Branching in Nanotubes

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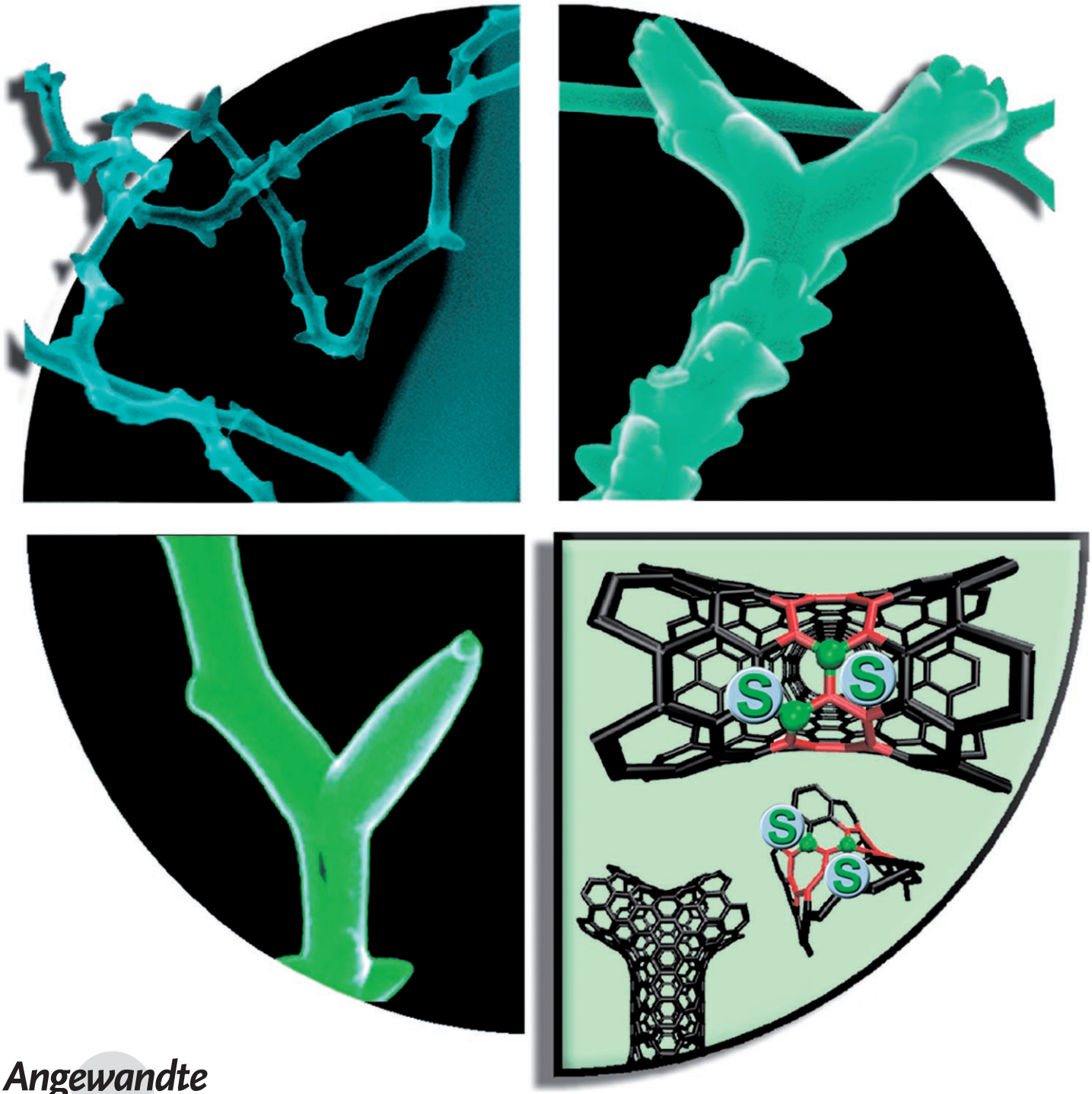
An Atomistic Branching Mechanism for Carbon Nanotubes: Sulfur as the Triggering Agent**

*José M. Romo-Herrera, Bobby G. Sumpter, David A. Cullen, Humberto Terrones, Eduardo Cruz-Silva, David J. Smith, Vincent Meunier, and Mauricio Terrones**



