

Fabrication of Metal Nanowires in Carbon Nanotubes via Versatile Nano-Template Reaction

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Received November 24, 2007; Revised Manuscript Received January 3, 2008

ABSTRACT

A nano-template reaction has been developed to fabricate metal nanowires using metallofullerene nanopeapods (i.e., carbon nanotubes (CNTs) encapsulating endohedral metallofullerenes) as starting materials. In this nanometer-scale reaction, the structure of resulting products should possess specific low-dimensional structures, because of their uniform starting orientation of metallofullerene molecules and the rigid restriction of reaction space by the presence of walls of CNTs. Using the nano-template reaction, we have fabricated various Gd nanowires, including a single Gd atomic chain, a one-dimensional alignment of Gd squares, and Gd nanowires that correspond to a one-dimensional segment of the bulk close-packed structure. The same reaction, in principle, can be applied to fabricate more than 20 different types of metal nanowires in the CNTs, which simply are dependent on the use of the corresponding different types of metallofullerenes as encapsulates in the CNTs. The present novel reaction will provide a wide variety of unusual low-dimensional nanowires and nanomaterials in the CNTs, which have not been synthesized via the fabrication techniques that have been reported so far.

Considerable efforts have been devoted to fabricate low-dimensional nanostructures, such as nanowires and nano-clusters, primarily because of the fundamental interest in their electrical and magnetic properties (which are qualitatively different from those at larger dimensions), as well as their versatile and promising applications toward nanoelectronic and nanospintronic devices.^{1–6} In particular, stability and controllability of these nanostructures are prerequisites for the investigation of their properties and device performance. For this purpose, we have developed a nano-template reaction technique to fabricate metal nanowires using metallofullerene nanopeapods, i.e., carbon nanotubes (CNTs) that encapsulate the so-called endohedral metallofullerenes.⁷ Metal nanowires synthesized via this reaction are determined to be exceptionally stable, because of encapsulation by CNTs, and the diameter of nanowires can be controlled by varying the diameter of the CNTs, which ranges from a single atom chain to nanowires 5 nm in diameter. Here, we report the details of the nano-template reaction and the structures of metal nanowires that can be fabricated.

Our strategy for creating a one-dimensional nanostructure is to use a well-aligned one-dimensional array of Gd-metallofullerenes (Gd@C₈₂) in CNTs (these are the so-called metallofullerene nanopeapods).⁸ Gd@C₈₂ were synthesized by DC arc-discharge and were purified using multistep high-performance liquid chromatography (HPLC) with toluene as

an eluent.⁹ The purity of Gd@C₈₂ metallofullerene was checked by both positive and negative laser desorption time-of-flight mass spectrometry, as well as via high-performance liquid chromatography (HPLC) analyses. Various carbon nanotubes with diameters in the range of 0.64–1.9 nm, synthesized by arc-discharge (FH-P, Meijo Nano Carbon, Inc.), pulsed laser vaporization, and chemical vapor deposition methods have been utilized for the current study. Encapsulation of Gd@C₈₂ into CNTs has been performed via the gas-phase reaction method, and a high filling ratio of Gd@C₈₂ was confirmed by high-resolution transmission electron microscopy (HRTEM) observations.¹⁰

Figures 1a and 1b show high-resolution transmission electron microscopy (HRTEM) images of (Gd@C₈₂)_n@CNT peapods. As clearly seen in the images, Gd@C₈₂ molecules have been densely packed in the CNT, giving rise to the formation of a one-dimensional (1D) crystalline array, and the cross-sectional image of a bundle of the peapods clearly shows that Gd@C₈₂ molecules are indeed encapsulated in the CNTs. A typical filling ratio of Gd@C₈₂ estimated from HRTEM images is >90%. In comparison to empty CNTs, the X-ray diffraction (XRD) pattern of (Gd@C₈₂)_n@CNT shows a significant reduction of a characteristic (10) diffraction peak, which is consistent with the high filling ratio estimated by HRTEM observations (see Figure S1 in the Supporting Information).¹¹

Using this 1D crystalline array of Gd@C₈₂ in CNT as a precursor, various metal nanowires have been synthesized

