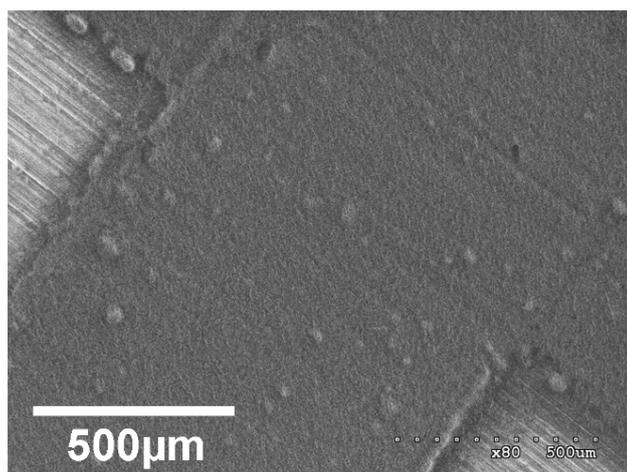


# Supplementary Information

## 1. Mask coating

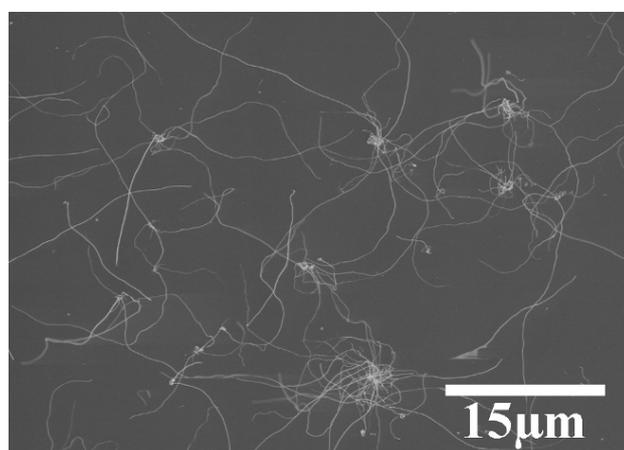
Fig. S1 shows the SEM image of a patterned BNNT film on a steel substrate created by mask coating. In this process, B ink was brushed on the substrate through a tape mask, and then the substrate was annealed at 1100 °C for 0.5 h in  $N_2+15\%H_2$  gas.



**Figure S1.** SEM image of a BNNT film pattern created by B ink mask coating.

## 2. Low density BNNT coating by spraying B ink

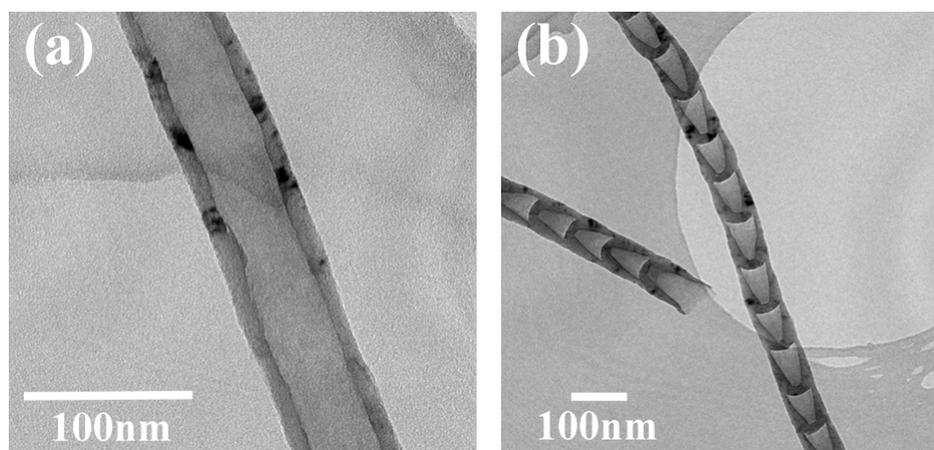
Fig. S2 shows a low density or sparse coating of BNNTs on a  $SiO_2/Si$  substrate by spraying B ink (30 mg of B in 0.02 M  $Fe(NO_3)_3$ ). The nanotubes were produced in  $N_2+15\%H_2$  gas at 1100 °C for 0.5 h.



