Thin single-wall BN-nanotubes formed inside carbon nanotubes

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Supplementary Figures

Figure S1 | Band structures of Yb atomic wire encapsulated (10,0) nanotube.
Optimized unit cell structures and corresponding band structures of (a) (10,0)SWBNNT, (b) Yb@(10,0) SWBNNT, and (c) Yb@(10,0) SWCNT. In these calculations, density functional theory (DFT)-based band structure calculations were applied with the generalized gradient approximation (GGA) and a plane-wave basis set with a cutoff energy of 400 eV. Interaction between the ionic cores and valence electrons was treated by the projector augmented-wave (PAW) method in the implementation of Kresse and Joubert. Structure relaxation was carried out using 40 irreducible \( k \) points with a coordinate \((0, 0, n/80)\times(2\pi/T)\) \((n=0,1,\ldots 30)\), where \(T\) is the translational period. For the band-structure calculation, 100 irreducible \( k \) points were used. The nanotubes were placed on a rectangular grid separated by 1.5 nm vacuum, which results in negligible intertube interactions. Gaussian smearing with the parameter \(\sigma = 0.01\) eV was applied to broaden the one-electron eigenenergies. Fermi level was set to 0 eV. All calculations were carried out using the Vienna ab initio simulation package (VASP).
As seen in (a), calculated band gap of BNNTs is ca. 4 eV, which is consistent to previous works. In the case of Yb@(10,0) SWBNNT ((b)), $s$ and $f$ state of encapsulated metal atoms locate between the top of valence band and the bottom of conduction band due to the large band gap; as a result, the $s$ state of Yb atomic wires is identical to that of isolated freestanding Yb atomic wire. In contrast, in the case of Yb@(10,0)SWCNTs, there is a significant overlap between the $s$ state of Yb atomic wires and $\pi$ states of SWCNTs, which leads to charge transfer from Yb atomic wire to SWCNTs. This system is, therefore, expected to show electronic properties that are different from those of isolated freestanding Yb atomic wire.
Figure S2  |  Structure models of ABC molecules and (6,5)SWBNNT encapsulated inside (14,7)SWCNT.

Schematic representation of packing structure of ABC molecules in (14,7) SWCNT depicted as (a) ball-and-stick model and (b) space-filling (CPK) model.  (c) Close-up image of a CPK representation of the packing structure of ABC molecules inside the SWCNT.  (d) Structure model of ABCs@(14,7)SWCNT shown from the direction perpendicular to the nanotube axis.  Based on this structure model, the atomic ratio was calculated to be B:C:N = 8:84:8.  (e) Structure model of (6,5)SWBNNT@(14,7)SWCNT shown from the direction perpendicular to the tube axis. Using this structure model, the expected atomic ratio was calculated to be B:C:N = 17:66:17.
Figure S3 | Surface $\pi$-plasmon of SWBNNT@SWCNTs.

EELS spectra of SWCNTs (black) and SWBNNT@SWCNTs (red) near Zero-loss energy region. The inset shows magnified spectra, where the plasmon loss region is highlighted. Peaks observed at 5.9 and 22 eV in the SWCNTs spectrum correspond to the $\pi$ plasmon and the excitation of plasma oscillation of all valence electrons ($\pi+\sigma$ plasmon), respectively. In the case of SWBNNT@SWCNTs, new peak appears at 7.0 eV, which corresponds to the $\pi$ plasmon of BNNT whose diameter is less than 8 nm$^4$. 
To determine the chirality of SWBNNT@SWCNT shown in Fig. 4(a), we performed a systematic simulation of TEM images and electron diffraction patterns. (a) shows fast Fourier transformation (FFT) image of TEM image of the SWBNNT@SWCNTs, and Fourier filtered image of the TEM image. In the Fourier filtering, we used the red framed region shown in the FFT image. Based on the TEM and FFT images, the diameters and chiral angles of the SWBNNT@SWCNT were estimated. Considering the diameters (outer tube is 1.45 nm, and inner tube 0.80 nm) and chiral angle (outer tube is 27 deg., and inner tube is 25 deg.), the possible chiralities of SWBNNT@SWCNT were selected. (b)–(f) Simulated electron diffraction patterns and TEM images of (b) (6,5)SWBNNT @ (12,10)SWCNT, (c) (7,5)SWBNNT @ (12,10)SWCNT, (d) (6,6)SWBNNT @ (12,10)SWCNT, (e) (6,5)SWBNNT @ (11,10)SWCNT, and (f) (6,5)SWBNNT @ (12,9)SWCNT. After the careful comparison between the observed and simulated images, (6,5)SWBNNT @ (12,10)SWCNT was selected as the most possible structure of the SWBNNT@SWCNT.
Figure S5 | Thermal gravimetric analysis of SWBNNT@SWCNTs.

