

Electronic Supplementary Information

Transformation of Ionic Liquid into Carbon Nanotubes in Confined Nanospace

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1. Experimental details

The high-purity grade (99%) 1-butyl-3-methylimidazolium bromide (bmimBr) ionic liquid was purchased from Merck KGaA (Darmstadt, Germany). This bmimBr was further purified carefully in our laboratory by recrystallization. Single-walled CNTs (SWNT) with ca. 1.9 nm in diameter were synthesized by the extended direct injection pyrolytic synthesis (*J. Phys. Chem. B* **2006**, *110*, 5849), and the raw SWNT products were subsequently annealed in vacuum at 1200 °C for 24 hours to remove the residual Fe catalyst nanoparticles and the amorphous carbon impurities. Before encapsulation, the SWNTs were heated under a dry air flow at 550 °C for 30 min to remove the end-caps. Open-ended SWNTs and bmimBr were separately loaded in an H-type quartz tube. The opened SWNTs were degassed by heating at 300 °C for 3 h

under dynamic vacuum line (1×10^{-5} Pa). Then, the SWNTs and bmimBr were mixed together and the H-type was vacuum-sealed. The mixture was kept at 200 °C for 72 h, at this temperature; the melted bmimBr was encapsulated within the interior channels of the SWNTs. The as-prepared products were washed with methanol to remove any bmimBr adsorbed on the outer surface of the SWNTs and then dried at 80 °C in vacuum for 12 h, obtaining the sample bmimBr@SWNTs (bmimBr encapsulated in SWNTs).

The filling of C₆₀ into bmimBr@SWNTs was carried out according to the reported C₆₀ peapods preparation in the literature (*Chem. Phys. Lett.* **2001**, 337, 48). The bmimBr@SWNTs and a C₆₀ powder were sealed in a glass tube at 1×10^{-5} Pa and kept at 420 °C for 24 h to complete the encapsulation. The confined bmimBr remained inside the channel while the C₆₀ were mainly inserted at the ends of the nanotube. Excess C₆₀ molecules were then washed with toluene. The final product was bmimBr/C₆₀@SWNTs. Transformation of the confined bmimBr into inner CNTs was achieved by thermal annealing the bmimBr/C₆₀@SWNTs at 1200 °C under a dynamic vacuum line (1×10^{-5} pa) at different transformation time.

2. Characterizations

Transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy and electron energy loss spectroscopy (EELS) measurements were performed using a JEOL JEM 2100F microscope equipped with a super-atmospheric thin-window X-ray detector. TEM images were acquired at an electron acceleration

voltage of 80 keV. The samples for TEM observations were prepared by dripping a drop of the nanotube-hexane suspension onto the commercially available carbon-coated copper grids.

Raman spectra were measured on a Jobin Yvon HR-800 micro-Raman spectrometer with a 633 nm (1.96 eV) excitation source under ambient conditions. For comparison, the same batch of the pristine SWNT was used to avoid any changes due to the different diameter distributions of the parent tubes. During Raman measurements, the nanotube samples were used in the form of thick bundles deposited on a silicon substrate, in order to ensure that the characteristics of the overall nanotube distribution spectra were acquired.

The XPS spectra were collected using an XPS spectrometer (ESCA-300; Scienta, Uppsala, Sweden) with a monochromatized Al K α X-ray source ($h\nu=1486.6$ eV) at a power of 2.4 kW and a base pressure of 7.3×10^{-8} Pa in the analytical chamber. The analyzer slit width and the pass energy were 0.5 mm and 150 eV, respectively.

