A universal wet – chemistry route to fill boron nitride nanotubes with metal nanostructures

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SUPPLEMENTAL INFORMATION

Synthesis of metal filled BNNTs: BNNTs are synthesized using our recently reported Extended Pressure Inductively Coupled (EPIC) plasma method. As-grown BNNTs are first refluxed in a nitric acid bath at 120 °C for 3 hours to remove boron impurities and

open nanotube tip ends. After rinsing in deionized water, the BNNTs are left overnight in a bath of 0.5 M of metal-salt precursors (H_2PtCl_6, $AuCl_3$, $PdCl_2$, $AgNO_3$, $In(NO3)_3$, and $Co(NO3)_2$ from Sigma – Aldrich with high purity (99.9999 %)) dissolved in ethanol. The products are then vacuum filtered and subsequently thermally reduced in a 200 sccm flow of H_2 at 600 – 800 °C for 1 – 4 hours to obtain metal nanostructures. The resulting materials are sonicated in isopropyl alcohol and drop cast onto lacey carbon grids for characterization by high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) (JEOL JEM 2010 operating at 80 kV and FEI TitanX working at 300 kV). The composition of the product has been evaluated with sub-nm resolution by a combination of energy dispersive X–ray (EDS) and electron energy loss (EELS) spectroscopies.

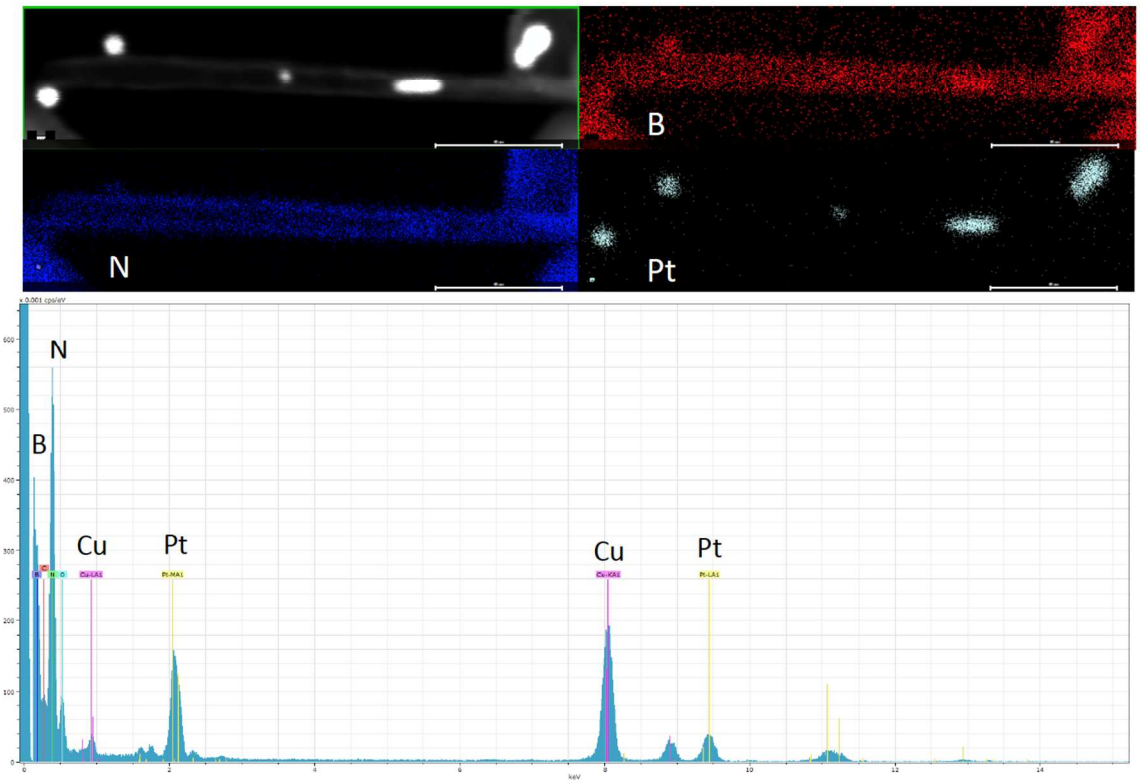

Figure S1. HAADF image, and EDS mapping and spectrum of Pt@BNNT. Cu peaks in EDS spectrum are from the copper TEM grid.