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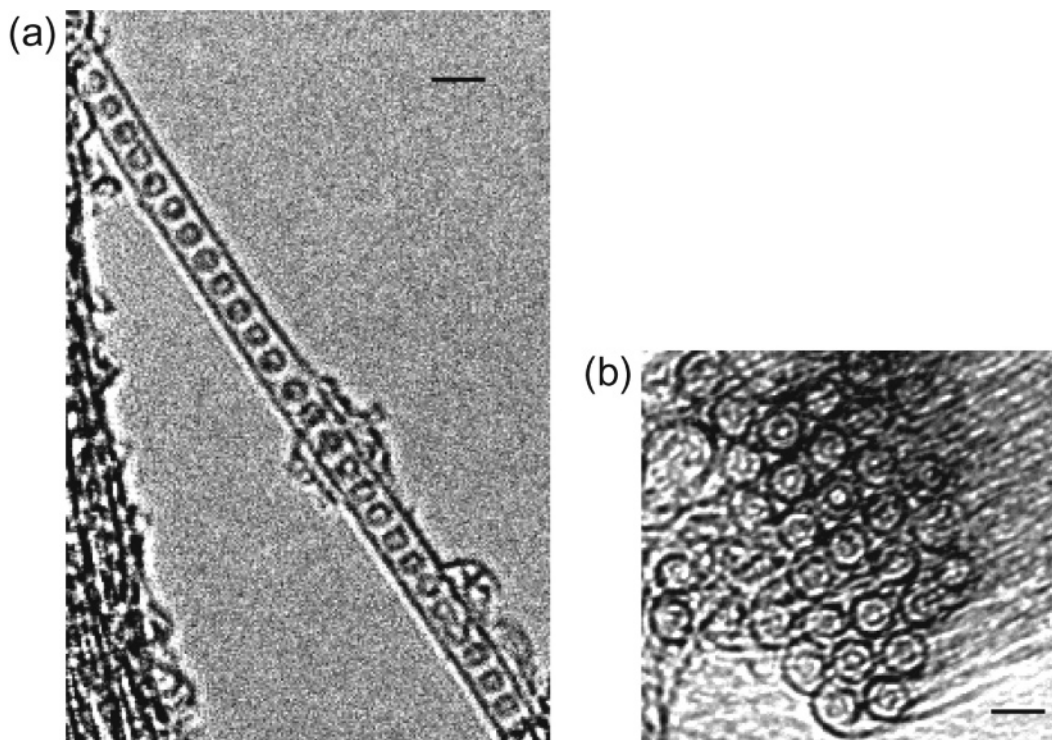


Figure 1. (a) HRTEM image of $(\text{Gd@C}_{82})_n\text{@CNT}$. (b) Cross-sectional image of a bundle of $(\text{Gd@C}_{82})_n\text{@CNT}$. Scale bars = 2 nm.

via high-vacuum high-temperature heat treatment. Because of the starting uniform orientation of Gd@C_{82} molecules and the rigid restriction of reaction space by the presence of walls of CNT, the structure of the resulting products should possess specific low-dimensional structures, which have never been realized in the bulk synthesis.¹² Namely, chemically and thermally stable CNT provides us an ideal reaction space for nano-template reactions for metal nanowire synthesis.¹³ The reaction conditions, such as temperature, background pressure, and time duration used in the present study were typically 1300–1400 °C, 10^{-6} Torr, and 0.5–3 days, respectively.

Raman spectra of $(\text{Gd@C}_{82})_n\text{@CNT}$ and the corresponding $(\text{Gd@C}_{82})_n\text{@CNT}$ heat-treated at an excitation wavelength of 632.85 nm are shown in Figure 2. The Raman bands at $\sim 150\text{--}170\text{ cm}^{-1}$ are assigned to the radial breathing modes (RBM) of the CNTs, which shows that the structure and quality of the CNTs remain the same after the heat treatment. However, new Raman bands at $\sim 280\text{--}330\text{ cm}^{-1}$ appear and become evident after 12 h of heat treatment, which can be attributed to the RBM of CNTs with smaller diameters. The diameters of such CNTs are within the range of 0.89–0.75 nm, based on the known relationship

$$d = \frac{248}{w}$$

where d represents the diameter (given in nanometers) and w represents the Raman shift (in units of cm^{-1}). The evolution of such new RBM modes originating from the CNTs with much smaller diameters is evidence that a fusion reaction of encapsulated Gd@C_{82} molecules occurs in

