Supporting Information

Growth of carbon nanotubes inside boron nitride nanotubes by coalescence of fullerenes: towards the world's smallest co-axial cable

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S1 **Analysis of as-received BNNTs** 2
S2 **Preparation of open BNNTs** 4
S3 **Preparation of C_{60}@BNNT** 7
S4 **Preparation of CNT@BNNT** 9

S1 Analysis of as-received BNNTs

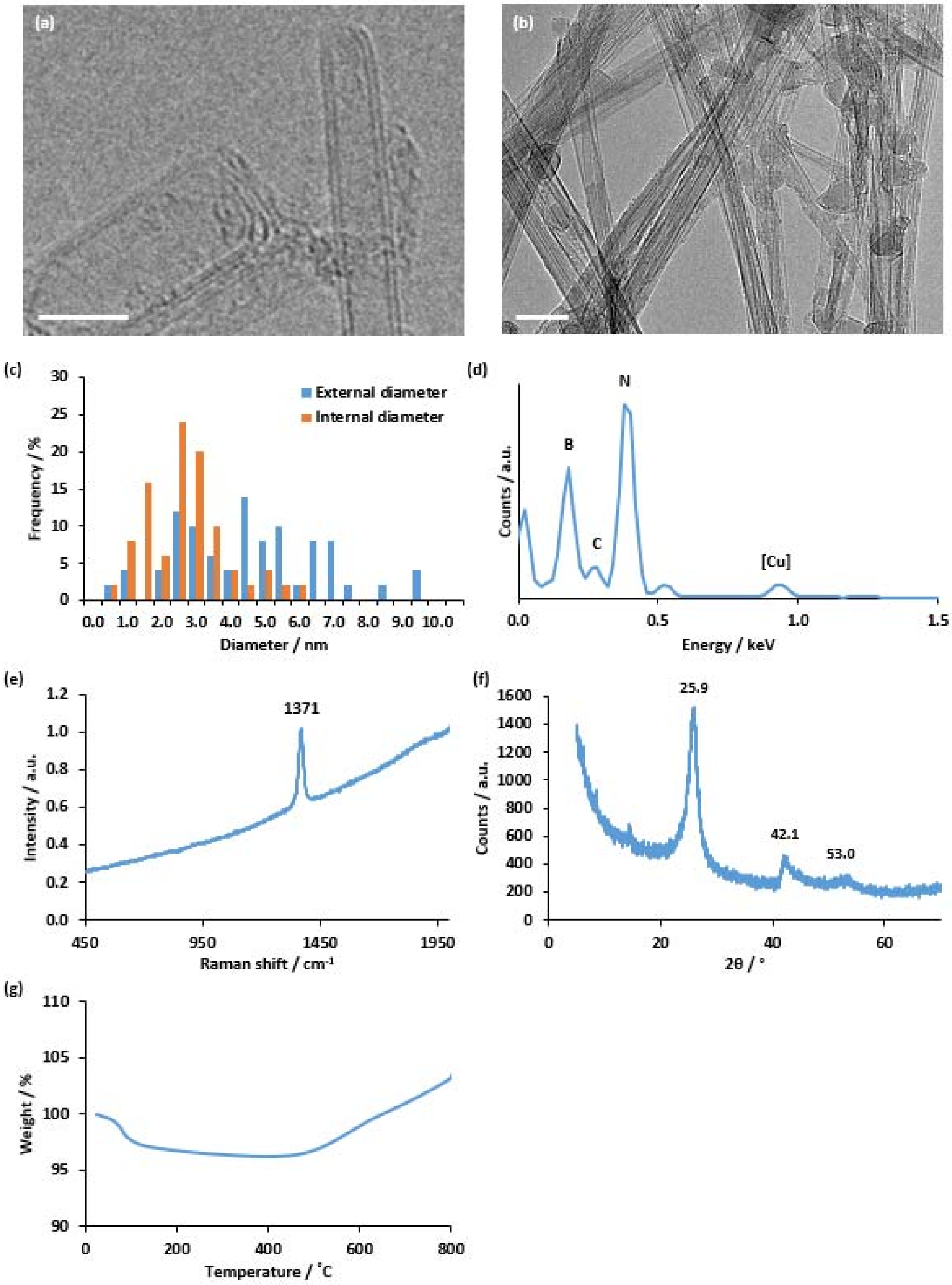

Figure S1. Microscopy, spectroscopy and gravimetric analysis of as-received BNNTs. Transmission electron microscopy (TEM) analysis shows (a) the closed termini of BNNTs (scale bar is 5 nm) and (b) the broad range of BNNT diameters and boron impurities present (scale bar is 20 nm). A measured d-spacing of 0.34 nm is consistent with the (0002) lattice plane in hexagonal boron nitride. (c) Statistical analysis of multiple micrographs reveals that the mean internal and external diameters of BNNTs are 2.45±1.19 and 4.32±2.09 nm respectively, the number of walls range between 1 and 5 (with 2 or 3 the most common) and the mean length is greater than 200 µm. (d) Energy dispersive X-ray (EDX) analysis indicates that the ratio of B:N is 61:39, confirming the presence of elemental boron as an impurity. (e) The Raman spectrum shows the characteristic peak at 1369 cm^{-1} which corresponds to a B-N stretching vibrational mode of