Molecular encapsulation from the liquid phase and 6-armchair graphene nanoribbon growth in carbon nanotubes

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Abstract

Growing graphene nanoribbons from small organic molecules encapsulated in carbon nanotubes can result in products with uniform width and chirality. We propose a method based on encapsulation of 1,2,4-trichlorobenzene, from the liquid phase, and subsequent annealing. This procedure results in 6-armchair graphene nanoribbon without byproducts. The presence of nanoribbons was proven by Raman spectra both on macroscopic samples and on the nanoscale by tip-enhanced Raman spectroscopy, and high-resolution transmission electron microscopic images.

Graphene nanoribbons (GNR) are one-dimensional objects cut from graphene sheets with important applications in nanoelectronics. As their electronic properties vary with
their size and conformation, reproducible fabrication methods are essential. GNR can be either produced from graphene by top-down methods or from small molecules by bottom-up procedures\(^1\). Top-down methods are various forms of lithography, electron or ion beams or scanning probe tips\(^2\). Oriented chemical reactions on surfaces, starting from small planar molecules, were the first attempts at bottom-up techniques\(^3\). Another possibility is growing nanoribbons in a confined environment, where, besides the precursor, the container’s internal diameter will determine the nanoribbon width. Carbon nanotubes (CNT) are suitable templates for this purpose, because their diameter matches the size of the most popular nanoribbons 6-AGNR or 7-AGNR. Lim et al.\(^4\) first suggested a two-step mechanism for the formation of inner nanotubes from encapsulated small molecules, where initial mild heat treatment produced GNRs that, on vigorous annealing, formed inner nanotubes through a twisted helical intermediate product. Besides leading to inner tubes of specific chirality, this study also suggested a method for producing encapsulated GNRs by stopping the process after the first step. Although intuition would dictate that fusion reactions of polyaromatic hydrocarbons would all follow this reaction path, this is not the case; only some specific ones go through these intermediates, e.g. coronene\(^5\)–\(^7\), or perylene. Later, several other starting materials with different structure were found, e.g. ferrocene\(^8\), as well as precursors containing halogens\(^9\),\(^10\) and sulfur\(^11\),\(^12\). These molecules show a surprising variety of structures, including non-six membered rings and functionalized fullerenes. The full understanding of the mechanism of this self-assembly into GNRs inside nanotubes is an open topic for experimental and theoretical efforts in the future.

In this work we show that graphene nanoribbons with length several tens of nanometers can be grown using a simple procedure from 1,2,4 trichlorobenzene (TCB). The encapsulation process results in a high filling ratio and does not require washing steps. We characterized the prepared GNRs, specifically the 6-AGNR, using Raman spectroscopy, tip-enhanced Raman spectroscopy and high-resolution transmission electron microscopy.

To obtain a nanoribbon with a controlled size and dimension, using CNTs as templates,
it is very important to choose an appropriate encapsulation method. Such methods have been reviewed in our previous work\textsuperscript{13}. High temperature procedures can lead to the formation of undesired byproducts\textsuperscript{6}. This can be particularly problematic in the case of GNR precursors, as GNR formation is generally initiated inside the nanotube by annealing the precursors. However, the molecules may start to react with each other already close to the sublimation temperature, leading to the outer walls of the nanotubes being covered with larger polycyclic aromatic hydrocarbons. Their removal can be problematic, as their solubility is rapidly decreasing with their size. Encapsulation from a solution of the precursor molecules overcomes this problem as it can be performed at low temperature and is suitable for a broad range of guest molecules. Its major disadvantage stems from the presence of the solvent that can also enter the nanotube channels. This not only leads to lower encapsulation ratios compared to direct encapsulation methods, but can also alter the reaction pathway of the precursor inside the cavity. Leaking of the guest molecules can also be problematic during washing steps, which are necessary to remove the non-encapsulated precursors. Not only can the filling ratio decrease further, but more solvent can also enter the nanotubes during the washing step. An ideal GNR precursor candidate would be a compound that is liquid at room temperature, therefore it can directly fill the immersed CNTs, and volatile enough, so the non-encapsulated molecules can be removed from the outer surface of the nanotubes by evaporation in mild enough conditions. We found that 1,2,4-trichlorobenzene is suitable for this purpose.

