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Template Synthesis of Linear-Chain Nanodiamonds Inside Carbon Nanotubes from Bridgehead-Halogenated Diamantane Precursors

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Abstract: *A simple method for the synthesis of linear-chain diamond-like nanomaterials, so-called diamantane polymers, is described. This synthetic approach is primarily based on a template reaction of dihalogen-substituted diamantane precursors in the hollow cavities of carbon nanotubes. Under high vacuum and in the presence of Fe nanocatalyst particles, the dehalogenated radical intermediates spontaneously form linear polymer chains within the carbon nanotubes. Transmission electron microscopy reveals the formation of well-aligned linear polymers. We expect that the present template-based approach will enable the synthesis of a diverse range of linear-chain polymers by choosing various precursor molecules. The present technique may offer a new strategy for the design and synthesis of one-dimensional nanomaterials.*

Carbon nanotubes (CNTs), nanometer-scale cylinders composed of rolled-up graphene sheets, provide an ideal platform to create one-dimensional (1D) nanostructures. Over the past decade, we have developed a synthetic method for 1D nanostructured materials utilizing the inner spaces of CNTs, in so-called nanotemplate reactions.[1–11] Precursor species are first filled into the cavities of CNTs and then transformed into linear structures by thermal annealing or electron beam irradiation. To date, various kinds of 1D nanomaterials have been synthesized, including metal nanowires with atomic thickness,[4–6] ultrathin boron nitride nanotubes,[10] and well-defined CNTs.[11] These exhibit unique architectures and properties that are entirely different from those of their bulk counterparts. Exploring novel 1D nanomaterials by means of the nanotemplate reaction opens new avenues of research in materials science.

As a part of our continuing efforts to prepare novel 1D nanomaterials inside CNTs, we have been working on the synthesis of linear forms of crystalline diamond from diamondoids, linear-chain diamondoid nanowires with diamond topology. Diamondoids consist of face-fused adamantane (a ten carbon cage structure) building blocks, regarded as the smallest unit of the diamond crystal lattice[12–16] that shows a variety of topologies.

Recently, the fabrication of ultrathin graphene nanoribbons, straight-edged stripes of graphene, has been achieved through the coalescence of aromatic molecules by nanotemplate reactions.[17,18] Analogous to the successful synthesis of nanomaterials with sp^2 hybridized carbon atoms, we thought that diamondoids may serve as building blocks for a diverse range of C(sp^3) nanostructures. Indeed, we have demonstrated that diamantane-4,9-dicarboxylic acid can be transformed into superfine diamond nanowires with sub-nanometer diameters inside CNTs.[19,20] These advances hint at the possibility of producing new types of 1D diamond nanostructures by nanotemplate reactions. Studies of structural variations of 1D C(sp^3) nanomaterials are much less common than those of the sp^2 hybridized counterparts.[21] Creating other new classes of 1D diamond nanostructures is crucial for systematic studies on the properties of diamond-like nanomaterials.[14]

Herein, we report the nanotemplate synthesis of linear-chain nanodiamonds, in which intact diamantane skeletons are connected with each other through C–C bond linkages[22] starting from apical-bridgehead-halogenated diamantane precursors. Under vigorous heating, the sublimed precursors are dehalogenated to form linear-chain diamantane polymers inside CNTs (Figure 1). Using experimental and theoretical techniques, we reveal that the diamantane skeletons are linked together inside the nanotubes. The template synthesis of this new class of diamond nanomaterial may offer a new direction for nanodiamond research as well as a new strategy for the design and synthesis of 1D nanomaterials in general.

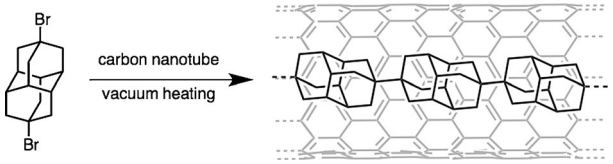

Figure 1. Schematic representation of the nanotemplate reaction for the synthesis of nanodiamond polymers from 4,9-dibromodiamantane within carbon nanotubes.

