Thin single-wall BN-nanotubes formed inside carbon nanotubes

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We report a high yield synthesis of single-wall boron nitride nanotubes (SWBNNTs) inside single-wall carbon nanotubes (SWCNTs), a nano-templated reaction, using ammonia borane complexes (ABC) as a precursor. Transmission electron microscope (TEM), high angle annular dark field (HAADF)-scanning TEM (STEM), electron energy loss spectra (EELS) and high resolution EELS mapping using aberration-corrected TEM system clearly show the formation of thin SWBNNTs inside SWCNTs. We have found that the yield of the SWBNNT formation is high and that the most of ABC molecules decompose and fuse to form the thin BNNTs at a temperature of 1,673 K having a narrow diameter distribution of 0.7 ± 0.1 nm. Optical absorption measurements suggest that the band gap of the thin SWBNNTs is about 6.0 eV, which provide the ideal insulator nanotubes with very small diameters.

Boron nitride nanotubes (BNNTs) are intriguing nanotube materials consisting of hexagonal boron nitride sheets. One of the most important features of BNNTs is that BNNTs possess a large band gap (~6.0 eV) irrespective of the number of walls, diameters and chiralities. In addition, BNNTs are chemically and mechanically stable. Thin single-wall BNNTs (SWBNNTs) can, therefore, widely be used as an ideal nanotube for exploring nanoscience in 1D materials such as chemical vapor deposition, laser ablation, arc-discharge and thermal decomposition of boron and metal nitrate, selective production of thin SWBNNTs has never been realized so far, which is in stark contrast to the presence of the well-established synthesis technique of thin SWCNTs.

Here, we report a novel synthesis method of thin SWBNNTs having an almost uniform diameter distribution of 0.7 ± 0.1 nm. Our strategy to synthesize thin BNNTs is to incorporate the so-called nano-templated reaction using SWCNTs which we have developed during the past decade. The present high yield preparation of BNNTs using the nano-templated reaction is schematically shown in Figure 1. In this reaction, precursor molecules containing boron and nitrogen are encapsulated first in SWCNTs followed by a thermal decomposition/fusion reaction inside the SWCNTs. The key idea here is to use a 1D array of ammonia borane complexes (ABC) molecules as a reactant, and a confined space of SWCNTs as a template for expecting the SWCNTs accelerate the formation of SWBNNTs due to their structural affinity which is confirmed in the pioneering work on multi-wall boron nitride and carbon hybrid nanotubes. These ideas lead to selective formation of thin BNNTs that have been difficult to synthesize in normal bulk scale reaction.
Results

Encapsulation of ABC molecules in SWCNTs. We used arc-grown SWCNTs having a diameter distribution of 1.4 ± 0.1 nm as a template to synthesize thin SWBNNTs. The uniform diameter distribution of SWCNT-templates is essential to realize a diameter selective synthesis of BNNTs; we can expect the thin SWBNNTs with typical diameter of 0.7 ± 0.1 nm using such SWCNTs. The encapsulation of ABC into SWCNTs was performed according to the previously reported gas phase process. After the encapsulation of ABC molecules, ends of SWCNTs were capped by C60 molecules in order for ABC not to escape from SWCNTs in the ensuing process. The sample was then washed with deionized water for 10 hours to remove surface-attached ABC molecules.

Figure 2a shows a low-magnification transmission electron microscope (TEM) image of ABC@SWCNTs. As clearly seen, the surface of SWCNTs is very clean showing an almost complete removal of residual ABC on the nanotube surface. High-magnification images in Figs. 2a and b show that short linear contrasts are observed along the SWCNTs axis. Electron energy loss spectra (EELS) obtained in the area presented as an inset of Figure 2d shows the presence of strong peaks at 197, 284 and 400 eV that are assigned to K-edge absorption of boron, carbon and nitrogen, respectively (Fig. 2d). The atomic ratio calculated from the background subtracted EELS spectrum (shown as red spectra in Fig. 2d) is B : C : N = 10 : 81 : 9. The ideal atomic ratio calculated assuming a closed packing structure of ABC molecules in (14, 7) SWCNTs (the structure is shown in supplementary Fig. S2) is B : C : N = 8 : 84 : 8 which well reproduces the observed atomic ratio. On the basis of these results, we conclude that the observed short linear contrasts in the SWCNTs should arise from encapsulated ABC molecules and that the filling yield of ABC molecules is very high.