Raman spectroscopy is the most widely employed method to detect subtle changes in nanotubes upon physical or chemical interaction with their environment\textsuperscript{14–16}. Encapsulation of molecules can be easily detected by observing the shift of the radial breathing mode (RBM), as the molecules inside the nanotube cavity influence the radial expansion and contraction of the nanotube. Data are available for a wide variety of encapsulated molecules\textsuperscript{17–19}. In the case of individual nanotubes, the RBM of the filled tubes was always blueshifted by up to 2 cm$^{-1}$ compared to the empty ones. Shift of the RBM can be also detected on bundles of
tubes upon filling, though identifying the origin of the shift is more complicated in this case, as the interaction between the nanotubes also alters their RBM. For example, Almadori et. al. observed shifts up to 7.5 cm$^{-1}$ upon encapsulation of various oligothiophenes in SWCNTs with internal diameters between 1.2 to 1.6 nm. In our work, after exposing the SWCNTs to 1,2,4-trichlorobenzene, a significant blueshift of the RBM mode (around 7 cm$^{-1}$) was detected with 532, 633 and 785 nm lasers (Figure S1).

To identify the ideal temperature at which GNRs form, we annealed the sample from 100 °C to 1200 °C in 100 °C increments and recorded the Raman spectrum after cooling to room temperature following each annealing step. Based on the excitation profiles reported by Kuzmany et. al$^8$, a 633 nm laser can induce a resonant Raman process in 6-AGNRs. We used the CH in-plane bending (CH-ipb) mode to track the GNR formation during the annealing process (Figure 1, Figure S2). Formation of 6-AGNRs was first detected after annealing to 500 °C, with the most intense ribbon peaks appearing at 600 °C formation temperature. For formation temperatures above 700 °C the ribbon modes start to diminish and they completely disappear at the 1100 °C annealing step, while new peaks appear in the RBM region indicating the presence of inner nanotubes. (Figure S3) The conversion into inner tubes indirectly confirms that the detected ribbons were formed in the nanotube interior.

For comparison, 6-AGNRs were observed to form from ferrocene at similar temperatures as from TCB. Perylene, perylene-3,4,9,10-tetracarboxylic dianhydride and coronene were observed to start forming ribbon fragments between 500 and 550 °C, and upon further annealing between 600 and 900 °C GNRs were present.$^4$-$^6$ 7-AGNRs from 10,10'-dibromo-9,9'-bianthryl were observed already after annealing at 300 °C.

To perform a thorough characterization, the TCB@P2-SWCNT samples were directly annealed to the temperatures where the signal from the CH-ipb peak was the highest (500-600 °C) and their Raman spectra were taken using 532, 633 and 785 nm excitation. The significant blueshift of the RBM observed on the TCB@SWCNT is not present anymore
after annealing (figure 2). Besides the CH-ipb mode, here the radial breathing-like mode of the 6-AGNR is clearly detected both with 633 and 532 nm excitation (figure 2a,d). The RBLM is located at 457 cm\(^{-1}\) with 633 nm excitation, which is slightly redshifted compared to 6-AGNR@SWCNT prepared from the ferrocene precursor\(^8\). Theoretical estimates for this mode are 457 cm\(^{-1}\)\(^\ldots\)\(^{18,20}\), 465.7 cm\(^{-1}\)\(^\ldots\)\(^{21}\) and \(\sim 453\) cm\(^{-1}\)\(^\ldots\)\(^{22}\). Using 532 nm excitation, the RBLM is centered at 446 cm\(^{-1}\). While the nanotubes used in our experiment would also be of suitable size for the growth of 7-AGNRs, and they should be close to resonance with the 532 nm laser, we did not observe their RBLMs, which would appear around 414 cm\(^{-1}\).