CNTs: there is a formation of inner thin CNTs in pristine CNTs. This inner tube formation is confirmed by HRTEM observations of $(\text{Gd@C}_{82})_n\text{@CNT}$ after the heat treatment. A similar inner tube formation has been known to occur in a high-temperature treatment of $(\text{C}_{60})_n\text{@CNT}$ and (ferrocene) @CNT .^{14,15} A close inspection of the RBM region at $\sim 150\text{--}170\text{ cm}^{-1}$ and the G-band (1591 cm^{-1}) reveals that the Raman bands exhibit a red shift after the high-temperature heat treatment; the amount of the shift is 3.9 and 6.7 cm^{-1} for the RBM and G-band, respectively, after 12 h of heat treatment. The observed shift strongly suggests the presence of charge transfer occurring from the encapsulated compounds to the outer CNTs.¹⁶

Figure 3a shows HRTEM images of heat-treated $(\text{Gd@C}_{82})_n\text{@CNT}$. As clearly seen in the figure, two columns of dark contrasts are regularly aligned along the tube axis. The contrast of the dark spots is stronger than that of carbon walls of the CNTs, which suggests that the dark spots are caused by heavier atoms. An energy-dispersive X-ray (EDX) spectrum obtained in this area (Figure 3e) shows the presence of strong peaks at 6.1 and 8.1 keV that are respectively assigned to the L_α and L_γ edge of the Gd atom. These peaks were not observed in empty CNTs. Therefore, we have assigned dark contrasts that are aligned in the CNTs to encapsulated individual Gd atoms. Using the layer-to-layer distance of graphite (0.335 nm) as a reference, we have performed direct lattice measurements from the HRTEM image, and the resultant Gd–Gd distances along and across the tube axis are 0.43 and 0.40 nm, respectively, with a standard deviation (SD) of 0.1 and 0.3 nm, respectively. This interatomic distance is significantly larger than those of bulk crystals of Gd and Gd-carbides (the interatomic distances