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Our strategy for creating linear-chain nanodiamond polymers relies on the vapor-phase reaction of an apically dibromo-substituted diamantane, 4,9-dibromodiamantane,[23] in the presence of either hollow single-wall CNTs (SWCNTs) or hollow double-wall CNTs (DWCNTs). At high vacuum and temperature (175 °C, 10^{-7} Torr), dibromodiamantane can be vaporized to form polymer chains inside the CNTs. High-resolution transmission electron microscopy (HR-TEM) images of the as-produced samples are shown in Figure 2.

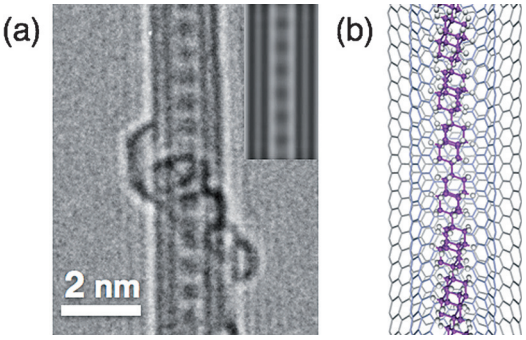

Figure 2. a) High-magnification TEM image of an as-produced sample; inset: simulated TEM image of a diamantane nanodiamond polymer confined in a DWCNT. b) Corresponding structural model.

Well-aligned dots are observed in DWCNTs with relatively thin inner tubes (Figure 2a). A close inspection of the space between individual dots reveals that the center-to-center distance d is 6.35 ± 0.2 Å, which is in excellent agreement with density functional theory (DFT) computations at the B3LYP (D3BJ)/cc-pVDZ level of theory ($d = 6.34$ Å), which we carried out in parallel with the TEM studies. The monomer separation was evaluated for the nanodiamond polymer as depicted in Figure 2b, in which two diamantane skeletons are linked between their apical bridgehead positions through covalent bonds between sp^3 hybridized carbon atoms (between their C4 and C9 positions; Figure 3, top). The dispersion-bound dimer with $d \approx 0.89$ nm (Figure 3, bottom) is incompatible with the much shorter inter-dot distance observed by TEM.[24] Indeed, the simulated TEM image is in good agreement with the observed images (Figure 2a, inset). These experimental and theoretical analyses indicate the formation of linear-chain diamantane polymers, whose structural features are distinctly different from those of an array of the precursor material.

Fourier transform infrared (FT-IR) spectra of the guest precursor, the host CNTs, and the hybrid material are shown in Figure 4. The IR spectroscopic vibrational bands of 4,9-dibromodiamantane observed at approximately 2900 cm^{-1} (blue), which were assigned to the C(sp^3)–H stretching modes, are also seen in the spectrum of the as-produced sample (red). Over the inspected range, unfilled CNTs have virtually no spectral contribution with appreciable intensity (black). The IR analyses strongly suggest that the structure of the resulting product should be related to the skeleton of the diamantane precursor. The slight shift and sharpening of the bands were attributed to the confinement of the molecular

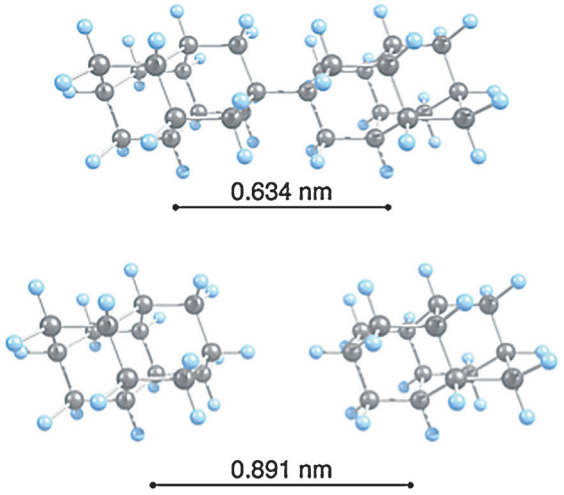

Figure 3. Comparison of covalently bound (top) and 1D dispersion-bound (bottom) diamantane dimers at the B3LYP(D3BJ)/cc-pVTZ level of theory. The center-to-center distance is in good agreement with our measurements only for the covalent species; its computed bond dissociation energy is 86.2 kcal mol^{-1}.