The controlled assembly of elongated nanostructures into ordered micronetworks constitutes a key challenge in nanotechnology. Two- and three-dimensional ordered networks based on carbon nanotubes (ON-CNTs) have been proposed and studied theoretically.[1] These types of carbon structures are of tremendous interest owing to their fascinating mechanical and electronic properties that could be used in the fabrication of nanodevices. Experimental realization of these types of networks can be quite challenging, and the most efficient and viable route appears to be by self-assembly. Although a number of chemical elements seem to play a key role in the formation of network nodes, little is known about their role in microscopic processes governing branch formation. Herein we systematically study, using a combination of theoretical and experimental techniques, the role of sulfur during nanotube network growth. We demonstrate that small concentrations of sulfur are sufficient to promote the formation of carbon heptagons during nanotube growth, and eventually to trigger the appearance of branching in nanotubes with stacked-cone morphologies. We have characterized the network samples using high-resolution electron microscopy and detailed elemental analyses, and observed the presence of minute amounts of sulfur at the branching point between straight nanotube sections. Our findings are rationalized and explained using molecular dynamics and other simulations based on density functional theory.

[*] J. M. Romo-Herrera, Prof. H. Terrones , E. Cruz-Silva, Prof. M. Terrones
Advanced Materials Department
IPICYT
Camino a la Presa San José 2055, Col. Lomas 4ª Sección, San Luis Potosí 78216 (México)
Fax: (+52) 444-834-2010
E-mail: mterrones@titan.ipicyt.edu.mx
B. G. Sumpter, V. Meunier
Computer Science and Mathematics Division and
Center for Nanophase Materials Sciences
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6367 (USA)
D. A. Cullen, D. J. Smith
School of Materials and Department of Physics
Arizona State University
Tempe, AZ 85287 (USA)

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Carbon nanotubes (CNTs) with multiterminal junctions (that is, junctions with at least three terminals) were first proposed theoretically as "Y" junctions.[2,3] They have prompted special interest because of their potential electronic properties in the fabrication of various nanodevices.[4,5] At present, great efforts are concentrated towards efficient synthesis for mass and controlled production of these networks.

After the first experimental observation of CNT branching in 1995,[6] there have been significant developments along three independent routes that are able to produce CNT junctions. First, different templates acting as molds were used to obtain three terminal junctions.[7] Second, it was demonstrated that by applying strong electron beams to crossing (overlapping) SWNTs, it was possible to fabricate three or four terminal CNT junctions.[8] Finally, and more recently, different synthetic approaches based on arc discharge or chemical vapor deposition (CVD) experiments have been developed to produce branched CNTs and networks.[9–17]

The overall morphology of CNT junctions obtained using the template method corresponds to the so-called "finger-like" shape,[7] with the branches growing parallel to one another. In addition, high resolution transmission electron microscopy (HRTEM) images indicate that this type of material has rather poorly graphitized sidewalls. These two characteristics are detrimental for exploiting the potential applications of ON-CNTs. On the other hand, while the electron beam irradiation approach[8] is the only clear report of a junction of single-walled nanotubes to date, it seems highly unlikely that it can be scaled up for mass production. Therefore, high-quality nanoscale branching seems to be the only viable approach if it is performed during controllable growth processes, in the presence of elements that could act as CNT welders so as to generate two- and three-dimensional CNT networks.

Rao and co-workers demonstrated for the first time that it is possible to produce Y-junction CNTs using a CVD process in the absence of templates by pyrolyzing nickelocene in conjunction with thiophene.[9] Several subsequent studies followed a similar approach of pyrolyzing a metallic catalyst, a carbon source, and most of the time including sulfur-containing species.[9,10,13,16,18] It was suggested that the presence of sulfur during the synthesis plays a key catalytic role in the branching mechanism.[9,10,13,16] Unfortunately, these studies were not able to detect sulfur concentrations using elemental characterization, possibly because of the low concentrations of sulfur incorporated in the carbon network (<1 atom %), and did not provide a branching model based on sulfur-mediated growth. Therefore, and to the best of our knowledge, an atomistic study analyzing the CNT branching phenomena using sulfur as the triggering agent has not been proposed.

Herein we present detailed HRTEM and elemental characterization of various Y junctions generated by pyrolyzing thiophene and nickelocene in an inert atmosphere (see Methods Section).[9] Sulfur atoms are mainly located in regions of the networks that present the largest curvature. These results were rationalized using first-principles density functional calculations.