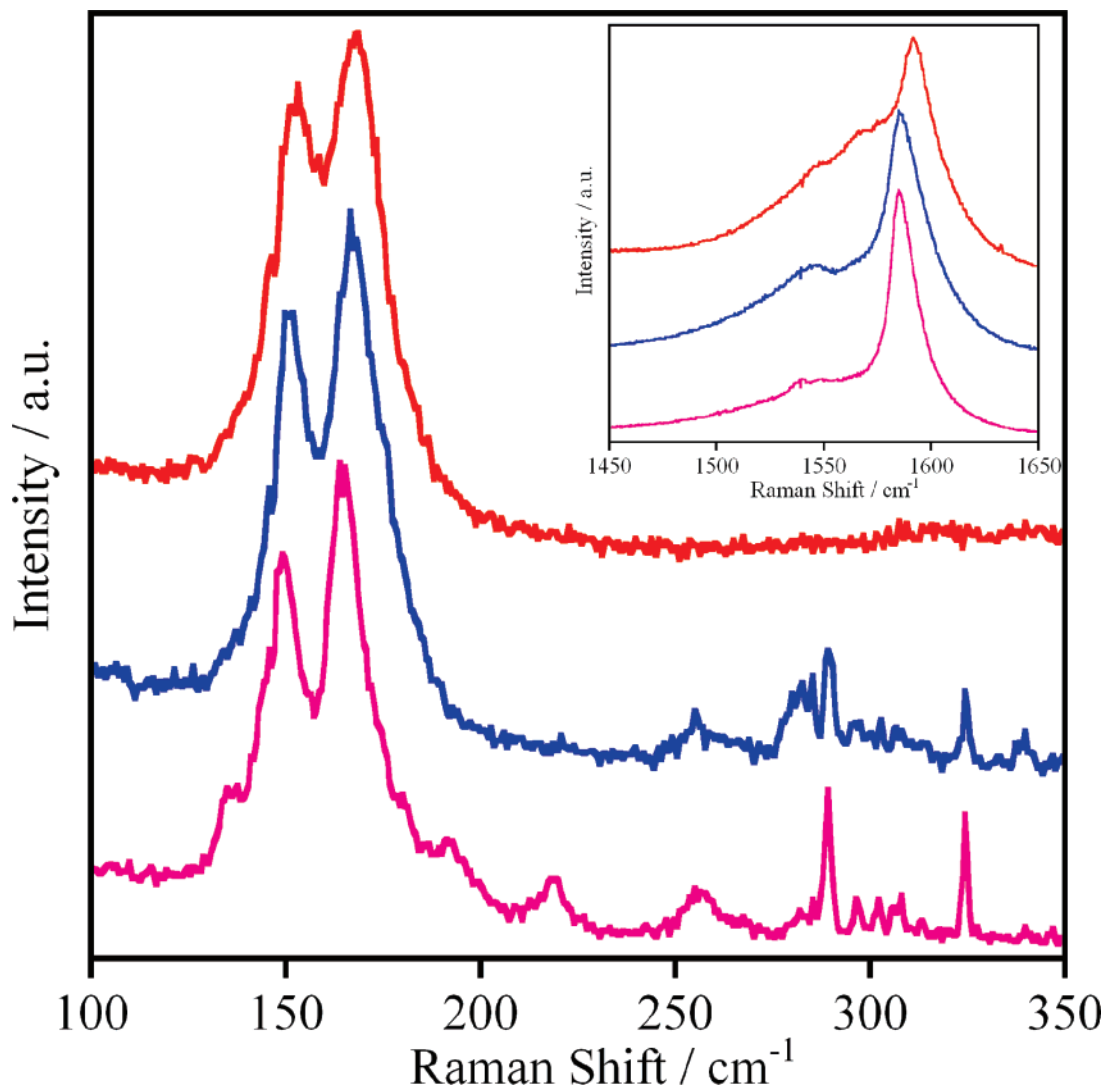


Figure 2. Raman spectra of pristine $(\text{Gd@C}_{82})_n\text{@CNT}$ (red line), $(\text{Gd@C}_{82})_n\text{@CNT}$ heat-treated at 1300 °C for 1 h (blue line), and $(\text{Gd@C}_{82})_n\text{@CNT}$ heat-treated at 1300 °C for 12 h (pink line), with an excitation wavelength at 632.85 nm at a radial breathing mode (RBM) region. The inset shows the G-band of corresponding samples.

of hexagonal close-packed (hcp) and body-centered cubic (bcc) crystals of Gd, and those of tetragonal and cubic Gd-carbides, are 0.357, 0.350, 0.372, and 0.363 nm, respectively). Most importantly, the present structure does not correspond to any known one-dimensional segments of a bulk Gd or Gd-carbide crystal.

Based on this HRTEM images, we have constructed a structure model of Gd-nanowires (see Figure 3b). Based on the constructed structure model, the present nano-template reaction can schematically be shown in Figure 4. In this structure model, Gd atoms are located at corners of a square with a Gd–Gd distance of 0.40 nm, and the squares are spaced at an average interval of 0.43 nm. The length of this nanowire structure evaluated from the HRTEM image is ca. 60 nm, and, therefore, the number of encapsulated Gd atoms is estimated to be ca. 560. This number is a reasonable value, because 560 Gd@C_{82} molecules packed closely in the CNTs correspond to a length of $\sim 0.6 \mu\text{m}$, which is an appropriate length of CNT used in this experiment. HRTEM image simulation using the multislice method, based on this

structure model at a defocus of 66 nm, well-reproduces both the observed dark contrast and its intensity (see Figure 3c).¹⁷ Ladder structures were excluded in the simulation, because the ladder model cannot reproduce the observed intensity ratio between dark spots in the CNTs and carbon walls of the CNTs. We have also simulated HRTEM images, assuming that the nanowire is Gd-carbide (see Figure S2 in the Supporting Information). The image simulation shows that the contrast of carbon atoms is very weak, compared to that of Gd atoms; therefore, there is no distinguishable difference between pure Gd-nanowire and Gd-carbide nanowires. Therefore, at the present time, we are unable to totally exclude the possibility of the formation of Gd-carbide nanowire.

