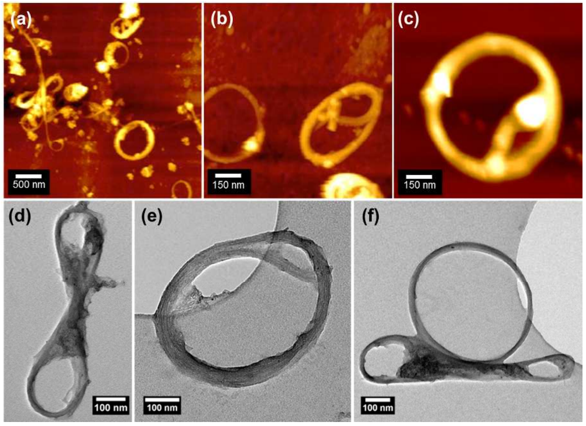

Fig. 2: SWCNT nanorings 300 to 700 nm in diameter, generated using a 20 mm VFD tube: (a-c) AFM height images of the rings, (d-f) TEM images of the different nanoring structures.

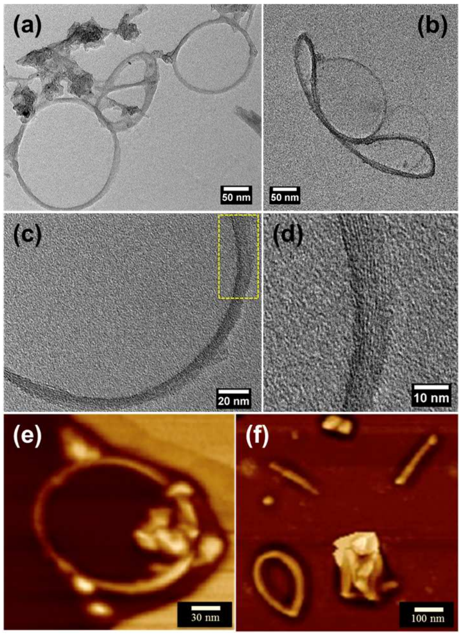

Fig. 3: SWCNT nanorings 100 to 200 nm in diameter (10 mm diameter VFD tube): (a-b) TEM images of the nanorings, (c-d) HRTEM images, AFM height images (e) nanoring, and (f) single SWCNT 'biting' its tail (lower left) along with some short SWCNTs, ca 120 nm in length.

Interestingly, the long axis of the figure of "8" structures is approximately twice the external diameter of the nanorings, and possibly arise from two toroids of SWCNT laden toluene in contact through common SWCNTs, at their limiting size under intense shear. Previous researchers have noted that the different structures of nanorings depend on the method of sample preparation, with rings collapsing at the edge of the substrate prior to solvent evaporation in forming the figure of "8" structure.[13] Formation of these structures has also been ascribed as resulting from further coiling and twisting of the toroid rings, as a secondary structure.[15]

As a control, sonication of a suspension of SWCNTs in toluene showed de-bundling of the nanotubes with occasional ring structures. However, these rings were unstable and slowly collapsed back to the post-sonication SWCNTs (See ESI for details †). Also SWCNTs in toluene, in the absence of water, and without the application of sonic energy, undergo aggregation/restacking. Clearly, sonication is essential to obtain well-dispersed SWCNT, and generating templating toroids of toluene laden with SWCNTs en route to forming the compact nanorings of SWCNTs under shear. VFD processing in the absence of the liquid-liquid interface under similar conditions, for a dispersion of SWCNTs in pure toluene, does not afford nanorings of SWCNTs, thereby establishing that the surface tension between the otherwise immiscible liquids is essential for generating nanorings of SWCNTs (see ESI for details †).

High-resolution TEM (HRTEM) images show that the nanorings are comprised of SWCNTs of diameters in the range 1 to 2 nm (Fig. 3c, 3d). These results are consistent with micro-Raman spectroscopy (Figure 4), at an excitation wavelength of 532 nm (≤ 5 mW).

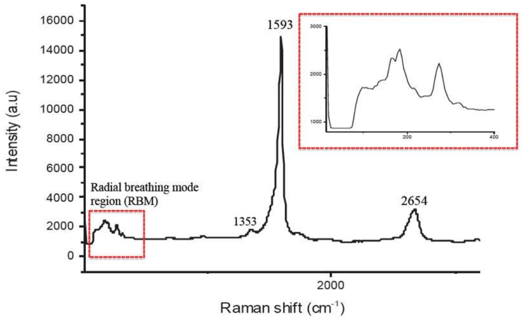

Fig 4: Raman spectra of SWCNT nanorings deposited on a glass slide. Inset: Radial breathing mode region whereby the frequencies correspond to diameter of the SWCNTs.[22]

The radial breathing mode (RBM) (Fig. 4 inset) as well as the G- and D-band on the spectra are markers for determining the diameters of the SWCNTs.[21] The peaks at 1353 cm^{-1} and the peak at 1593 cm^{-1} correspond to the D- and the G-bands respectively (Fig. 4). The D-band is the disorder-induced band which provides information regarding amorphous impurities and is a measure of the amount of disorder and defects on the walls of the nanotubes, whereas the G-band (graphite band) corresponds to the graphite E_{2g} symmetry band, affirming the structural integrity of the sp^2 hybridized carbon atoms of the nanotubes.[22] Focusing on the RBM of the spectra, the frequencies at ca 97.3 cm^{-1}, 164.1 cm^{-1}, 182.1 cm^{-1} and 277.8 cm^{-1} respectively, $\nu_{RBM} = A/d_t + B$, where the RBM frequency is in cm^{-1}, d_t is the diameter of the CNT, and A= 223.5 cm^{-1} and B= 12.5 cm^{-1} which have been determined experimentally,[23] enable the determination of the diameter of the SWCNTs forming the rings. Thus, the frequencies of the RBM region correspond to SWCNTs present approximately 2.64 nm, 1.47 nm, 1.32 nm and 0.86 nm in diameter respectively, in accordance with HRTEM data. The irregular thicknesses (Fig. 2 and 3) of the ring walls relate to aggregation of more than one nanotube, consisting of semiconducting and metallic nanotubes of a range of diameters, stacked at the van der Waals limit. The rings produced in the 20 mm VFD had a nanoring wall thickness of ca 30 to 60 nm, comprised of approximately 20 to 30 stacks of nanotubes of diameters between 1 to 2 nm, noting that some of the nanotubes are likely to coil more than once in each nanoring. The smaller diameter rings, generated using a 10 mm diameter VFD tube, have 7.0 to 8.0 nm thick walls, being similarly built up of about 3 to 8 stacks of nanotubes of 1 to 2 nm in diameter.

In summary, we have developed a simple and novel one-step method to fabricate SWCNT nanorings using the shear generated in thin films within a vortex fluidic device. This is under ambient conditions and avoids the use of reactive chemicals for processing, and the need for surfactants to stabilize the nanorings, with the ability to control the ring size, depending on the diameter of the rapidly rotating tube. Nanorings of SWCNT have promise in a number fields including in polymer composites, sensing devices and more importantly electronic circuits,[12-14] and this is closer to a realization with the availability of such material herein, which can be readily scaled up, noting the ability for the VFD to operate under continuous flow conditions.[16]

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