As shown in fig. 2, the 6-AGNR modes are more intense in the 500°C annealed sample using 532 nm excitation, while using 633 nm excitation the 600°C annealed sample has stronger GNR signals (figure ??). We presume this is caused by the presence of shorter ribbons at 500°C, which results in a blueshift of their bandgap.\(^{23}\)

The products formed inside the carbon nanotubes can be visualized using transmission
Figure 2: Raman spectra of P2@SWCNT annealed to 500 and 600 °C compared with opened and filled P2 as references. Spectra form the RBM and CH-ipb-D regions a-c, GNR samples measured with 532 nm laser d-f, GNR samples measured with 633 nm laser. g-i, GNR samples measured with 785 nm laser. Low energy region spectra a, d, g are normalized to the RBM and b, c, e, f, h, i spectra to the G mode of the SWCNT.

electron microscopy. The encapsulated nanoribbons are sensitive to the electron beam, they twist upon illumination, which can help identify these structures. Such twisting ribbons can be observed both in the 500°C and 600°C annealed sample (figure 4). Confirming our spectroscopic observations, shorter ribbons were observed in the sample annealed at 500°C than in the 600°C annealed one. TEM time sequences are shown in Figure S4. Energy-dispersive X-ray (EDX) spectra (Fig. S5) confirm the presence of Cl in the ribbons, indicating some chlorine termination, but quantitative information cannot be drawn from them.
Figure 3: GNR@P2-SWCNT formed at 500°C and 600°C measured with 532 and 633 nm laser excitation. GNR intensity ratio of the 500 and 600°C annealed sample changes with the excitation wavelength, probably caused by the presence of mostly shorter ribbons in the sample annealed to a lower temperature.

To further prove that the products measured in the macroscopic sample using Raman spectroscopy correspond to the ribbons identified by TEM, nanoscale measurements were also performed using tip-enhanced Raman spectroscopy (TERS). In figure 5 one can see the overlap of the ribbon signal and the nanotube signal along a small nanotube bundle. Panels b to d correspond to the optical image of Stokes photons scattered by different Raman modes, the nanotube RBM, the ribbon RBLM and the G mode. In the latter region both the nanotubes and the ribbons contribute to the signal. One can see that the ribbons are formed all along the nanotubes, confirming the expected high filling ratio. In Fig. S6, we
In conclusion, we report a method for growing 6-armchair graphene nanoribbons inside carbon nanotubes from 1,2,4-trichlorobenzene, a liquid at room temperature. The 6-AGNRs were characterized by Raman spectroscopy, tip-enhanced Raman spectroscopy and transmission electron microscopy. The characteristic RBLM and CH-ipb modes of the 6 AGNR were detected by Raman and tip-enhanced Raman spectroscopy. Following the Raman intensity of the CH-ipb peak it was possible to determine the ideal temperature for ribbon formation, and within that window, to follow the increase in length with increasing formation temperature. As the encapsulation step involves lower temperature than sublimation-based methods, and no additional solvent, it results in fewer potential by-products and higher purity.

**Experimental methods**

The precleaned nanotubes were opened, degassed and immersed in 1,2,4-trichlorobenzene. The excess precursor was removed by filtration followed by evaporation of the solvent at room temperature.
Figure 5: Tip-enhanced Raman scattering of GNR@SWCNT. a) Topographic image acquired simultaneously with the near-field image. b)-d) Optical image of Stokes photons scattered by different Raman modes, namely b) the nanotube’s RBM, c) the nanoribbon’s RBLM and d) the overlapping G-mode of the nanoribbon and nanotube. The locations marked in d) indicate where the spectra shown in figure S3 have been acquired. The length of the scale bars correspond to 200 nm.