Nano-templated reaction and structure characterization. ABC@SWCNTs was annealed at 1673 K for 3 days in vacuo; hereafter we refer to the annealed ABC@SWCNTs as a-ABC@SWCNTs. Figures 3a, b and c show TEM images of the a-ABC@SWCNTs. The low-magnification TEM image (Fig. 3a) shows that the surface of the sample is clean without any residual surface attached ABC molecules after the annealing process. Figures 3b and 3c are typical high-magnification TEM images of the a-ABC@SWCNTs, where the inner tube formation is clearly confirmed. Figure 3d is the corresponding EELS spectrum from isolated a-ABC@SWCNT (shown in the inset of Fig. 3d), indicating the presence of signals arising from B, C and N K-edges. The EELS spectra shows several peaks that are assigned to π*, σ* and fine structures. The observed conspicuous spectral shape of π* and σ* peaks in boron and carbon K-edge signals is characteristic to sp2 bonding of hexagonal boron nitride and graphene sheets. The ratio of integrated intensities of π* (Iπ*) and σ* (Iσ*) at the Boron K-edge (189–194 eV and 197–207 eV, respectively) represents the bonding environment of boron; the ratio of Iπ*/Iσ* increases as sp2 bonding character increases. The observed Iπ*/Iσ* of a-ABC@SWCNT and ABC@SWCNT is 0.36 and 0.32, respectively, which is consistent with the idea that ABC molecules decompose and fuse to form BNNTs inside SWCNTs. Furthermore, the observed atomic ratio of B, C and N is found to

Figure 1 | Schematic images of the nano-templated reaction for the synthesis of thin SWBNNTs using internal nano-space of SWCNTs.
Cap-opened single-wall carbon nanotube (SWCNT, left) is considered as a nano-scale container, and ammonia borane complexes (ABC) are introduced into them to form ABC encapsulated SWCNT (ABC@SWCNT, center). Then, the ABC@SWCNT is annealed at high-temperature under the vacuum to form single-wall boron nitride nanotube (SWBNNT) structure inside SWCNT (SWBNNT@SWCNT, right). B and N atoms are illustrated as pink and purple spheres, respectively.

Figure 2 | TEM images and EELS spectrum of ABC@SWCNTs. (a) Low magnification TEM image of ABC@SWCNTs. No any impurities can be confirmed on the surface of the sample. (b), (c) High magnification TEM images of ABC@SWCNTs. Something amorphous like structures can be confirmed inside SWCNTs. (d) EELS spectrum of ABC@SWCNTs taken at inset region. Green filled spectrum, black dashed line, and red solid line correspond to the original spectrum, background comes from Zero-loss or plasmon peaks, and the background subtracted data from the original spectrum, respectively.
be 14 : 71 : 15 which is comparable to an expected atomic ratio of B : C : N = 17 : 66 : 17; to calculate the expected atomic ratio, we employ (6,5) SWBNNT@(14,7) SWCNT as a typical product having inner and outer diameters of 0.76 and 1.45 nm, respectively (the diameters were calculated using C-C distance of 1.42 Å and B-N distance of 1.44 Å). In addition to the characteristic π* and σ* peaks, a new peaks arising from π plasmon of BNNTs is observed at energy loss of 7.0 eV in an EELS spectrum of a-ABC@SWCNT (supplementary Fig. S3). These results strongly support a successful fabrication of SWBNNT inside SWCNTs (i.e., SWBNNT@SWCNTs).

To investigate the structure of a-ABC@SWCNT in detail, we performed high magnification TEM observation. Figure 4a is a high magnification TEM image of the sample, where lattice fringes arising from the atomic structure of the specimen are visible. The observed lattice image is similar to that of the moiré patterns usually observed in double wall CNTs⁴⁹,⁵⁰, indicating that a tubular structure possessing honeycomb network is formed inside SWCNT; the diameters of the outer and inner tube are determined to be 1.45 and 0.80 nm, respectively. The observed lattice image and diameter are consistent with the formation of a double-wall nanotube with chiralities of (6,5) and (12,10) for the inner BN and outer carbon nanotubes, respectively (supplementary Fig. S4). A multi-slice-based TEM image simulation of (6,5) BNNT@ (12,10) CNTs well reproduce the observed image (Figs. 4a and b), which strongly supports the formation of thin SWBNNTs in SWCNTs. To further obtain information on the detailed structure of BNNT@CNT, we conducted linear EELS mapping along the line perpendicular to the nanotube axis.