Using CNTs that have a different diameter, we can fabricate various types of Gd-nanowires in CNTs. For example, as presented in Figure 5a, a single column of dark contrasts with regular intervals is observed in CNTs with a very small diameter (0.64 nm). EDX spectra also show that these dark contrasts are attributable to encapsulated Gd

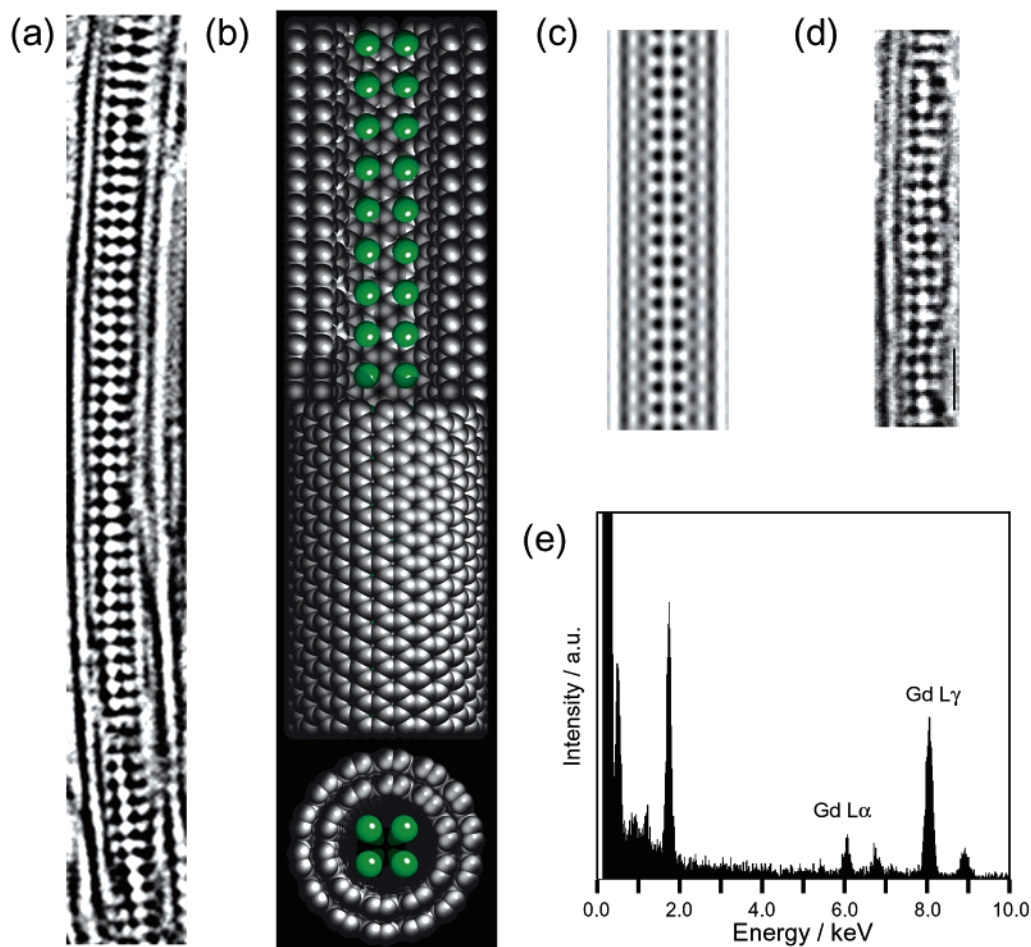


Figure 3. (a) HRTEM image of heat-treated $(\text{Gd}@\text{C}_{82})_n@\text{CNT}$ (a diameter of the CNTs is 1.17 nm). Fourier filtering treatment was applied to remove amorphous materials attached to the surface of CNTs from the image. Scale bar = 2 nm. (b) Structure model of observed HRTEM image represented by the space-filling model. Upper and lower picture shows the structure model perpendicular and parallel to tube axis, respectively. In this figure, gray balls represent carbon atoms and green balls represent gadolinium atoms. (c) Simulated HRTEM image of the model by multislice method at Scherzer defocus. (d) Unprocessed Scherzer defocus HRTEM image. Scale bar = 2 nm. (e) EDX spectrum obtained from heat-treated $(\text{Gd}@\text{C}_{82})_n@\text{CNT}$.

atoms. Direct measurement of the lattice size from the HRTEM image shows that the Gd–Gd distance is 0.41 nm, with a corresponding standard deviation of $\text{SD} = 0.1$ nm. This bond length is also larger than that of bulk Gd crystals.