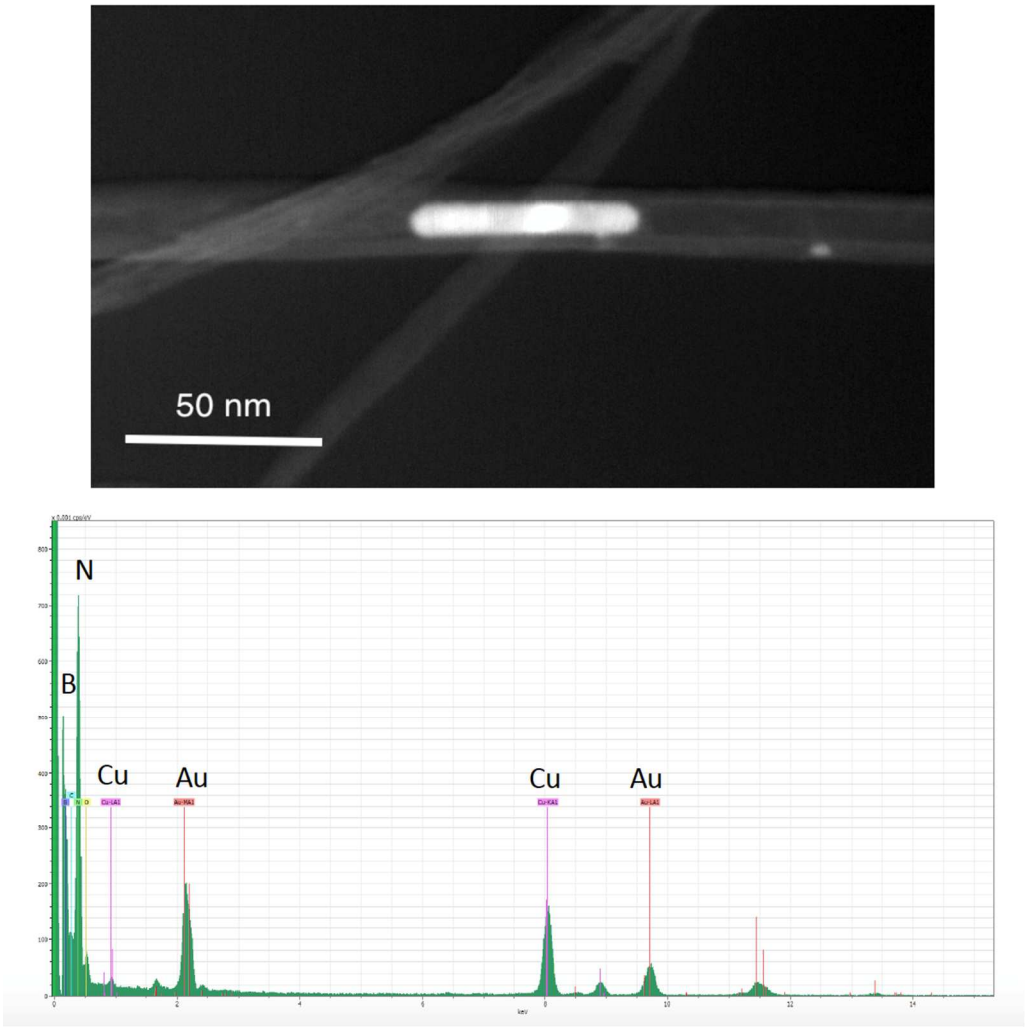

Figure S2. HAADF image and EDS spectrum of a Au nanorod within a BNNT showing only Au signals with negligible trace of O and Cl. Cu peaks in the spectrum are from the

copper TEM grid.