Figure 1 shows the overall morphologies of the junctions that are produced; the branching morphologies are similar to those reported previously.[9,10,12–13,15–17] Junctions of variable thickness (Figure 1 a,b,d,e) and with multiple branching, where the density of branches increases considerably (Figure 1 c,f), were produced. Figure 1 g,h depicts scanning electron microscopy (SEM) images and bright field STEM images of one of the produced junctions. Figure 1 i corresponds to a TEM image of a junction, showing highly crystalline material.

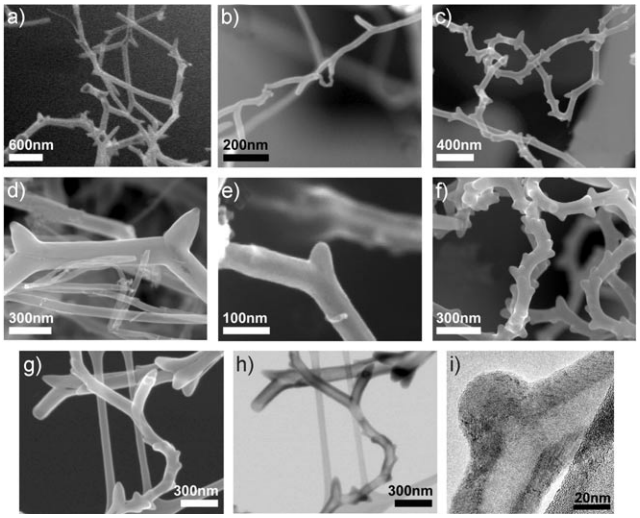

Figure 1. General morphology of carbon nanostructure junctions. a) and d) SEM images of thick junctions (diameters ca. 200 nm), b) and e) thinner junctions (diameters ca. 50 nm), c) and f) networks with a higher density of branching points. g) SEM and h) bright field STEM, showing the hollow interior of the junctions. i) TEM image, showing the general structure of an opening junction.

A detailed elemental characterization revealed the presence of sulfur at the emerging branches of structures (highly curved surface), which also motivated theoretical calculations to understand, at the atomic level, the role of sulfur as a branching promoter. These studies, together with HRTEM structural analysis, provide novel and important information that explains the mechanism of nanotube junction formation.

Figure 2 a–d shows results obtained using high-resolution energy-dispersive X-ray spectroscopy (EDX) line scans. These scans confirm the presence of sulfur within the emerging CNT branch (Figure 2 b). To ensure the reliability of the measurement, we compared an EDX point measurement in vacuum (marked as point A in Figure 2 a and the spectrum shown in Figure 2 c) with a point located at the tip of the branch (B in Figure 2 a and in Figure 2 d). In the case of point B, a clear signal was observed at 2.3 keV (Figure 2 d), which is characteristic of sulfur.

The TEM and HRTEM images in Figure 2 e, f show how the formation of a new branch induced by the presence of sulfur atoms results in a tensile force at the opposite side which modifies the graphitic structure. In every branch, a deformation in the stacking of the graphene layers at the opposite side is always observed. A black line and a white line (marked on the HRTEM image of the lower panel in