E_{2g} symmetry. (f) Powder X-ray diffraction (PXRD) analysis shows peaks at 25.9, 42.1 and 53.0 ^{o} corresponding to the (002), (100) and (004) planes of BNNTs respectively. (g) Thermogravimetric analysis (TGA) highlights the excellent thermal stability of BNNTs in air. The small increase in mass above 500 ^{o}C is caused by oxidation of boron ($B + O_2 \rightarrow B_2O_3$) and boron nitride ($BN + O_2 \rightarrow B_2O_3 + NO + NO_2$) in the presence of atmospheric oxygen.

S2 Preparation of open BNNTs

Method 1: Oxidation in air

As-received BNNTs (3.86 mg) were heated from room temperature to 800 °C at 10 °C min^{-1} in air and then held at 800 °C for 60 min. The initial grey, fluffy BNNTs turned white and brittle after heating. Mass = 4.12 mg.

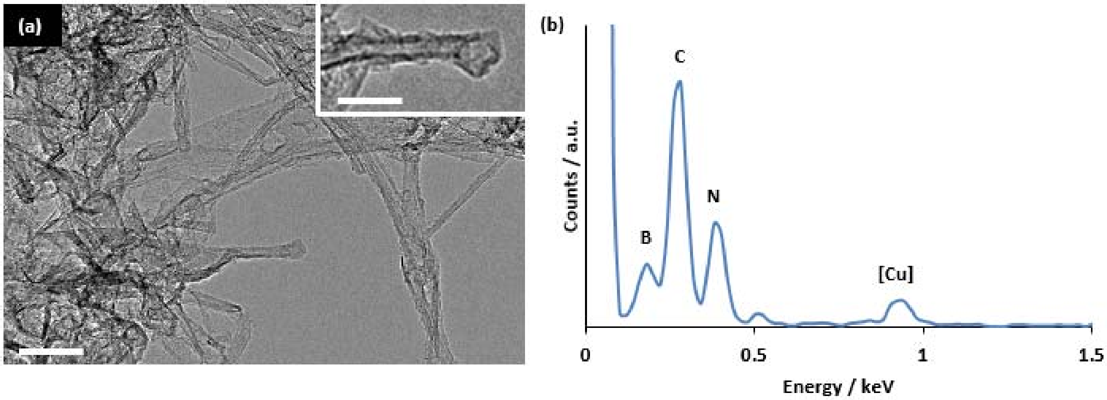

Figure S2. (a) TEM analysis of BNNTs heated to 800 °C in air indicates that the termini remain closed, with no discernible reduction in length observed. Scale bar is 50 nm (inset is 20 nm). (b) EDX analysis shows the ratio of B:N to be 87:13, consistent with the formation of B_2O_3 under these conditions.

Method 2: Ball milling

As-received BNNTs (5.05 mg) were loaded in a hardened steel jar (1.5 mL capacity) equipped with a hardened steel ball (10 mm diameter) and milled (10 Hz, Retsch Mixer Mill MM400) for 90 min at room temperature. Mass = 4.35 mg.