**Encapsulating 1,2,4-trichlorobenzene into carbon nanotubes** P2-SWCNT with 1.2-1.6 nm diameters range were purchased from Carbon Solutions. 1,2,4 trichlorobenzene (TCB) was purchased form Sigma Aldrich. Before filling, P2-SWCNTs were placed in a quartz tube and heated at 420°C for 20 min in air to open the ends of the tubes. After removing the nanotube caps, functional groups that may block the open tube ends were removed by vacuum annealing. The tubes were place under dynamic vacuum and inserted into a preheated furnace at 800 °C for 1 hour annealing and cooled down to ambient temperate in steps of 5 °C/min. When the cleaned nanotubes reached room temperature,
1,2,4 trichlorobenzene (TCB) was introduced to the quartz tube through a valve, without the nanotubes being exposed to air. The mixture (TCB@SWCNT) was sonicated for 10 min and filtered after 24 hours. To remove the molecules adsorbed on the walls, the TCB@SWCNT was left open to air for four days.

**Preparation of GNR@SWCNT** To determine the ideal temperature for the ribbons’ formation, TCB@SWCNT were annealed from 100 °C to 1200 °C at 100 °C increments in a closed quartz tube. Each annealing temperature was kept for 12h, the heating and cooling rate was 5 °C/min. After each annealing step the sample was analyzed using Raman spectroscopy through the quartz tube. Once the ideal ribbon formation temperature was determined (fig. 1), another portion of the filled sample was annealed directly to 500 and 600 °C. We observed that by starting the annealing directly at the target temperature instead of gradually increasing it, resulted in a higher GNR yield. During annealing one end of the quartz tube was kept at a cooler temperature, to allow condensation of desorbed guest species and reaction products, if any.

**Raman characterization** was carried out with a Renishaw InVia micro Raman spectrometer equipped with 532, 633 and 785 nm lasers. The measurements shown in Fig 2 were done using a sealed quartz ampoule. The samples were kept in the ampoule throughout the annealing sequence to prevent contamination. The micro Raman spectra were obtained through the quartz using 20x magnification objectives. Regular measurements were performed in air with 100x magnification objective. Laser power was kept low to prevent heating induced shift of the Raman peaks.

**Tip-enhanced Raman spectroscopy** Samples for TERS were prepared by bath sonication in toluene (1 hour at 45 kHz 100 W followed by 30 min at 45 kHz 30 W). While still sonicating, a drop of the solution was pipetted onto the surface of distilled water and transferred to a glass coverslip with gold markers for TERS measurements. TERS measurements were performed using a home-built setup described in24. Spectra were recorded with 633 nm excitation. The radially polarized laser beam was tightly focused by a high numerical
aperture (NA 1.4) oil-immersion objective, that generates a nanoscale excitation source at the apex of an optical nanoantenna. The antenna is attached to a piezoelectric tuning fork and positioned in close proximity to the sample surface with a shear-force feedback system. Spectral images were recorded by raster scanning and using an avalanche photodiode (APD) combined with a narrow-band bandpass filter to detect scattered light in the desired spectral region (G mode, RBM and RBLM area). For all measurements an LP633 filter in front of the APD was used. For the G mode an additional BP700/13 filter was used, for the RBM an additional BP632/22 filter, and for the RBLM a combination of LP647 and BP645/30. Spectra were recorded at certain points by a CCD-equipped spectrometer.

**High resolution transmission electron microscopy** High-resolution TEM imaging was performed using a JEOL 2100F TEM (field emission gun source, information limit <0.19 nm) at 100 kV at room temperature. EDX spectra were recorded using an Oxford Instruments 30 mm2 Si(Li) detector or an Oxford Instruments x-Max 80 SDD running on an INCA microanalysis system. Samples for TEM and EDX were prepared by casting several drops of a suspension of nanotubes onto copper-grid mounted “lacey” carbon films.

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**Supporting Information Available**

The following files are available free of charge.
• S1: additional Raman spectra, TEM time sequences, far- and near-field Raman spectra

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