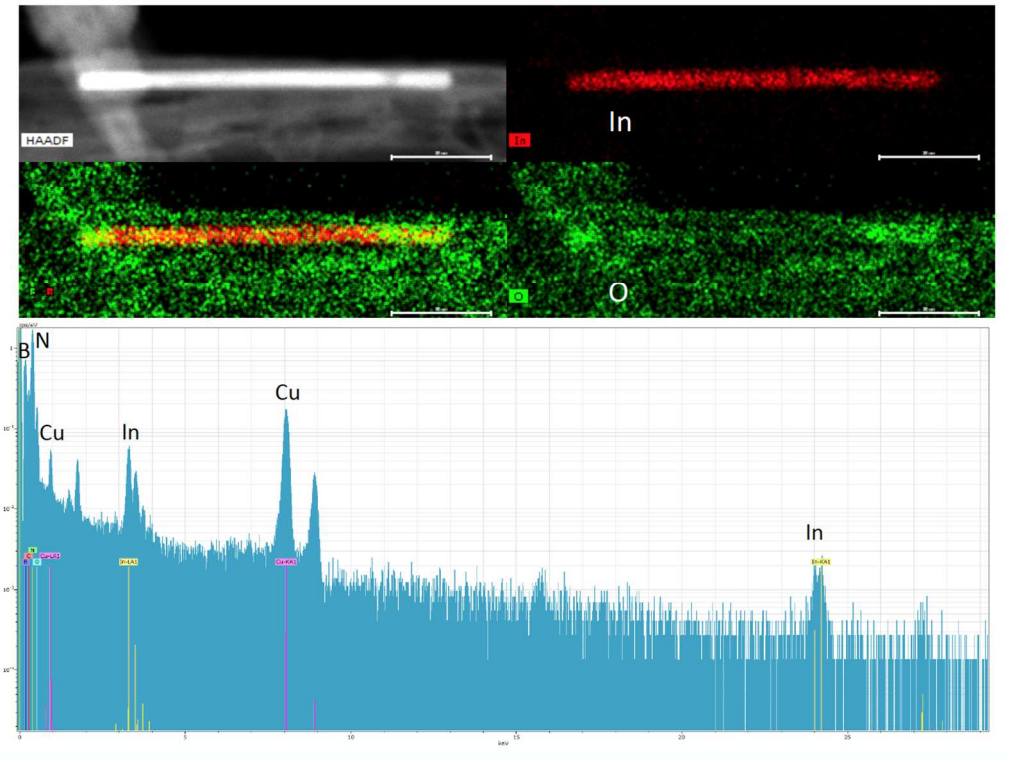

Figure S3. HAADF image, EDS mapping and EELS spectrum of In@BNNT. Indium oxide is indicated at the two ends of In nanorods. This suggests that pure In nanorods were initially formed and subsequently oxidized in the presence of either ambient oxygen or resultant products of the salt reduction inside the BNNT after thermal reduction was carried out. Cu peaks in EELS spectrum originate from the copper TEM grid.

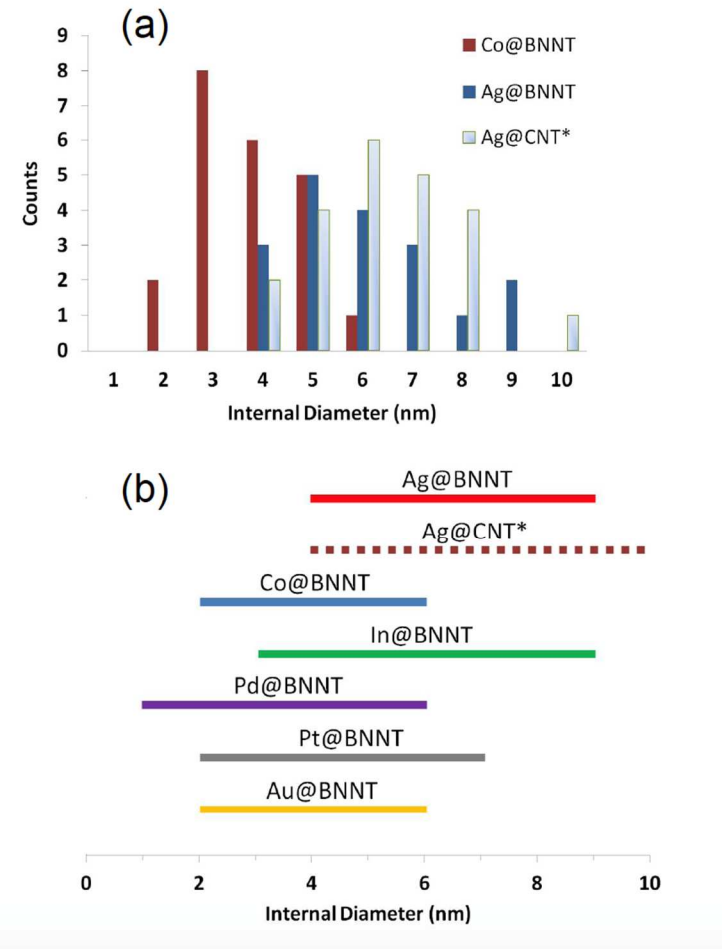

Figure S4. (a) Histogram of the diameter distribution of the internal cavity of BNNTs encapsulating Co and Ag. (b) Typical ranges of internal cavity diameters of BNNTs containing various filling metals. For comparison, the distribution and diameter ranges for Ag within CNTs (denoted Ag@CNT*) is taken from Ref. 32.

Calculation of theoretical maximum filling efficiency based on volume reduction from metal salts to elemental metals: Assume the total number of metal atoms (and therefore its mole) is conserved according to the thermal reduction reaction: $MX_n \rightarrow M$ (1)

Where X is either (-Cl) or ($-NO_3$) and n is the oxidation state of metal M (n = 1, 2, 3, etc.). From (1) assume we start from 1 mole of MX_n we will end up getting 1 mole of M. Therefore the initial volume of metal salt and resultant volume of metal will be: (M + nX)/D and (M/d) respectively where M, X are atomic/molecular weight (g) of M and X, and D,d are densities (g/cm^3) of the metal salt and metal..

The maximum filling factor will be:

(M/d)/[M+nX)/D] * 100 (volume%)

Take an example for the case of $AuCl_3$ → Au:

Molecular weight of $AuCl_3$ = 303.5 g/mol

Molecular weight of Au = 197.0 g/mol

Density of $AuCl_3$ = 4.70 g/cm^3

Density of Au = 19.3 g/cm^3

Therefore:

The volume of 1 mole of $AuCl_3$ salt is: (1 mol * 303.5 g/mol)/(4.70 g/cm^3) = 64.57 cm^3

The volume of 1 mole of Au metal is: (1 mol * 197.0 g/mol)/(19.3 g/cm^3) = 10.20 cm^3

The theoretical maximum filling factor is: (10.20/64.57)*100 = 15.8 (volume%)

Similarly, we have a table of maximum filling factor for other metals:

Metals	Maximum filling factor (volume %)

Pt	5.4
Au	15.8
Pd	20.0
Ag	26.2
Co	9.0