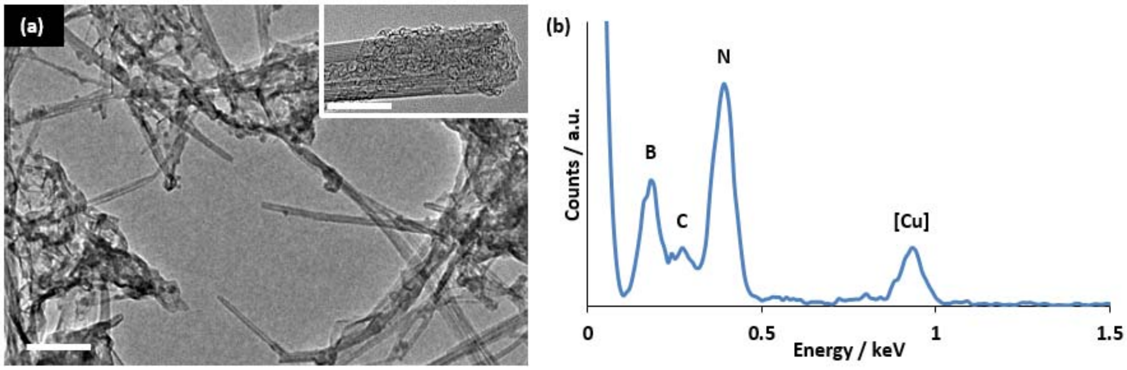

Figure S3. (a) TEM analysis of BNNTs subjected to ball milling indicates that the afforded BNNTs were largely open (80%) and significantly shorter (mean length is 1.98±0.78 μm) than the as-received material. Scale bar is 100 nm (inset is 10 nm). (b) EDX analysis shows the ratio of B:N to be 57:43.

Method 3: Hydrolysis followed by oxidation in air

To as-received BNNTs (100 mg) was added an aqueous solution of ammonium hydroxide (200 mL, 10 % in water) and the suspension homogenised by tip ultrasonication (20 kHz, 130 W Sonics Vibracell CPX150 ultrasonic processor) at room temperature for 4, 10 or 24 hr. Any visible clumps of BNNTs which had not dispersed were discarded. The resultant suspended grey/brown solid was collected by vacuum filtration (0.2 μm PTFE membrane) and washed with deionised water (20 mL). This was further heated at 800 ^{o}C for 1 hr, washed with hot (~90 ^{o}C) deionised water (~500 mL) and collected by vacuum filtration (0.2 μm PTFE membrane). Mass = 52 mg.

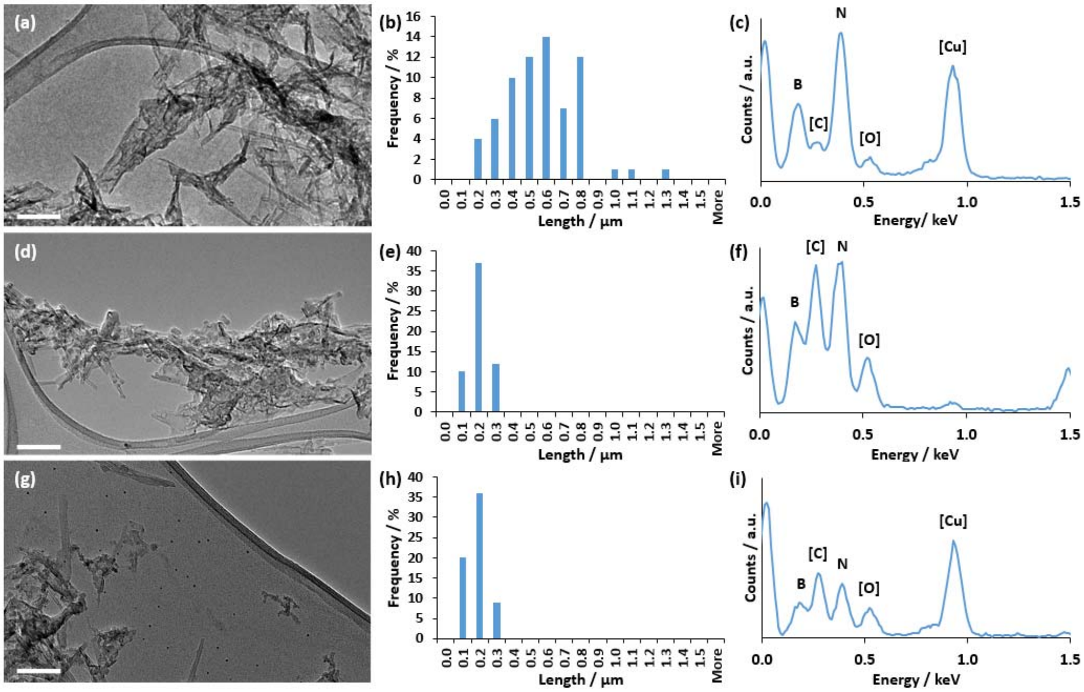

Figure S4. TEM/EDX analysis of BNNTs purified by (a) 4, (d) 10 and (g) 24 hr sonication in aqueous ammonium hydroxide solution, followed by oxidation in air, indicates that this method is effective for the removal of the nanotube endcaps, resulting in a reduction of the mean nanotube length (b, e and h respectively) and removing the boron-containing impurities (c, f and i respectively). As 4 hr sonic treatment is sufficient to open, shorten and purify BNNTs, extended sonication is not required and may facilitate further damage to the nanotube sidewall structure. Scale bars are 100 nm.

