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# Synthesis of graphene nanoribbons inside boron nitride nanotubes

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We report on bottom-up synthesis of graphene nanoribbons inside boron nitride nanotubes, using coronene molecules as building blocks. The synthesized ribbons are one or two coronene molecules wide, depending on the diameter of the host nanotube. The encapsulated carbon nanostructures can be eliminated from the inner cavity of the filled boron nitride nanotube via oxidation without any damage to the nanotube structure.

**1 Introduction** The clean and homogenous quasi one-dimensional inner cavity of a nanotube provides a unique opportunity for encapsulation of small molecules. The encapsulated guest material is confined to have special dimensions and/or packing, which do not exist in the unconfined condition [1, 2]. Previous studies have shown that carbon-based small molecules (i.e., fullerenes, coronene), encapsulated in single walled carbon nanotube (SWCNTs) can be transformed to nanotubes or graphene nanoribbons (GNRs) in a bottom-up approach [3–7]. The resulting hybrid nanostructure, in particular GNRs encapsulated in SWCNTs, has made it possible to combine the properties of two exciting materials. In addition, he bottom-up synthesis of GNRs has attracted attention in recent years and has been recognized as a relatively easy approach to the synthesis of narrow GNRs with well-defined edges [8–10].

Boron nitride nanotubes (BNNTs) are very similar to carbon nanotube (CNTs) as a quasi one-dimensional material with high aspect ratio and clean inner cavity; however, BNNTs exhibit significantly higher chemical and thermal stability compared to CNTs [11]. These exceptional properties together with wide band gap of BNNTs make them a potential candidate for protecting materials encapsulated in their inner cavity.

Here we report bottom-up synthesis of GNRs inside BNNTs, via polymerization of coronene molecules. The encapsulation and thermal polymerization of coronene molecules are driven in a single step by exposing the BNNT to the vapor of coronene in vacuum [12]. The encapsulated GNRs can be burned away by annealing the sample in air (oxidized) at temperature above $500\,^\circ$C, while the BNNTs remain intact.

**2 Methods** Highly crystalline BNNTs, mainly two- or three wall, with outer diameter ranging from 2 to 6 nm, are first synthesized using the extended pressure inductively coupled plasma method [13]. The close ends of as-synthesized BNNTs are opened via acid treatment [14] and further annealing at $800\,^\circ$C in air for 1 h. The BNNTs are mixed with coronene (97% purity from Sigma–Aldrich) and sealed in a quartz ampule at $10^{-5}$ torr. The quartz ampule is placed in an oven at $430\,^\circ$C for 3 days. The coronene filled BNNTs are annealed at $500\,^\circ$C in air for 10 min to oxidized excess coronene molecules on the outer wall of the nanotubes. For transmission electron microscopy (TEM), coronene filled BNNTs are dispersed in IPA and drop cast on the TEM grid. For testing the oxidation of encapsulated coronene-based structures, the sample is dispersed on a 300 mesh gold TEM grid, covered with a holey SiO film. After TEM examination, the grid is annealed at $650\,^\circ$C in air for 30 min and the sample is further examined by TEM. High resolution TEM imaging is performed using a JEOL 2010 operated at 80 keV.

**3 Results and discussion** Figure 1a illustrates a TEM image of a three-walled BNNT initially filled with coronene molecules. The tube has an inner diameter of 1.63 nm and shelters a 0.79 nm wide GNR.

Figure 1b schematically illustrates a coronene molecule. Coronene is a flat molecule with a diameter of 0.75 nm. Similar to fullerene molecules, coronene can also be encapsulated in a nanotube; however, due to the flat geometry, coronene molecules form regular arrangements, only if the diameter of the host tube is close to the diameter of the coronene molecule. For instance, coronene molecules encapsulated inside SWCNTs (diameters between 1.5 and 2 nm) form close packing by stacking parallel to each other along the nanotube axis [15–17]. The orientation of coronene molecules (the angle between coronene and tube axis) inside SWCNTs depends on diameter of the host tube [18]. Such a highly close packed coronene molecules in a small diameter tube can then transform to GNRs, via thermal polymerization. The width of the GNR in Fig. 1a is close to the diameter of a coronene molecule. This indicates that molecules were initially stacked parallel to each other and then transformed to a GNR at elevated temperature. We note that the GNR in Fig. 1a is twisted along its length (indicated by the arrow in the figure), which is frequently observed in GNR encapsulated in nanotubes [5, 19].

Figure 2a illustrates a TEM image of a larger diameter BNNTs initially filled with coronene molecules. The upper right double-walled tube has an inner diameter of 2.1 nm and shelters a 1.43 nm GNR. The middle three-walled tube and lower left double-walled tube are 3.2 and 2.32 nm in diameter, respectively. The encapsulated structures in the middle tubes have indistinct morphology with a semi-amorphous structure. The lower tube, which has smaller diameter, is, however, partially filled with a ribbon like structure (as shown by the arrow in Fig. 2a). It has been shown that coronene molecules encapsulated in large diameter nanotubes (inner diameters larger than 2 nm) form short-range packings, randomly oriented inside the tube, which upon thermal polymerization transform to semi-amorphous structures [19, 20]. This explains the semi-amorphous nature of the encapsulated materials observed in middle and lower tubes of Fig. 2a. This is in line with the previous works on coronene filled carbon nanotubes [18]. Interestingly, the width of the GNRs in the upper right tube in Fig. 2a is almost two times the diameter of a
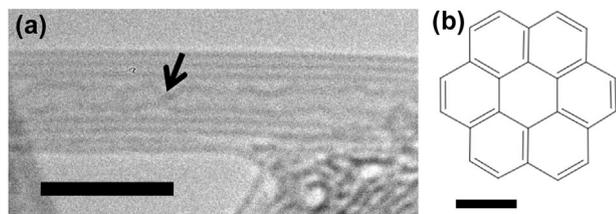