**Figure S2.** SEM image of low density or sparsity of BNNTs on  $SiO_2/Si$  substrate by spraying.  
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### 3. The structure of BNNTs produced in $N_2+15\%H_2$ gas

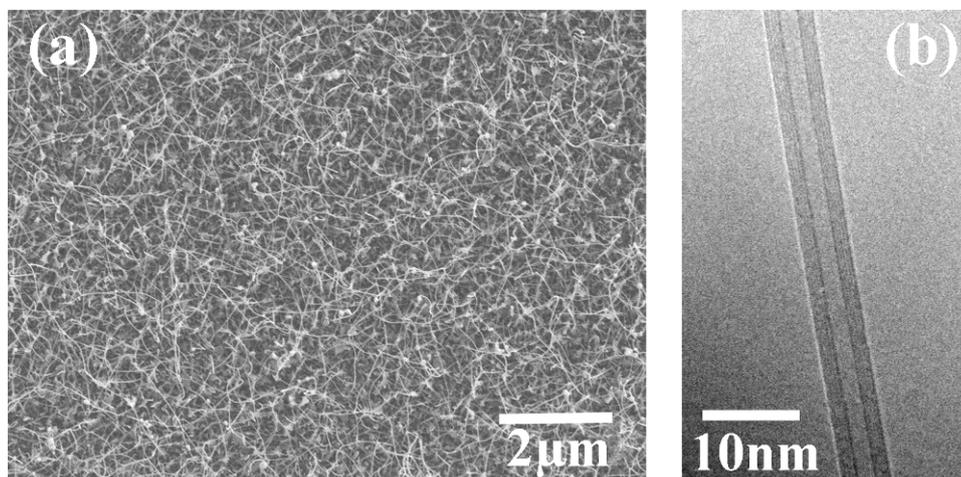
The BNNTs produced in  $N_2+15\%H_2$  atmosphere can have a multi-walled cylindrical or a bamboo-like structure. TEM images in Fig. S3a and S3b show the two BNNT structures produced using  $N_2+15\%H_2$  gas at 1100 °C. The different structures are probably caused by the different migration or precipitation rates of BN in the catalyst.



**Figure S3.** (a) TEM image of a BNNT with cylindrical structure; (b) TEM image of two BNNTs with bamboo-like structure.

### 4. BNNT film produced in $NH_3$ gas at 1300 °C

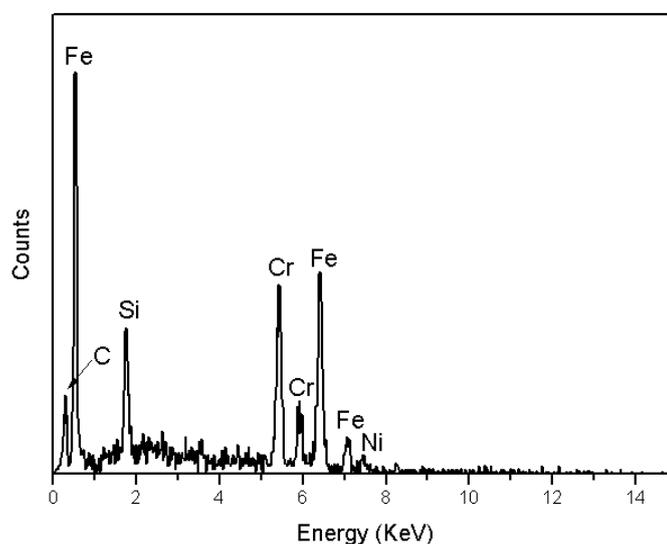
Small diameter cylindrical BNNTs with good crystallinity can be synthesized by annealing the B ink coating in  $NH_3$  gas at 1300 °C. Fig. S4a shows a SEM image of such BNNTs coated on a  $SiO_2/Si$  substrate, and Fig. S4b shows a typical TEM image of a small diameter cylindrical BNNT. The B particles produced using the same milling parameters can give rise to different structure and size of BNNTs if different annealing conditions and atmospheres are used. This suggests that the structure and size of BNNTs are much more dependent on the annealing conditions and reactive gas used rather than the size of milled B particles. The different nitriding reaction rate during  $NH_3$  annealing gives rise to the formation of finer nanotubes.