S3 Preparation of C_{60}@BNNTs

Open and purified BNNTs (10 mg) and C_{60}-fullerene (10 mg) were sealed under vacuum ($3.2x10^{-5}$ mbar) in a Pyrex tube and heated at 600 ^{o}C for 20 hr. The solid was collected by vacuum filtration (0.2 μm PTFE membrane) and washed extensively with toluene until the filtrate became colourless. Mass = 8.2 mg.

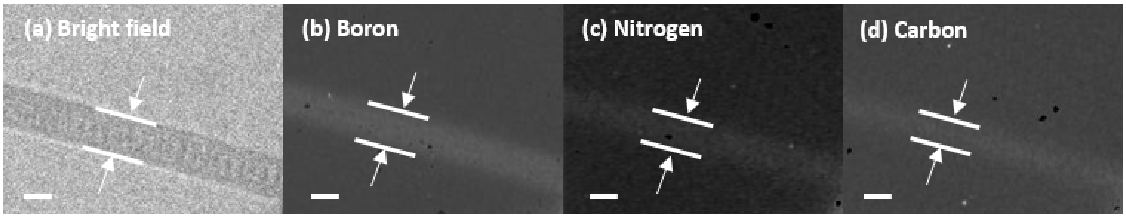

Figure S5. (a) Bright field and (b-d) energy filtered TEM images of a BNNT. The line widths are as follows: bright field=3.3 nm, boron=3.3 nm, nitrogen=3.2 nm and carbon=2.2 nm. This analysis confirms the encapsulation of C_{60} within BNNTs. Scale bars are 2 nm.

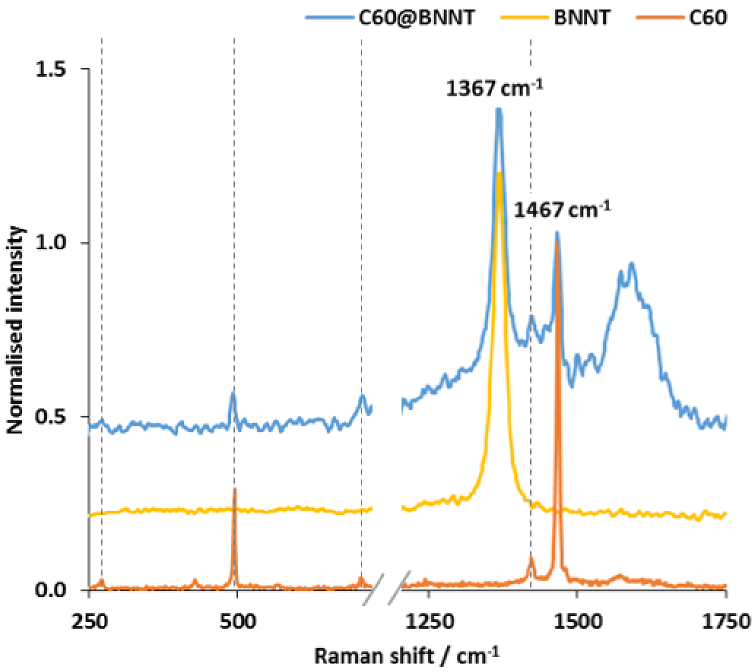

Figure S6. Raman spectra of BNNT, C_{60} and C_{60}@BNNT at room temperature collected using 355 nm excitation (due to extreme luminescence, C_{60}@BNNT can only be measured with UV excitation). The presence of C_{60} is evident in the spectra of the filled tubes.