**Figure 2** (a) TEM image of three coronene filled BNNTs with three different inner diameter from upper right to lower left: 2.1, 3.2, 2.32 nm, respectively. The right BNNT has small enough diameter to transform coronene molecules to GNR, while the diameters of the other two are larger than the limit (2.2 nm) for GNR formation. (b) Schematic of dicoronylene (dimer of coronene). Scale bar in (a) is 5 nm and in (b) is 0.25 nm.

coronene molecule. This suggests that the nanoribbon is most probably formed by polymerization of dicoronylene (a dimer of coronene, see Fig. 2b). In fact coronene molecules can form dimers at temperatures ranging from 450 up to 550° C [12, 21]. Considering that the dimerization process depends on pressure and concentration of coronene in the reaction chamber, it is possible that in our experiment the dicoronylenes are formed during the filling step inside the quartz ampule. This is also confirmed by the appearance of red deposit on the walls of the quartz ampule, which is the color of dicoronylene formation [21]. Similar to coronene, dicoronylenes may also form long range parallel stacking, if the diameter of the host tube is close to the dicoronylene width.

Figure 3a is a histogram showing the width distribution of GNRs synthesized inside BNNTs. The inner diameter distribution of the host BNNTs is also shown by histogram in Fig. 3b. Although the inner diameters of the BNNTs, hosting GNRs, are ranging from 1.47 to 2.29 nm; the width of the encapsulated GNRs can be divided into two subgroups. First, GNRs with width close to 0.75 nm and second, GNRs with width close to 1.40 nm. The first group is attributed to



**Figure 1** (a) TEM image of a 0.79 nm wide GNR encapsulated in three-walled BNNTs. (b) Schematic showing a coronene molecule. Scale bar in (a) is 5 nm and in (b) 0.25 nm.
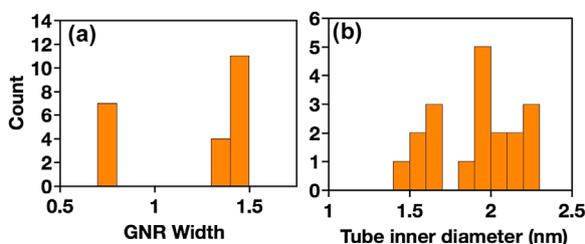


**Figure 3** Histograms indicating (a) the width distribution of encapsulated GNRs and (b) the inner diameter distribution of the host BNNTs.
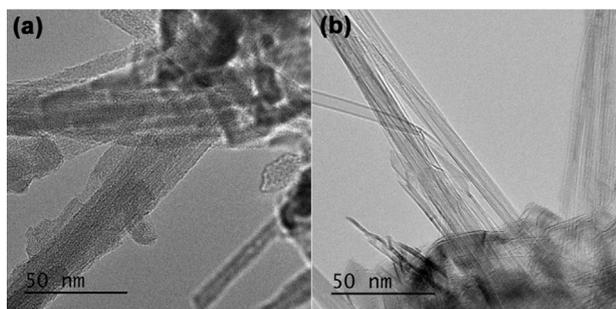
**Figure 4** TEM images of (a) BNNT bundles filled with coronene and (b) same area of the TEM grid after it was annealed at 650 °C in air for 30 min.

polymerization of coronene molecules and the second one can be attribute to polymerization of dicoronylenes. Since a dicoronylene has lower symmetry compared to coronene, the width of the GNRs formed by polymerization of dicoronylenes might show slightly different diameter, depending on the orientation of encapsulated dicoronylenes. All BNNTs with diameter larger than 2.29 nm are mainly filled with semi-amorphous structures.

Interestingly, high temperature stability of the BNNTs make it possible to oxidize (burn away) the encapsulated carbon-based structure at temperatures above 500° C without causing any damage to the BNNTs structure. Figure 4a indicates bundles of BNNTs filled with coronene. Figure 4b shows same bundles after 30 min annealing at 650 °C in air. We note that after annealing the BNNT bundles are slightly dislocated. Our TEM examinations revealed that BNNTs remain robust even after 1 h annealing at 800 °C in air. This provides a new potential application for BNNTs, as robust nanocavities, with high thermal and chemical stabilities, for studying physical and chemical properties of encapsulated nanomaterials.

**4 Conclusions** We prepared encapsulated GNRs inside electrically insulated BNNTs via polymerization of coronene molecules. We have showed that encapsulated coronene transforms to a GNR if the inner diameter of the host tube is between 1.47 and 2.29 nm while tubes with diameters above 2.29 nm were filled by semi-amorphous structures. Furthermore, the inner cavity of the filled tube can be cleaned by oxidation of encapsulated material at temperatures above 500° C.

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