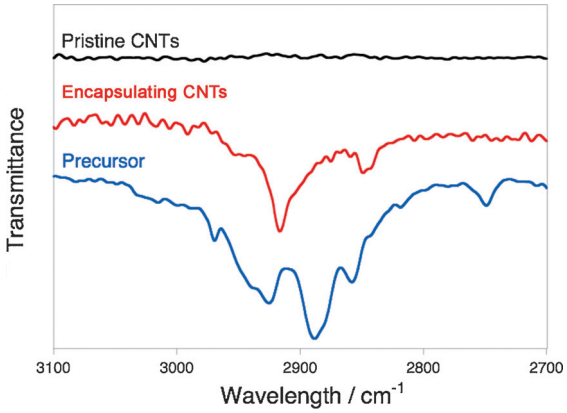

Figure 4. FT-IR spectra of 4,9-dibromodiamantane (blue), an as-produced sample (red), and pristine DWCNTs (black).

motion in the narrow interior of the DWCNTs. Similar changes in IR spectra have also been observed for the encapsulation of various diamondoid precursors.[19,20,25] Note that residual outside molecules have been removed and thus make no spectral contribution. After the reaction, the outer surfaces of the DWCNTs were thoroughly washed with an organic solvent (see the Supporting Information). The complete removal of residual precursor was confirmed by the IR spectrum of the control sample, in which the precursor was heated with end-closed DWCNTs. The corresponding IR spectra of the control samples showed no characteristic bands after washing (Supporting Information, Figure S1). The origin of the detected bands must therefore be attributed to the encapsulated products.

In the as-produced samples, on the other hand, the C–Br stretching vibration modes of the sublimed precursor are obscured by C–C stretching and C–C and C–H bending modes (600–1500 cm^{-1}; Figure S1). Although it is difficult to

extract reliable information on the C–Br bonds from the fingerprint region, it is reasonable to assume that the disappearance of these characteristic peaks is the result of the linear-chain polymer formation. In addition to the IR analyses, energy-dispersive X-ray (EDX) spectra indicate the absence of bromine atoms in the linear products (Figure S2). These elemental analyses confirmed our assumption that the dehalogenated intermediates link up with each other to produce linear-chain polymers.

Histograms illustrating the inner diameter distributions of the encapsulating and pristine DWCNTs are shown in Figure 5. The average inner diameter of the encapsulating

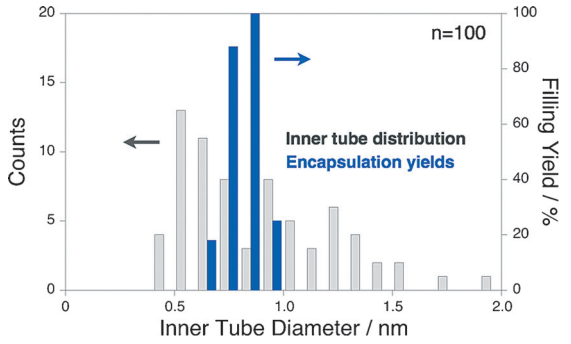

Figure 5. Histograms of the inner diameter distributions of pristine and encapsulating DWCNTs. The diameters were estimated based on TEM observations.

DWCNTs is approximately 1 nm, and the distribution lies within a narrow range. Polymer formation largely depends on the inner diameter of the DWCNTs. One of the key factors for the diameter-selective polymerization is the essentially weak interaction of the diamondoids with the CNT interior. The hydrogen-terminated diamondoids, which have a low affinity for the internal surface of the CNT wall, are unlikely to remain inside CNTs with a large diameter, as they can readily exit the CNTs. In cavities with suitable sizes, however, the diamondoids would be substantially stabilized by van der Waals (vdW) interactions. In this case, the linear-chain polymers should assemble preferentially in these closely fitting interiors, whereas CNTs with a larger diameter remain empty or encapsulate amorphous carbon material derived from the decomposed precursor (Figure 6c,d). Once formed inside the CNTs, the polymers become geometrically and energetically stable. As a consequence, the linear-chain diamantane polymers are entrapped within the CNTs. This is consistent with the fact that the bisapical diamantane dimer is very stable, as also indicated by its high melting point of 360 °C.[22b] The London dispersion interactions between the diamantane moieties substantially contribute to this stability.