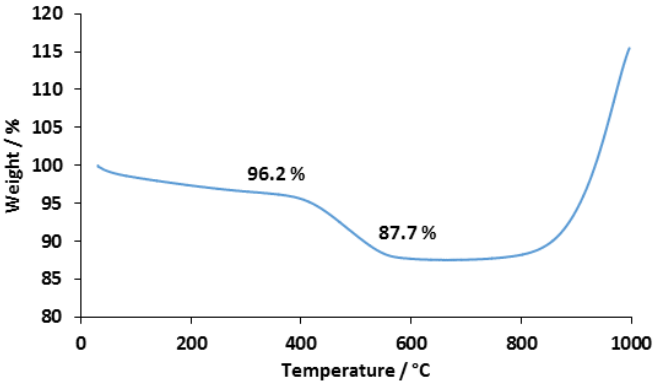

Figure S7. TGA of C_{60}@BNNT in air indicates a weight loss of 8.5 % between 360 and 600 °C consistent with the oxidation of carbon within BNNTs ($C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$).

S4. Preparation of CNT@BNNT

Table S1. Comparison of the methods used to form CNT@BNNT from C_{60}@BNNT.

Method	Conditions	Filling / %	L_{CNT} / nm
1	Heat C_{60}@BNNT at 1200 °C for 6 hr	ca. 25	4.3±2.9
2	Heat C_{60}@BNNT at 1400 °C for 6 hr	ca. 25	4.2±2.5
3	Heat C_{60}@BNNT at 1200 °C for 10 hr	ca. 25	4.5±2.7
4	Heat C_{60}@BNNT at 1200 °C for 6 hr, repeat C_{60} filling then heat C_{60}@BNNT at 1200 °C for 6 hr	> 25	3.8±2.6

Method 1

C_{60}@BNNT (9.0 mg) was sealed under Ar (0.7 bar) in a quartz ampoule and heated at 1200 ^{o}C for 6 hr. Mass = 7.1 mg.

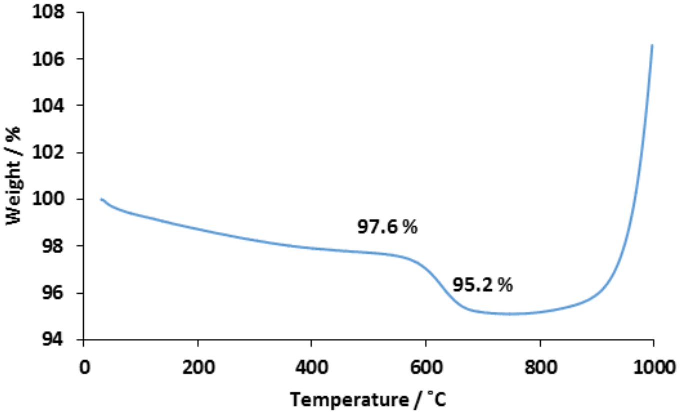

Figure S8. TGA of CNT@BNNT in air indicates a weight loss of 2.4 % between 530 and 700 °C consistent with the oxidation of carbon nanotubes within BNNTs ($C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$). This carbon loading is approximately four times lower than in C_{60}@BNNT, consistent with the loss of C_{60} from the internal channel of BNNT during the high temperature treatment.

Method 2: Higher temperature

C_{60}@BNNT (5.0 mg) was sealed under Ar (0.7 bar) in a quartz ampoule and heated at 1400 ^{o}C for 6 hr. Mass = 4.0 mg.

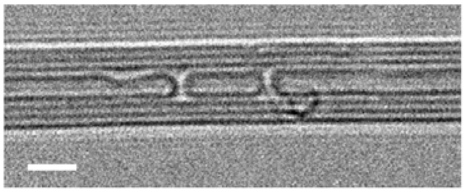

Figure S9. TEM of single-walled carbon nanotubes formed inside a triple-walled BNNT from C_{60}@BNNT when heated at 1400 °C for 6 hr. Scale bar is 2 nm.

Method 3: Increased heating time

C_{60}@BNNT (5.0 mg) was sealed under Ar (0.7 bar) in a quartz ampoule and heated at 1200 °C for 10 hr. Mass = 4.0 mg.

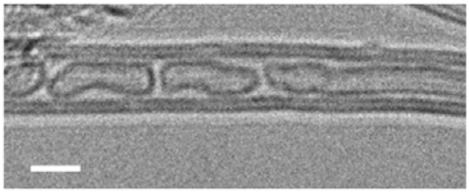

Figure S10. TEM of single-walled carbon nanotubes formed inside a double-walled BNNT from C_{60}@BNNT when heated at 1200 ˚C for 10 hr. Scale bar is 2 nm.