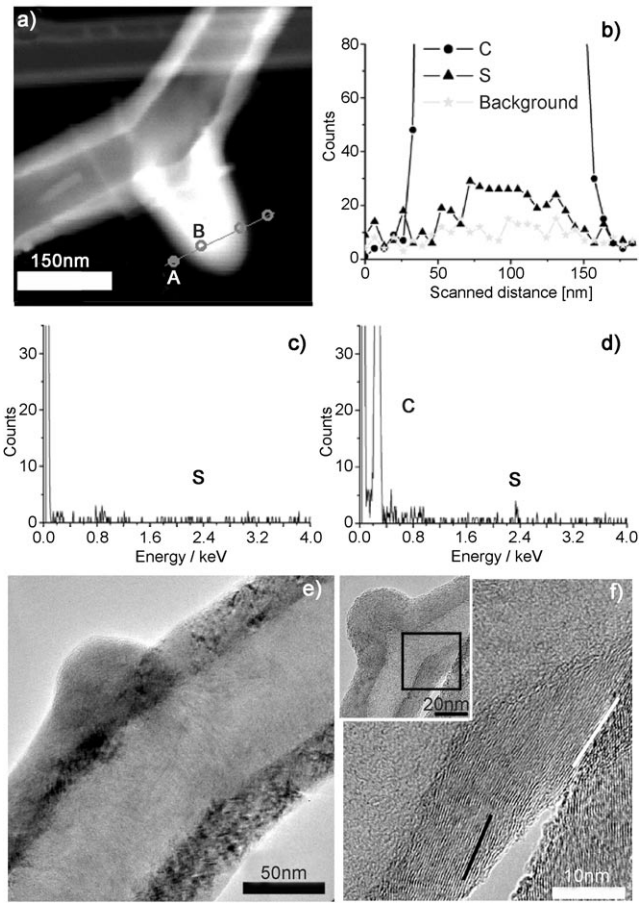

Figure 2. a)–d) Elemental characterization at an opening branch, where sulfur presence was detected: a) Position of the performed line scan; b) the sulfur signal above the background signal. c),d) Confirmation of the presence of sulfur at 2.3 keV, by comparing the EDX spectrum of c) point A (vacuum) and d) point B (over the branch tip). e),f) Structural changes at the opposite side of the CNT arising from the emerging branch: e) Low-magnification TEM image showing a directional change in the main stem just at the branching point; f) HRTEM image showing a variation in angle of the stacked graphene layers, indicated in the large magnified view by the black and white lines.

Figure 2 f) indicate the graphite plane stacking variations at different angles occurring in front of the emerging branch.

The presence of sulfur in these branched structures motivated us to perform extensive simulations based on first-principles density functional theory (both static and dynamic, see Methods Section for details) to fully understand the role of sulfur at the atomic level. First, molecular dynamics (MD) calculations revealed that sulfur widens the diameter of a nanotube by inducing the formation of heptagons (see Figure 3 a). This widening could also be responsible for inducing the formation of graphitic stacked cones (Figure 3 b). All the sulfur-catalyzed tubular structures exhibit a stacked-cone morphology.[9,10,12,15–17,20] The formation of a pentagon and a heptagon is observed in detailed analysis of the MD results, suggesting that sulfur promotes the creation of nonhexagonal rings in the sp^2 carbon network. In addition, when a sulfur atom is placed in a graphene layer, it tends to come out from the carbon network, causing the