**Figure S4.** (a) SEM image of BNNTs with small diameters and a cylindrical structure grown on SiO<sub>2</sub>/Si substrate; (b) a corresponding TEM image of a BNNT in the film.

### 5. EDS results of the metal particles shown in Fig.4b

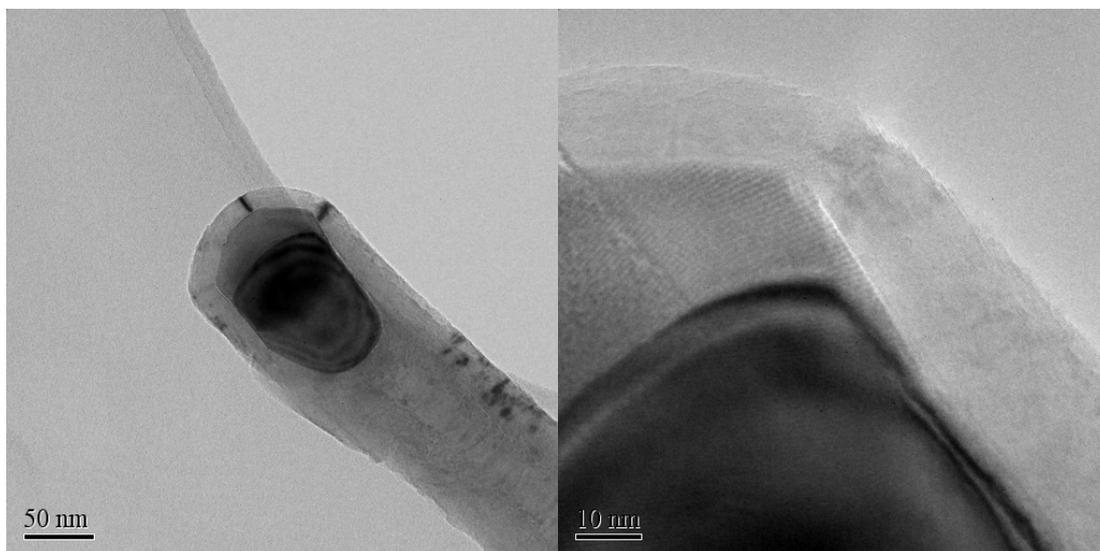
EDS spectrum showing the elemental composition of the metal catalyst shown in Fig. 4b. This sample used the B ink (31.3 mg mL<sup>-1</sup> of B in 0.04 M Fe(NO<sub>3</sub>)<sub>3</sub> ethanol). The C and Si signal may partly come from contamination.



**Figure S5.** EDS spectrum of the metal catalyst shown in Fig. 4b.

### 6. TEM image showing tip growth

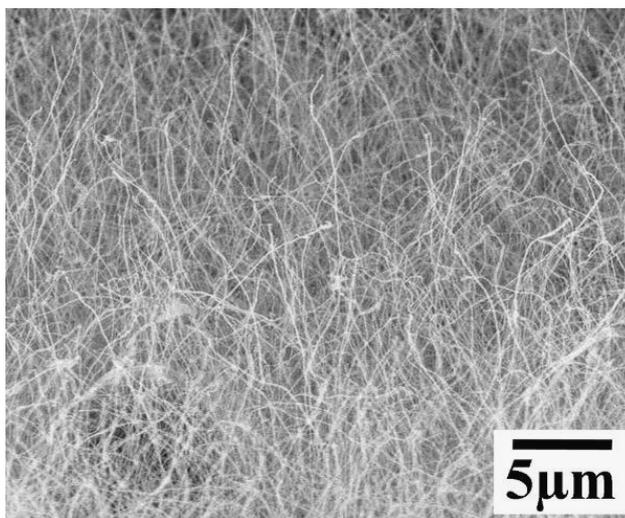
Two TEM images show the tip growth of a BNNT in the sample.



**Figure S6.** TEM images showing a BNNT grown from tip catalyst.

### 7. SEM image of the inside of the needle

The internal channel of the steel needle was also coated by semi-erect BNNTs.



**Figure S7.** SEM image of the BNNT coating on the internal surface of the needle.