Figure 5a also shows a structure model and the simulated image of the model based on the multislice method, which shows that the mixed-chain structure (a single Gd atom and a zigzag chain) encapsulated in CNTs can well reproduce the observed image. Note that a theoretical investigation on the filling of rigid spheres into a cylinder space shows that a zigzag or a double-helix structure is stable when the diameter of the cylinder is small.¹⁸ In fact, a double-helix structure has been observed in I_2 molecules that are aligned in CNTs.^{19,20} This mixed-chain structure, with larger Gd–Gd distances than that of bulk Gd crystals (which cannot be understood by the simple filling of rigid spheres), indicates that the interaction between encapsulated Gd atoms and a wall of CNTs has a crucial role in stabilizing the observed Gd-nanowires. This is consistent with the Raman spectroscopy results (Figure 2), which indicates that there might be a substantial charge-transfer interaction between encapsulated Gd atoms and CNT. To the best of our knowledge, the Gd-

nanowire structures previously presented are the thinnest rare-earth metal structures ever reported.

Figure 5b shows an HRTEM image of nanowires formed in a larger-diameter nanotube (1.8 nm). As shown in this figure, four linear arrays of dark spots that are aligned along the tube axis are observed in CNT. Because of several possible structures that can exist in the case of nanowires with a large diameter, we have not yet determined the detailed structure. However, preliminary investigations based on comparison between the observed and simulated images suggest that a 1D segment of a close-packed structure (such as bcc, fcc, and hcp) is one of the best candidates for the structure model. This result is reasonable, because the structure of encapsulated nanowires is expected to become more and more similar to the bulklike crystal structure as the diameter of the nanowires increases. In fact, Gd-nanowires fabricated in CNTs with a diameter of 5 nm is well understood by a 1D segment of a bulk hcp structure.

Figure 6 shows the HRTEM image of the nanowire. As clearly illustrated in the figure, the encapsulated Gd-nanowire