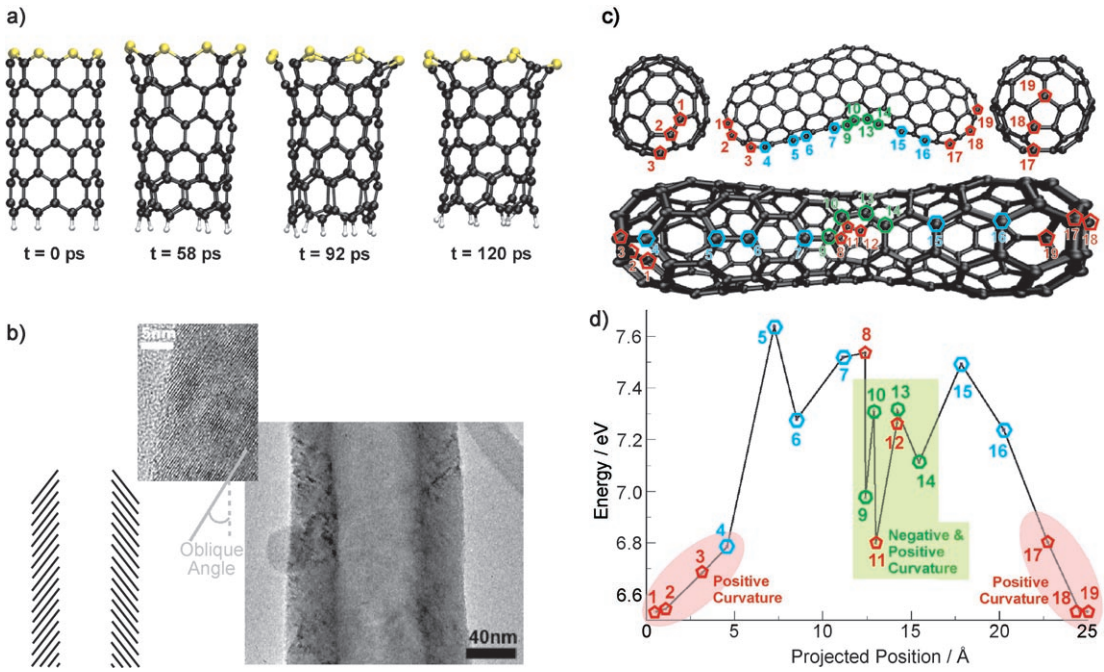

Figure 3. Theoretical calculations explaining the role of sulfur at the atomic level. a) Snapshots from quantum molecular dynamics simulations, showing the effect of widening the CNT diameter in the presence of sulfur. b) Stacked-cone structure promoted by sulfur widening the CNT. The angle caused by the heptagons ((a), at 120 ps) is very close to those observed in the stacked-cone morphologies (b). c) The position of a sulfur atom within a carbon nanotube lattice marked to indicate if it is in a pentagon (red), hexagon (blue), or heptagon (green), and d) the total energy for the resulting system (details of the calculations are given in the Methods Section).

formation of a bump on the graphene layer (not shown). Furthermore, this bump results in the cleavage of a S–C bond, leaving two open hexagons. This would cause the formation of heptagons at that site in the presence of carbon feedstock and a thermal gradient; that is, conditions similar to our experiment. Finally, the energetic stability of a substitutional sulfur atom in a sp^2 carbon network was calculated for different types of local environment (different types of curvature; that is, pentagons, hexagons, or heptagons (see Methods Section for details). The results are illustrated in Figure 3c,d. DFT calculations revealed that sulfur energetically favors pentagonal rings and heptagonal rings over hexagons, thereby introducing negative curvatures (heptagons, branch opening) or positive curvatures (pentagons, closing its tip).[19] These results suggest that sulfur is likely to induce the appearance of a bud along the structure and to promote the formation of junctions. This finding is consistent with the EDX line scan shown in Figure 2, indicating the presence of sulfur within the branch tip. Previous experimental studies have also indicated that sulfur is necessary for the formation of Y junctions,[9,10,13,16] but compositional analysis using electron energy loss spectroscopy (EELS) at the junctions were not able to detect traces of sulfur, possibly because the concentrations of sulfur are lower than the detection limit of the instrument used (<1 atom %).[21,22] However, our EDX analyses using a nanoprobe (0.5 nm) and long acquisition times were able to detect minute amounts of sulfur in strained areas of the junctions.

The HRTEM analysis (Figure 4) highlights the main structural features of the Y junctions. Figure 4a reveals how a branch opening is accompanied by a change in direction of the main stem. This is consistent with the variation of the stacking angle of the graphene layers. Figure 4c shows the structure of the developing branch. It also depicts graphitized layers that appear to be very well stacked with a hollow core. The resulting Y junction shown in the Figure 4b consists of an array of graphene layers that are organized along two new arms at a given angle. By annealing these conical junctions, defects are removed, but the formation of loops (coalescence) on the open edges occurs; that is, the cones never become tubular structures.[23]

With the evidence presented above, we propose the branching mechanism summarized in Figure 5. Our model starts with the formation of the main cylindrical stem with a stacked-cone structure, which is favored by the presence of sulfur in the system leading to a widening effect on the nanotube (see Figure 3a). Accumulation of sulfur atoms on a cone wall then promotes the formation of a bump, which induces deformations on the opposite side of the growing tubule. The bump formation is supported by the fact that sulfur tends to promote heptagonal and pentagonal rings in the sp^2 carbon network. This step is essential for achieving negative curvature at the emerging branch and positive curvature close to the branch tip, as indicated by the theoretical results. Following the initial stage of bump formation, the graphitic walls on the opposite side experience strong deformations which in turn cause a change in the stacking angle of the graphene layers. This change alters the growth direction of the main stem, thus promoting the formation of the second arm (Figure 5c). As the emerging