3. Supporting figures

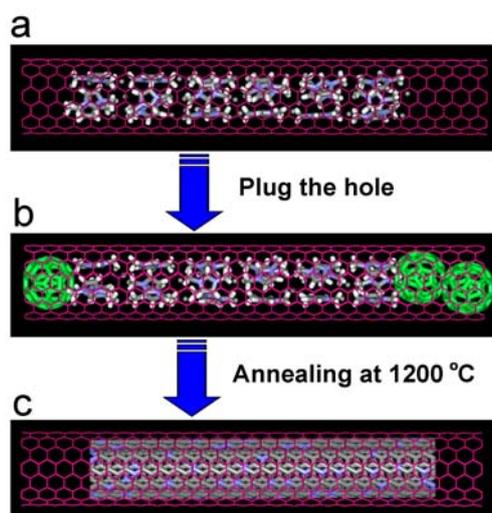


Fig. S1 Schematic diagram for the nanotube growth from the confined ionic liquid in a SWNT template. (a) bmimBr filled SWNT; (b) the open tips of the bmimBr@SWNT were plugged by filling C₆₀ at the ends of the tube; (c) the inner tube grows from the confined ionic liquid at high temperature. N atoms on the carbon network (indicated by violet color) were originated from the imidazolium rings of bmimBr.

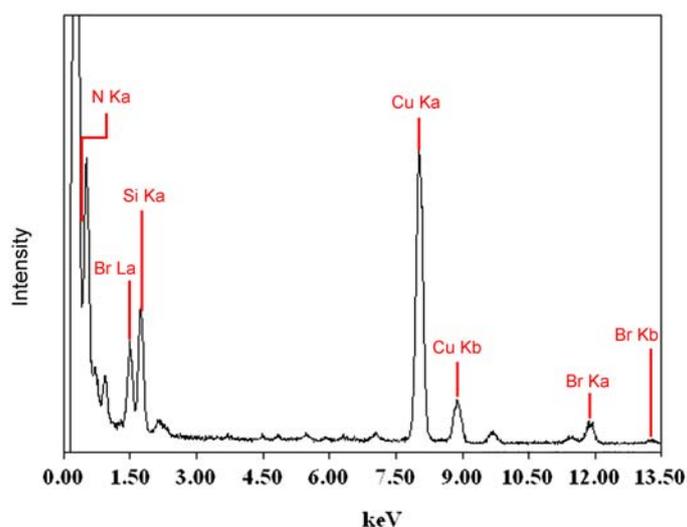


Fig. S2 A typical energy dispersive X-ray (EDX) spectrum of the bmimBr/C₆₀@SWNTs.

