

Self-assembly of a sulphur-terminated graphene nanoribbon within a single-walled carbon nanotube.

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Graphene nanoribbons (GNRs) possess many of the unique properties of the parent material but with the added advantage of the ability to tune these properties through modification of the nanoribbon width and its edge structure.^{1,2} As a result, the potential applications of GNRs in electronic devices extend well beyond those of graphene,³⁻⁵ which has stimulated a significant current effort in the preparation of GNRs. Until very recently most approaches were based on a “top-down” methodology⁶⁻⁸ offering only a limited degree of control over the GNR’s atomic structure, but a recent breakthrough in the “bottom-up” direction has enabled assembly of GNRs with well-defined atomic structures utilising molecules as the carbon source.⁹ As the structure of a GNR appears to be strictly determined by the structure of the initial molecules, this method requires the careful preparation and pre-organisation of the molecular precursors on atomically flat surfaces under precisely controlled ultra-high vacuum conditions.

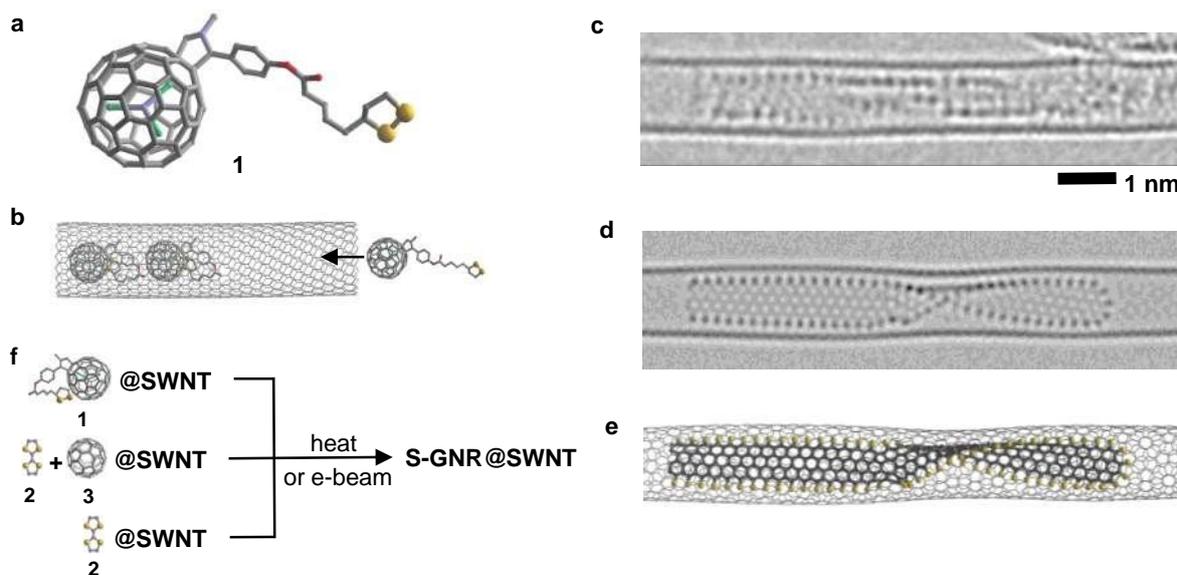
In our study¹⁰, we demonstrate that a GNR can self-assemble spontaneously from a random mixture of elements within a single-walled carbon nanotube (SWNT) that is utilised as both the reaction vessel and a 1D template for the growth of GNRs. We identify the two key principles that lead to the formation of GNR: (i) 1D confinement at the nanoscale ensures propagation of GNR only in one dimension, and (ii) incorporation of heteroatoms into the predominantly carbon-based elemental feedstock leads to the termination of dangling bonds, stabilising the structure and making the otherwise unstable nanoribbons thermodynamically viable over other possible forms of carbon.

The resultant structure GNR@SWNT represents a new, unexpected hybrid form of carbon, with potentially exciting functional properties. The width of the nanoribbon is strictly determined by the diameter of SWNT-nanoreactor, while its elemental composition is controlled by the molecular precursors loaded into the nanotube. Our electron microscopy imaging reveals remarkable structural and dynamic behaviour of the GNR@SWNT system, including elliptical distortion of the nanotube, helical twist and the screw-like motion of the nanoribbon along the nanotube. These unexpected effects offer new mechanisms for controlling properties of carbon nanomaterials, such as electronic band gap and concentration of charge carriers. A recent study indicated that hydrogen-terminated nanoribbons (H-GNR) can also be formed inside nanotubes by pyrolysis of polyaromatic hydrocarbons.¹¹

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Figures



Carbon nanotubes serve as containers and nanoreactors for molecules. Functionalised fullerenes **1** (a) bearing an organic group with sulphur atoms on their surface are spontaneously and irreversibly encapsulated into a SWNT (b) due to the strong van der Waals interactions between the fullerene cage and the interior of the host-nanotube. Under prolonged exposure to the e-beam, the functional groups and the fullerene cages decompose and re-assemble into a nanoribbon inside a (14,5)-SWNT (c). Sulphur atoms terminating the edges of the nanoribbon appear as chains of dark atoms (c – an experimental AC-HRTEM image, e – a model of S-GNR@SWNT and d – an image simulated from the model). Sulphur-terminated nanoribbons can be also formed from other sulphur-containing organic molecules, such as tetrathiafulvalene (TTF) **2** or a mixture of TTF **2** and C₆₀ **3** inserted in nanotube (f) and decomposed at high temperature (over 1000 °C) or under e-beam radiation. (In structural diagrams atoms of sulphur, oxygen, nitrogen and carbon are coloured in yellow, red, blue and grey respectively; atoms of hydrogen in structural diagram of **1** are omitted for clarity).