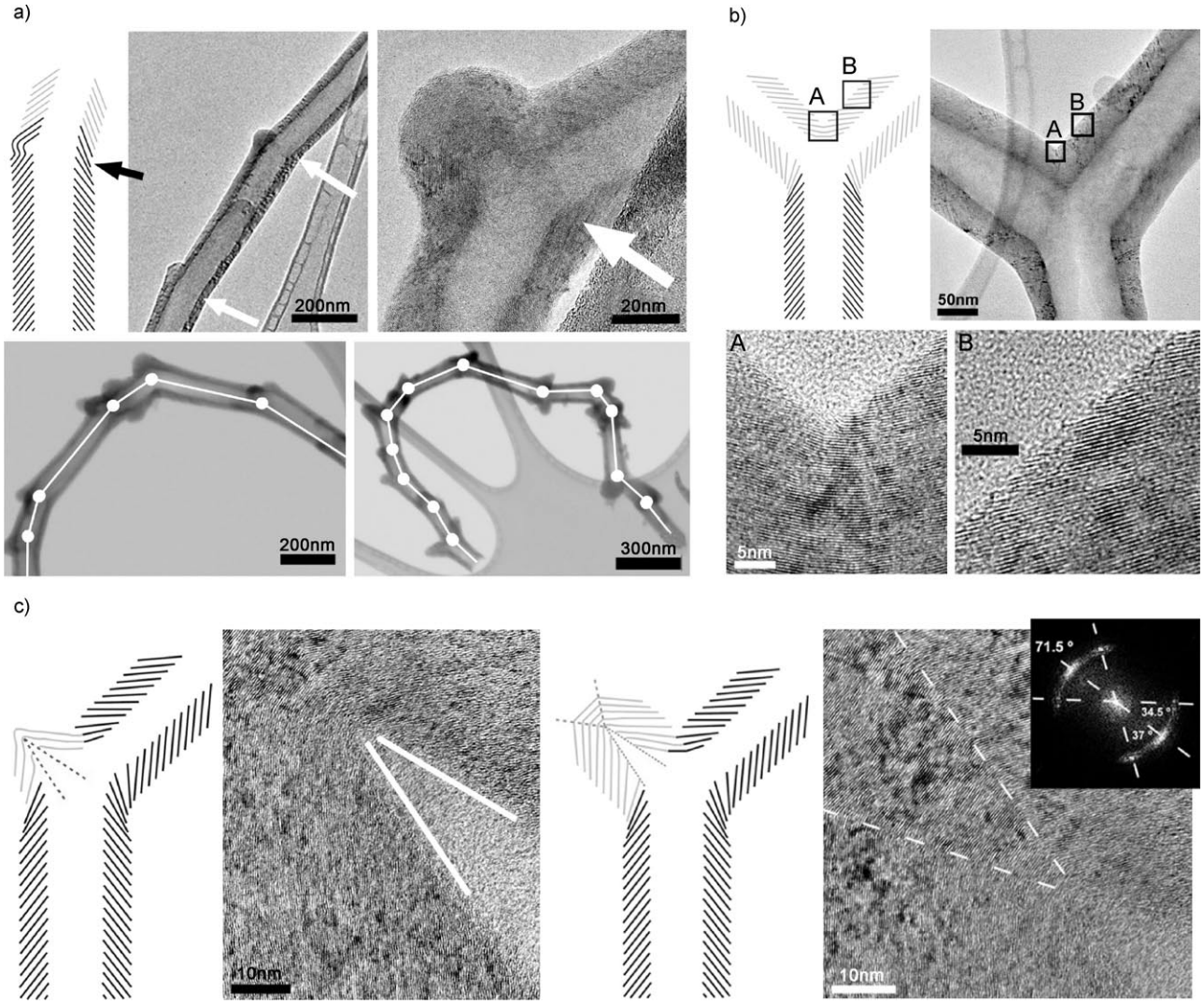

Figure 4. a) Low-magnification TEM pictures showing that every time a branch opening occurs, there is a direction change of the main stem (indicated by arrows and white dots). b) The final Y-junction, along with high-resolution views of the structure at the developed arms (panel B), and right at the angle between them (panel A). c) Structure of the developing branch at the graphene layer level. Inset: Fast Fourier transform calculation from the image, allowing the angle between the stacking direction of the graphene layers to be measured (34.5°: stacking change marked by left dashed line on HRTEM image, 37°: stacking change at the right dashed line).

bump continues to develop, it will become the third arm of the junction (Figure 5 d–f) to finally obtain the Y junction structure.

In summary, we have demonstrated that sulfur plays an important role in the formation of branched nanotube networks with stacked-cone morphologies. The growing branches possess minute amounts of sulfur that are sufficient to promote the formation of heptagons (negative curvature) and pentagons (positive curvature). The MD simulations show that sulfur atoms promote the formation of heptagonal rings, and are also more likely to be found in curved regions (either heptagons or pentagons). Other studies have used sulfur-containing precursors and produced CNT junctions[9, 10, 13, 16, 18] that exhibited stacked-cone morphologies.[9, 10, 12, 15–17, 20] However, none of those studies elucidated the underlying atomistic mechanism whereby sulfur atoms induce the formation of bumps during nanotube growth that ultimately develop into CNT junctions. In addition, the growth mechanism for stacked-cone structures has never been explained in terms of the presence of elements such as sulfur. We envisage that other elements will also promote the formation of novel and intriguing nanostructure morphologies, and further research should be conducted in this direction.