Figures 5a and b show, respectively, TEM and high angle annular dark field (HAADF)-Scanning TEM (STEM) images of annealed ABC@SWCNT taken at the same location, where an inner tube can be clearly observed. The diameters of the inner and outer tube are determined to be 0.77 and 1.45 nm, respectively, judging from the TEM image. An EELS mapping along the arrow shown in Fig. 5b is presented in Fig. 5c, consisting of 116 EELS spectra with a spatial step of 0.3 nm. In the EELS map, B, C and N K-edge spectra are clearly observed around 190, 290 and 400 eV, respectively. Figure 5d provides line profiles of the EELS map at the energy of 191.0, 284.6 and 405.4 eV corresponding to 1s → π* transitions of B, C and N K-edge EELS spectra, respectively. Figures 5d top, middle and bottom, respectively, show the line profiles of B, C and N after a subtraction of background due to the tails of zero loss and plasmon loss peaks. The observed line profiles of B and N are narrower than that of C, indicating that the inner tube is boron nitride and the outer tube is carbon. Two peaks observed at 1.14 and 2.58 nm in C-distribution correspond to side wall of outer SWCNTs, consistent with the diameter of outer tube determined from the TEM image. Widths of B- and N- line profiles are ca. 0.7 nm, which is also in good agreement with the diameter of the inner tube determined from the TEM image. Furthermore, the interlayer distance between the inner and outer tube determined from the liner profile is...
0.33 – 0.36 nm, which are similar to the typical interlayer distance of double-wall CNTs of 0.335 nm. All these results jointly show that thin BNNT nanotubes are formed in high yield inside the template made of SWCNTs.

**Discussion**

As shown above, the filling yield of ABC molecules in ABC@SWCNT is high; the atomic ratio of B, C and N is close to that of closed packing structure of ABC molecules in SWCNTs. However, the atomic ratio of B (or N) to C in an ideal SWBNNT@SWCNT should be 2.7 times higher than that of the closely packed ABC@SWCNT, suggesting that the number of boron and nitrogen atoms in ABC@SWCNT is insufficient to form a perfect SWBNNT having the same tube length as that of the SWCNT template. There should be, thus, single-wall area in a SWBNT@SWCNT double-wall nanotube, which has actually been observed in many TEM images.

Assuming that all ABC molecules react to form BNNTs inside SWCNTs, the theoretical ratio between double-wall and single-wall nanotube regions in the SWBNNT@SWCNTs is calculated to be $37 : 67$. To obtain experimental information on the ratio and diameter distribution, we have performed a TEM-based statistical analysis using 102 isolated nanotubes; partially filled nanotubes were excluded from this analysis. Figure 6 shows a histogram showing the diameter distribution of SWCNTs (Fig. 6a, blue), inner SWBNNTs (Fig. 6b, green) and outer SWCNTs (Fig. 6b, red). The observed ratio of double-wall nanotubes to single-wall nanotubes is found to be $54 : 47$, which is comparable to the theoretical ratio of double-wall and single-wall regions; the probability of finding double-wall and single-wall nanotubes is assumed to be proportional to the theoretical ratio between double-wall and single-wall regions. Considering the statistical error in the TEM-based sampling analysis, we conclude that the most of ABC molecules react to form BNNTs inside SWCNTs. The present nano-templated reaction proceeds very efficiently, which leads to the first production of thin SWBNNT in bulk scale; 0.5 mg of SWCNTs was typically used to obtain ca. 0.2 mg of the thin SWBNNTs (supplementary Fig. S5).

One of the most important aspects of the present reaction is that volatile ABC molecules remain inside SWCNTs to react each other under vacuum at high-temperature conditions. The main reason for this highly efficient formation reaction of BNNTs is that the end-capping using C$_{60}$ molecules prevents the encapsulated ABC molecules from escaping during the fusion reaction under vacuum high-temperature condition. The smallest diameter of SWBNNT formed in this reaction is 0.43 nm, which is close to the diameter of the thinnest stable SWBNNT; the ab-initio density functional theory (DFT) calculation on BNNTs and BN stripes shows that a (5,0) BNNT with a diameter of 0.4 nm is the thinnest stable BNNT$^{27}$. BNNTs is found to possess the diameter of $0.7 \pm 0.1$ nm, and, to the best of our knowledge, this is the thinnest SWBNNT synthesized in bulk scale so far.