(a) Weight loss (red solid line) and the first derivative (blue dashed line) of SWBNNT@SWCNTs as a function of temperature measured with thermal gravimetric analysis (TGA; Shimadzu, TGA-50). The measurement was performed from room temperature to 1000 °C with a heating rate of 2 °C/min. in a dry air flow of 100 cm³/min. The TGA curve shows an abrupt drop at 500-700 °C, which can be assigned to an oxidation of outer SWCNT. In this TGA measurement, a 0.73 mg sample was used and a 0.28 mg (about 38 %) residue was obtained as a transparent glassy material (B₂O₃) after the measurement. To investigate the observed abrupt drop of the TGA curve, TEM and EELS measurements were performed. (b) and (c) show HRTEM image and EELS spectrum of the gray-white material obtained after a thermal oxidation.
of SWBNNT@SWCNTs at 700 °C, respectively. As clearly seen in the EELS spectrum, carbon K-edge EELS peak disappeared, which means that SWCNT was completely oxidized and removed at 700 °C. In contrast, Boron and nitrogen K-edge peaks remained (atomic ration of B:N is 47:53) after the thermal oxidation. TEM image shows that tubular structure of SWBNNTs collapsed to form disordered BN structure during the oxidation process. These results show that the observed abrupt drop of the TGA curve arises from a thermal oxidation of outer SWCNTs.
Figure S6  |  Raman spectroscopy of SWBNNT@SWCNTs.

Raman spectra of SWCNTs (black), ABC@SWCNTs (blue) and SWBNNT@SWCNTs (red) measured at (a) 488 nm and (b) 633 nm excitation wavelengths using HR-800 spectrometer (Horiba Jobin Yvon). (c) and (d) are magnified spectra at the region of radial breathing mode (RBM, left) and $E_{2g}$ mode (G-band, right) of (a) and (b), respectively. All spectra were normalized at the peak of G-band. Whereas RBM peaks coming from SWCNTs were decreased after the encapsulation of ABCs and SWBNNTs, the interaction between the surrounding SWCNTs and inner materials can be estimated as little or nothing because significantly peak shifts could not be observed in the RBM and G-band regions. On the other hand, peaks at 1340 cm$^{-1}$ (D-band) of SWCNTs were increased after the SWBNNT syntheses inside them. These increasing may be caused by the etching of SWCNTs with hydrogen which was generated from annealing of ABC molecules because the D-band peak depends on the defects of SWCNTs. Peaks coming from SWBNNTs could not be confirmed in this time, which can be estimated as the peaks were submerged by those of SWCNTs.
Figure S7 | Encapsulation of 2,4,6-Trichloroborazine (TCB) into SWCNTs.
(a) TEM image and (b) EELS spectrum of TCB@SWCNTs; the encapsulation of TCB was performed with the gas phase reaction at 673 K. Green filled spectrum, black dashed line and red solid line in the EELS spectrum correspond to the original EELS spectrum, the background signal arising from the tail of Zero-loss or plasmon peaks and the background subtracted spectrum, respectively. The red solid spectrum was used to calculate the atomic ratio. Although several contrasts can be seen in SWCNT ((a)), the ratio of B and N are quite low (B:C:N = 3:96:1), which indicates that the filling yield of TCB at 673 K is low.
(c) TEM image, and (d) EELS spectrum of TCB@SWCNTs; the encapsulation was performed with the gas phase reaction at 873 K. In the case of TCB@SWCNTs prepared at 873 K, in addition to contrasts in SWCNTs ((c)), the strong boron K-edge peak was observed ((d)). However, peaks arising from nitrogen K-edge cannot be confirmed (B:C:N = 10:89:1), which indicates that the decomposition of TCB occurs at the encapsulation process. Based on these results, we have decided to give up to use TCB molecules as precursor.
Supplementary References