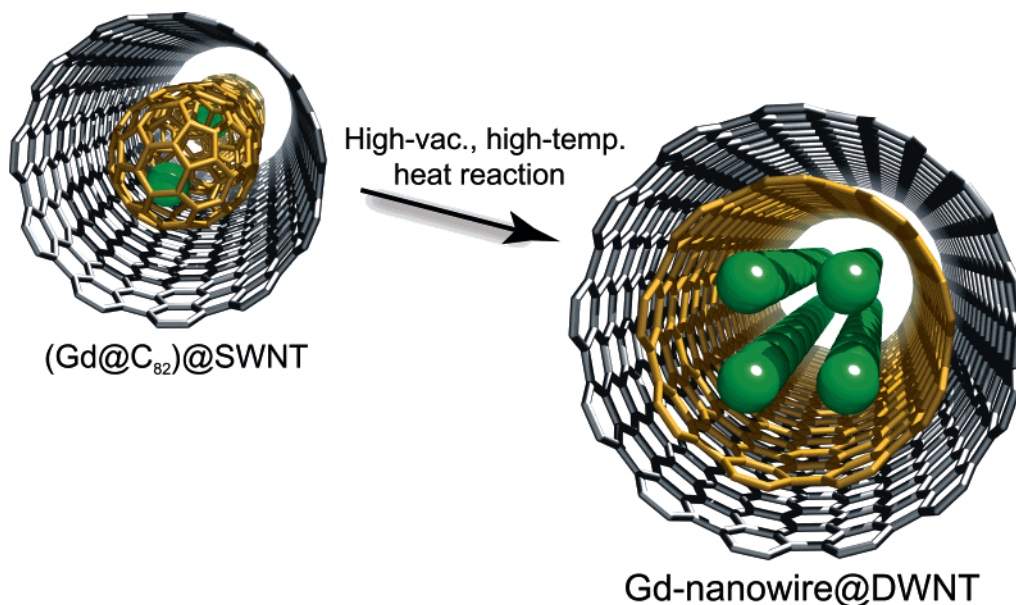


Figure 4. Schematic representation of the formation of Gd-nanowire via nano-template reaction on metallofullerene peapods. In the figure, the green balls represent gadolinium atoms, the gray sticks represent carbon atoms of the outer CNT, and the yellow sticks represent carbon atoms of the inner CNT.

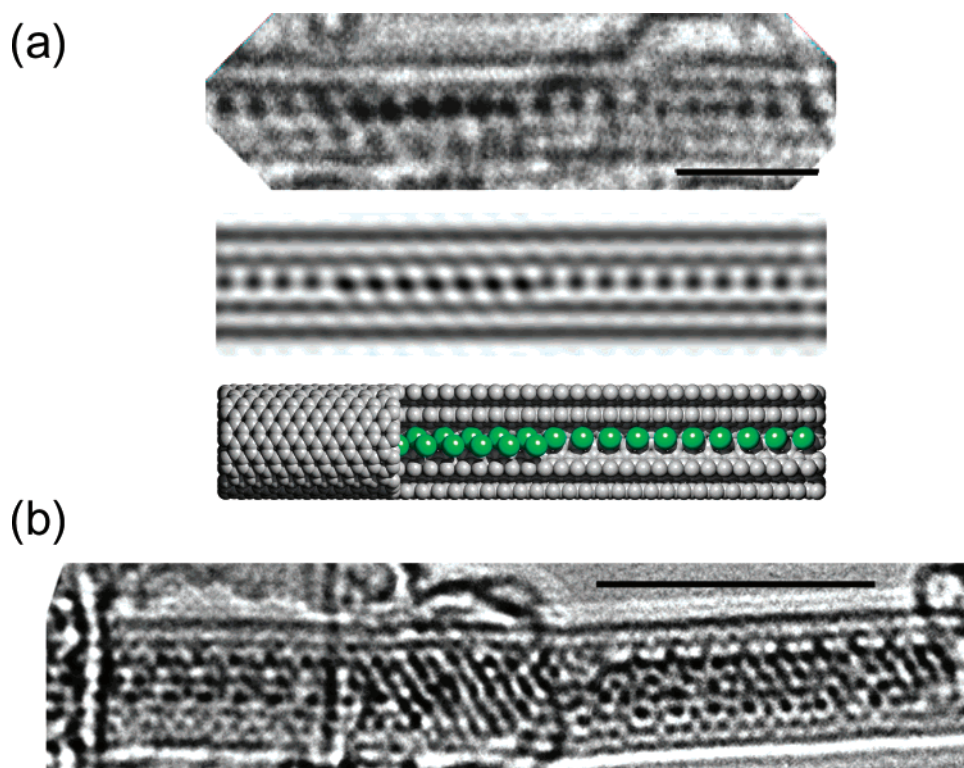


Figure 5. (a) Observed (upper) and simulated (middle) HRTEM image and proposed structure model (bottom) of mixed-chain structure (a single atom and a zigzag chain) formed in CNTs (diameter = 0.64 nm). Fourier filtering treatment was applied to the observed image to remove amorphous materials attached to the surface of the CNTs from the image. Scale bar = 2 nm. (b) HRTEM image of Gd-nanowire formed in CNTs with a diameter of 1.8 nm. Scale bar = 5 nm.

possesses hexagonal symmetry. Fast Fourier transformation (FFT) of the image shows the presence of the hexagonal pattern created by the $(1\bar{1}01)$, $(10\bar{1}0)$, and $(0\bar{1}11)$ lattice planes, which indicates that the crystal is oriented along the $[12\bar{1}3]$ direction of the Gd hcp structure; multislice image

simulation of the Gd hcp structure along the $[\bar{1}2\bar{1}3]$ direction well reproduce the observed image. This is also consistent with previous studies on transition-metal nanorods encapsulated in multiwall CNTs with large diameters, which possess a close-packed structure identical to the correspond-