In addition to the apically dibrominated diamantane, the corresponding dichloride and diiodide substrates were also used as precursors. Under similar conditions (175 °C), sublimed 4,9-dichlorodiamantane remained largely intact without forming linear-chain polymers. When heated under vacuum at temperatures above 200 °C, however, 4,9-dichlorodiamantane forms linear-chain polymers inside CNTs (Figure S3a,b). The difference in reactivity is in accord with the

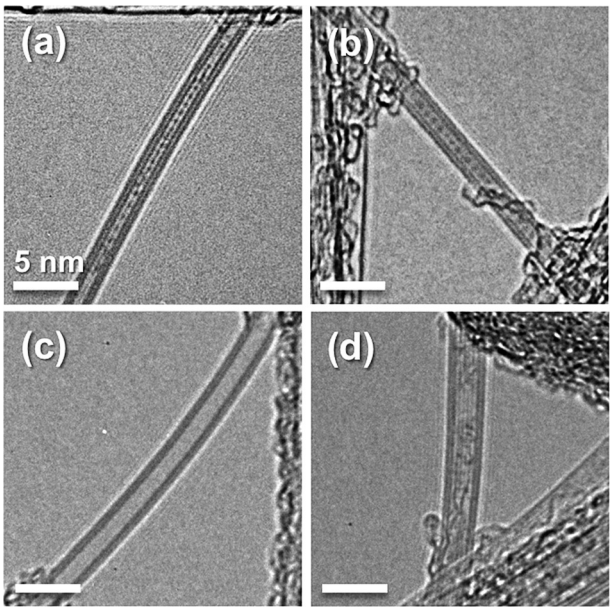

Figure 6. TEM images of a, b) DWCNTs with an inner diameter of 1.0 nm and c, d) DWCNTs with a diameter of 1.5 nm after encapsulation.

bond dissociation energy of the C–Cl bond (81 kcal mol^{-1}) compared with that of the C–Br bond (68 kcal mol^{-1}).[26] Similar experiments were also carried out with 4,9-diiododiamantane. Iodine vapor was observed during the reaction, and the polymer yield significantly decreased. Instead, amorphous inclusion compounds formed in high yields (Figure S3c,d). The C–I bond (52 kcal mol^{-1}) is much weaker than any other carbon–halogen bonds, and 4,9-diiododiamantane may already decompose during sublimation.

After the reaction, a mixture of mono-, di-, and tri-bromo-substituted compounds were found on the outer walls (Figure S4). All of these side products may be obtained through detachment, migration, and recombination reactions of the starting materials, suggesting that the polymerization proceeds through radical intermediates. To date, several studies have described the fabrication of graphene nanoribbons through the radical-mediated polymerization of dehalogenated aromatic molecules.[27–29] A similar process may also be occurring in the present reaction.

To our great surprise, the radicals are persistent and recombined with each other inside the CNTs. Under high-vacuum conditions, the deactivation should be suppressed with a concomitant increase in the lifetime of the radicals, in contrast to typical solvent environments, where free radicals tend to be rapidly quenched in the presence of other chemical species. Furthermore, the dehalogenation of the bisapical bridgehead positions generates exceptionally stable tertiary-carbon-centered radicals, which are much more stable than phenyl radicals.[30] The bridgehead biradical sites are the only configuration that enables an intermolecular coupling reaction within the confined 1D space. In the larger cavities, on the other hand, the biradical intermediates can rotate freely to form branched and disordered polymers or break down into amorphous carbon, as shown in Figure 6d.