Methods Section

The experimental data were obtained using SEM (XL30 SFEG FEI), STEM (XL30 SFEG FEI), HRTEM (Philips CM200) and High-Resolution EDX (Philips CM200; 0.5–1.0-nm probe size).

The synthesis follows the procedure reported by Satishkumar et al.,[9] in which nickelocene was sublimed in a first furnace heated from room temperature to 400 °C, and then introduced into a second furnace at 1000 °C by a carrier Ar–H_2 gas (5 % H_2 v/v), previously bubbled by a thiophene container (ca. 200 bubbles/min). CNT

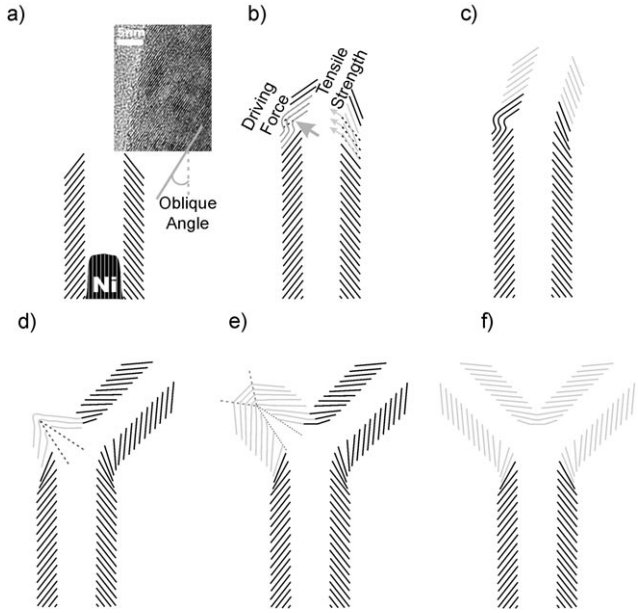

Figure 5. Schematic representation of the proposed branching mechanism. a) Main stem with a stacked-cone structure; b) sulfur-promoted formation of a bump as the main driving force to start branching, causing a tensile force at the opposite wall which changes the stacking angle of the subsequent graphene cones; c) a direction change in the main stem leading to formation of a second arm. d) The opening branch develops with a hollow interior; e) this third arm keeps growing by stacking of new graphene cones until f) the final Y-junction is obtained.

junctions and networks were observed in the material collected from the inlet and outlet of the second furnace, where a steep temperature gradient is present.

All calculations were performed using the periodic DFT program Vienna ab initio simulation package (VASP), v. 4.6.6.[24–27] The Kohn–Sham equations were solved using the projector augmented wave (PAW) approach and a plane-wave basis with a 400-eV energy cutoff.[28,29] The generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) was utilized.[30] Electronic convergence was defined as a consistency between successive cycles of less than 10^{-5} eV. Each nanotube system was placed in a cell that ensured at least 10 Å of vacuum in each Cartesian direction between the tube and its reflection. *k*-point sampling was restricted to the Γ point, a choice that is relevant for a cluster-like calculation as performed herein.

The nano-"peanut" studied (see Figure 3c) consisted of a capped (9,0) and a (5,5) nanotube joined with a pentagon–heptagon pair. The calculation consisted of placing a single sulfur atom at different substitutional positions in a defective structure (shown in red when part of a pentagon, blue hexagons, and green heptagons) to examine the energetics that underly the formation of heptagons and pentagons, and also to determine if sulfur concentrates at the tip. As the substitution of a carbon atom by a sulfur atom is associated with significant structural reorganization, full DFT relaxation for each case is performed. These results were also complemented by calculations based on first-principles molecular dynamics at temperatures relevant to the experimental synthesis (400–1000 K). The main observation of those simulations is that nanotubes with sulfur included in their lattice at small relative concentrations (< 5 %) leads to a defective structure that results from the cleavage of a S–C bond, leaving two open hexagons. Carbon feedstock and a thermal gradient as present in the experimental synthesis can then cause the formation of a heptagon (also shown to be energetically favored by the static calculations) at that site and the creation of the observed bud.

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