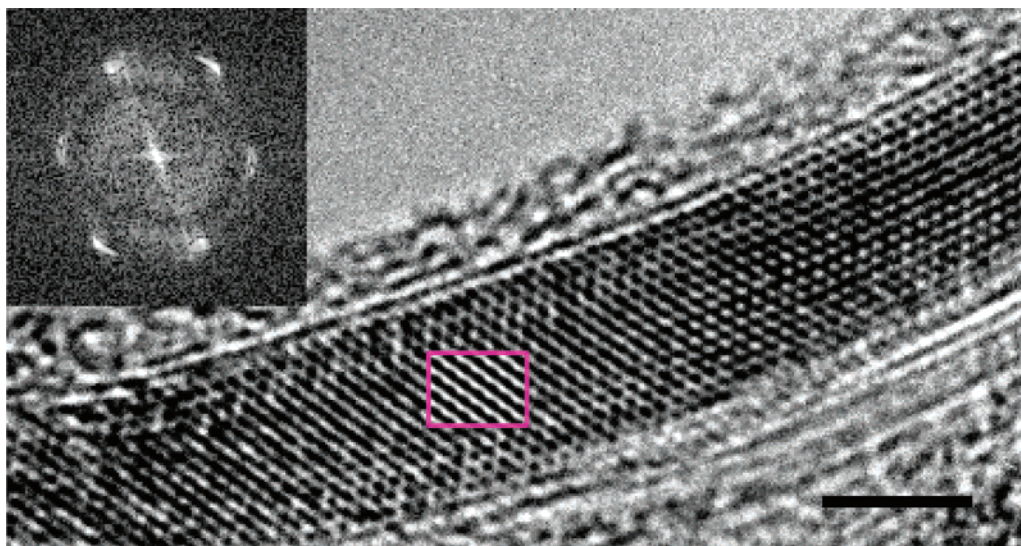


Figure 6. Observed HRTEM image of a one-dimensional (1D) segment of Gd close-packed (hcp) structure formed in CNTs (diameter = 5 nm); the HRTEM image surrounded by a pink square represents a simulated image of a bulk Gd hcp structure along the $[1\bar{2}13]$ direction. Inset shows the fast Fourier transformation (FFT) of this image, showing a hexagonal pattern. Scale bar = 2 nm.

ing bulk crystal.^{21,22} These results strongly suggest that the boundary between the structures specific to 1D and to the bulk may be located around 2–4 rows of atom nanowires.

Using a nano-template reaction developed in this study, we are able to fabricate various types of metal nanowires that are specific to the 1D space of CNTs and are 1D segments of bulk crystals. This reaction, in principle, can be applied to various metallofullerene peapods. Therefore, we can control the number of atoms that comprise the nanowires; the length of nanowire can be doubled and tripled when di- and tri-metallofullerenes are used as starting materials (i.e., peapods). Moreover, alloy nanowires can be synthesized using a mixture of different types of metallofullerenes. These various nanowires are stable because of the presence of the surrounding carbon walls, so that they can easily be individually dispersed in solution and be attached directly to electrodes and fabricated to nanodevices. The present nano-template reaction, using the high-temperature annealing of metallofullerene nanopeapods, will provide a new field in the fabrication of low-dimensional metal-nanowires, nanomaterials, and, thus, nanoelectronics.

Acknowledgment. This work has been supported by the JST CREST Program for Novel Carbon Nanotube Materials and partially supported by the Grant-in-Aid for Scientific Research A (No. 19205003) of MEXT, Japan. We thank H. Okimoto and Dr. Y. Ito for assistance in the synthesis and characterization of the Gd-metallofullerenes.

Supporting Information Available: Figure showing the X-ray diffraction (XRD) pattern of pristine single-wall carbon nanotubes, Gd-peapods, and Gd-peapods after 12 h (Figure S1). Figure showing the structure model of Gd-carbide nanowires encapsulated in CNTs, and the simulated image produced by the multislice method (Figure S2). (PDF) This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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NL073070D