To obtain further information on the growth mechanism of the linear-chain diamantane, we investigated the surfaces of the CNTs in an attempt to identify the source of radical generation. EDX measurements indicated the presence of residual Fe catalyst nanoparticles on the CNT surface that were involved in CNT growth (Figure 7). For comparison, we

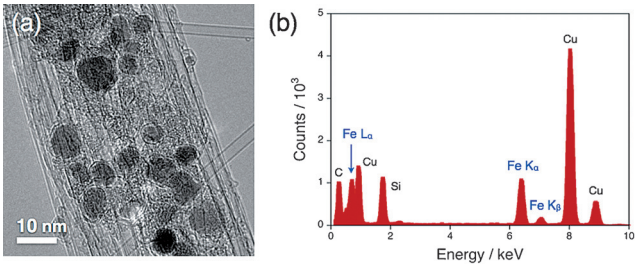

Figure 7. a) TEM image of Fe catalyst nanoparticles adsorbed on the outer walls of CNTs and b) EDX spectrum of the corresponding Fe nanoparticles. Peaks labeled Cu and Si are due to the TEM grid and the Pyrex tube used for polymer formation, respectively.

also studied purified, catalyst-free CNTs, where any residual Fe particles had been removed by annealing at 1200 °C,[31] to determine whether Fe was involved in the polymerization reaction. Despite extensive TEM monitoring, we did not observe the formation of the nanodiamond polymers in the cavities of the purified CNTs. Furthermore, no traces of the halogen gases were observed, indicating that the radicals were not generated. Even though the details of the reaction mechanism have not been fully clarified, it is evident that the Fe nanoparticles adsorbed on the outer walls play a crucial role in the radical generation process.

Based on the above results, the following growth mechanism for the linear-chain polymers is suggested (Figure 8): First, the bromide precursors are adsorbed on the outer walls of the DWCNTs and then diffuse relatively freely along the tube surfaces. A similar mechanism was found for the so-called C_{60} peapod formation.[32] During the diffusion process, the precursor is captured on the Fe nanoparticles to form the radial species, which subsequently enter the channels. This incorporation into the CNTs prevents the radicals from undergoing hydrogen abstraction and termination processes. Depending on the inner diameter of the CNTs, the inserted

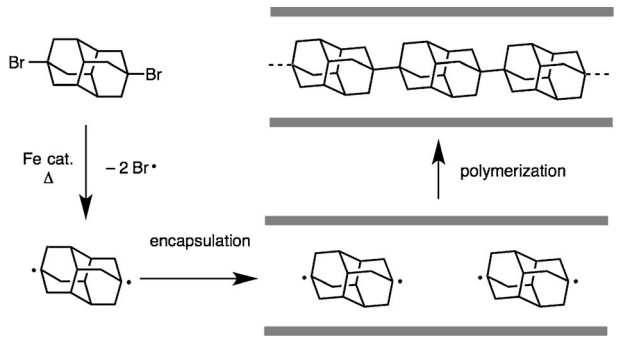

Figure 8. Suggested pathway for the formation of nanodiamond polymers by the nanotemplate reaction.

species can either be transformed into the linear-chain polymers or into amorphous carbon. Only in DWCNTs with a suitably narrow 1D space, the biradical intermediates are forced to align in the same direction and form carbon–carbon bonds between two adjacent monomers, resulting in the formation of the linear polymers.

In conclusion, we have reported a new strategy for the synthesis of a linear-chain diamantane, a new one-dimensional diamond nanomaterial formed inside CNTs from bridgehead-halogenated diamantane. In the presence of (residual) iron catalyst, the sublimed precursors were dehalogenated to form biradical intermediates, which subsequently entered the CNTs and formed C–C single bonds through radical–radical combination. The present template-based approach for the synthesis of linear-chain diamondoid polymers is entirely different from conventional chemical approaches.[22,33–36] We have also developed a method for extracting the products formed inside the CNT templates from the template through solution-phase sonication/extraction.[37] Studies on polymer extraction are currently in progress to investigate their tensile strengths or thermal transport properties. We also expect that the present template-based approach will provide access to a diverse range of novel 1D polymers. In principle, the present strategy is applicable to various dihalogen-substituted molecules. In fact, preliminary experiments indicate that the polymerization can also occur with other precursor molecules. The present synthetic method may offer a new strategy for the design and synthesis of one-dimensional nanomaterials.

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