The DFT study also predicts that the band gap of BNNTs does not vary depending on diameter and chirality (the predicted LDA band gap is about 4 eV) when a diameter of BNNT is larger than 0.6 nm$^{26}$. It is well known that the LDA calculation normally underestimates the band gap, which is predicted to be $5.5$ eV after the quasiparticle correction$^{26}$. The previous experimental studies have shown that thick BNNTs have the band gap of 6 eV$^{33}$, which is in good agreement with the theoretical calculation. Thin BNNTs synthesized in this study have an average diameter of 0.7 nm, and therefore, the thin BNNTs are also expected to possess a band gap close to 6 eV. Figure 7 shows absorption spectra of SWBNNT@SWCNT and SWCNT, where the intensity of absorption is normalized at 280 nm; the
sample was dispersed in 1,2-dichloroethane and the dispersion solution was sprayed onto the quartz substrate to obtain the absorption spectra. Apparently, in the absorption spectra of SWBNNT@SWCNT, a new peak appears at 6.1 eV that can be assigned to transitions due to π-π* bands of the BNNTs, indicating that thin BNNTs have a band gap of around 6 eV, which is in good agreement with the theoretical prediction\textsuperscript{26,27}. Raman spectra (supplementary Fig. S6) shows that the interaction between SWCNTs and SWBNNTs is small, which is consistent with the large band gap of BNNTs.

In summary, we have synthesized thin SWBNNTs with a narrow diameter distribution of 0.7 ± 0.1 nm using internal nanospace of SWCNTs as a nano-scale reactor. TEM, HAADF-STEM, EELS and EELS mapping using an aberration-corrected TEM have clearly shown the successful formation of SWBNNTs inside SWCNTs. In particular, the high resolution EELS mapping have proven to be a powerful technique to characterize the structure of the sample. Optical absorption measurements reveal that the band gap of the SWBNNTs is about 6 eV; The SWBNNTs is an ideal nanoscale template with a thin inter-cylinder space of 0.4 nm having stable structures, which is transparent to visible light. The nano-templated reaction used in this study can provide novel nanostructures that have been difficult to be synthesized by the conventional bulk-scale reactions. The current finding provides brand-new fields for further understanding on 1D nanosystems.

**Methods**

**Preparation of samples.** SWCNTs have been purchased from Meijo Nano Carbon Co. Ltd. and used after purification of heating at 1,473 K for 2 days under high vacuum (10\textsuperscript{−5} Torr). The purified SWCNTs were heated under dry airflow at 873 K for 30 min in order to remove the end-cap. ABC (97%, Sigma-Aldrich, Inc.) was annealed at 393 K for 12 hours to remove impurities. The annealed ABC was, then, sealed into a glass tube with cap-opened SWCNTs under high vacuum (10\textsuperscript{−6} Torr) followed by a heat treatment at 823 K for 3 days. After capped with those ends with C\textsubscript{60} molecules and washed with deionized water for 10 hours, ABC encapsulated SWCNTs (ABC@SWCNTs) were annealed at 1673 K for 3 days. In addition to ABC molecules, 2,4,6-Trichloroborazine (B\textsubscript{3}Cl\textsubscript{3}H\textsubscript{3}N\textsubscript{3}; Sigma-Aldrich, Inc.) was also used as a precursor (supplementary Fig. S7).

**Characterizations.** For structural characterization of obtained samples, TEM observations were performed using a high-resolution field-emission gun TEM (JEOL JEM-2100F).
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**Acknowledgements**

This work has been supported by the Grant-in-Aids for Specific Area Research (Grant No. 19080408) on Carbon Nanotube Nano-Electronics and for Scientific Research S (No. 22225001) of MEXT of Japan. R.N. thanks the Japan Society for the Promotion of Science for a Research Fellowship for Young Scientists. We thank Dr. Takashi Yamaguchi (No. 22225001) of MEXT of Japan. R.N. thanks the Japan Society for the Promotion of Science for a Research Fellowship for Young Scientists. We thank Dr. Takashi Yamaguchi for fruitful discussions on the synthesis of BNNTs.

**Author contributions**

R.N. performed the synthesis and spectroscopic characterization of the samples. R.N., R.K. and J.H.W. performed TEM experiments. R.N., R.K. and H.S. designed the study and co-wrote the paper. All authors discussed the results.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Nakashima, R. et al. Thin single-wall BN nanotubes formed inside carbon nanotubes. *Sci. Rep.* 3, 1385; DOI:10.1038/srep01385 (2013).