Method 4: Repeated filling

C_{60}@BNNT (5.0 mg) was sealed under Ar (0.7 bar) in a quartz ampoule and heated at 1200 °C for 6 hr. The sample (3.0 mg) was then sealed with C_{60}-fullerene (3.0 mg) in a quartz tube under vacuum (10^{-5} mbar) and heated at 600˚C for 16 hr, then sealed under Ar (0.7 bar) at 1200 °C for 6 hr. Mass = 2.0 mg.

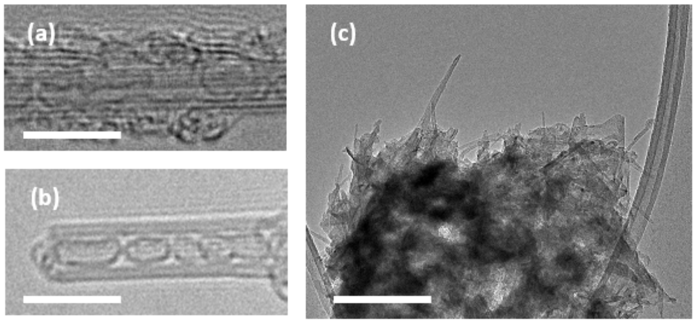

Figure S11. TEM of single-walled carbon nanotubes formed inside BNNTs using method 4. The newly formed carbon nanotubes (a and b) are of similar length to those produced in the original single filling procedure. The additional carbon added appears to coat the exterior of BNNTs as an amorphous layer (c). Scale bars are 5 nm.

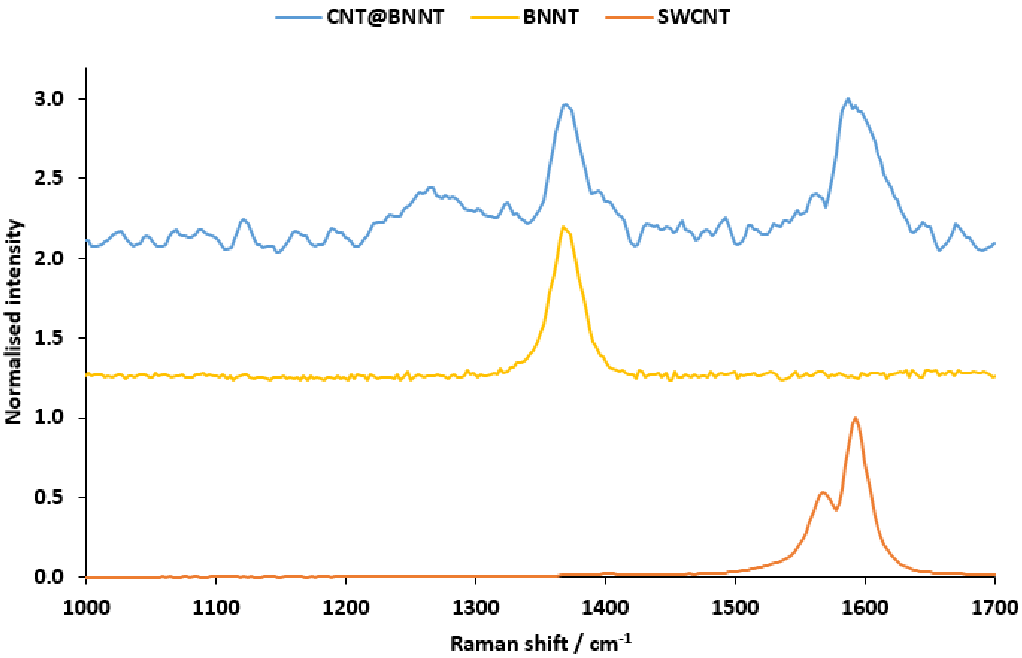

Figure S12. Raman spectra of BNNT and C_{60}@BNNT annealed at 1200 °C (forming CNT@BNNT) collected using 355 nm excitation. The two new bands in the annealed sample are assigned to carbon nanotube modes: the D mode – a ring breathing vibrational mode of A_{1g} symmetry in a disordered graphitic lattice that is activated by the presence of a defect – at around 1300 cm^{-1} and the G mode – a stretching mode of E_{2g} symmetry, present in all graphitic nanostructures (see for example the spectrum of SWCNT) – at around 1600 cm^{-1}. The presence and high intensity of the D band (relative to the G band) in the Raman spectrum of CNT@BNNT indicates a high level of structural disorder within the graphitic lattice that comprises the internal carbon nanotube.