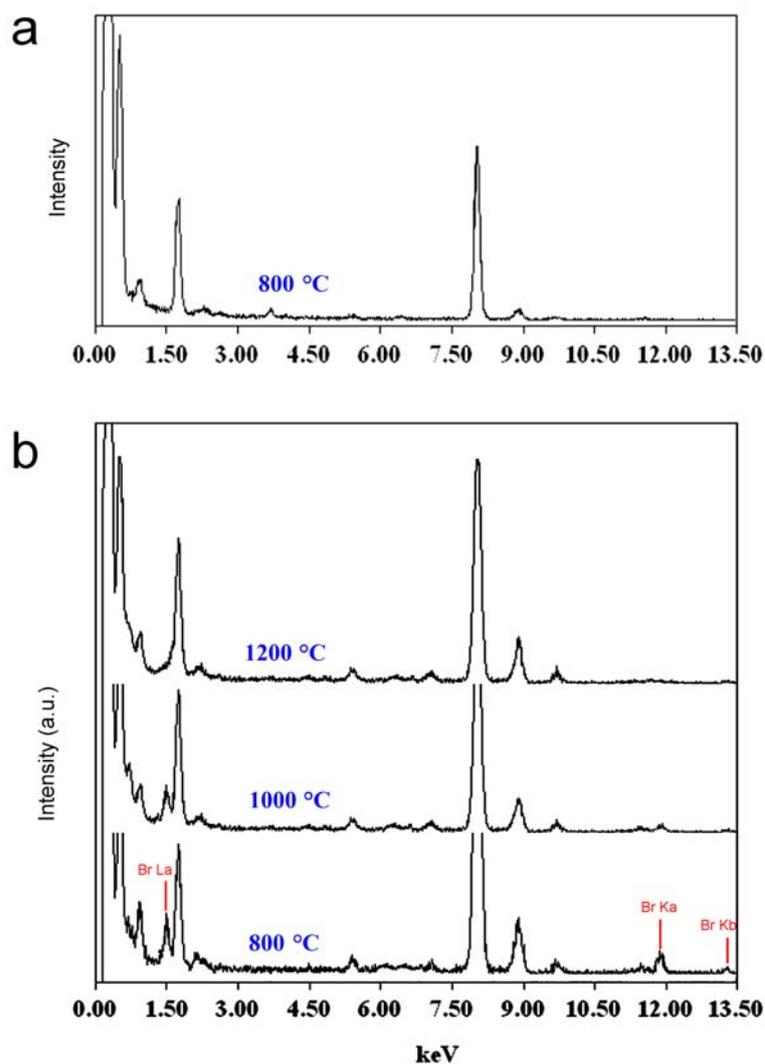


Fig. S3 Typical Energy dispersive X-ray (EDX) spectra of the bmimBr @SWNTs annealing at 800 °C for 2 h (a) and bmimBr/C₆₀@SWNTs annealing at 800 °C, 1000 °C and 1200 °C respectively for 2 h. There are no detectable EDX peaks of Br in spectrum a, whereas, the peaks were clearly observed in b. This indicates that the escape of the confined bmimBr during the heating treatment can be prevented with the insertion of C₆₀ molecules at the end of SWNT.

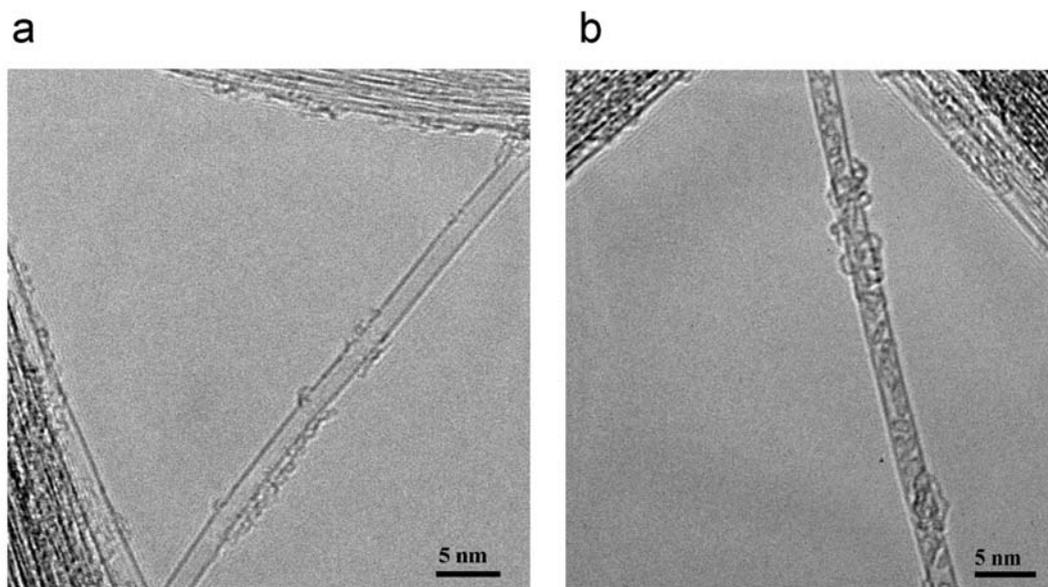


Fig. S4 Typical TEM images of bmimBr@SWNTs annealing at 800 °C for 2 h (a) and bmimBr/C₆₀@SWNTs annealing at 800 °C for 2 h (b). As shown in (a), if there is no C₆₀ inserted at the open ends of SWNT, the encapsulated bmimBr will be removed from the channel of SWNT after annealing.

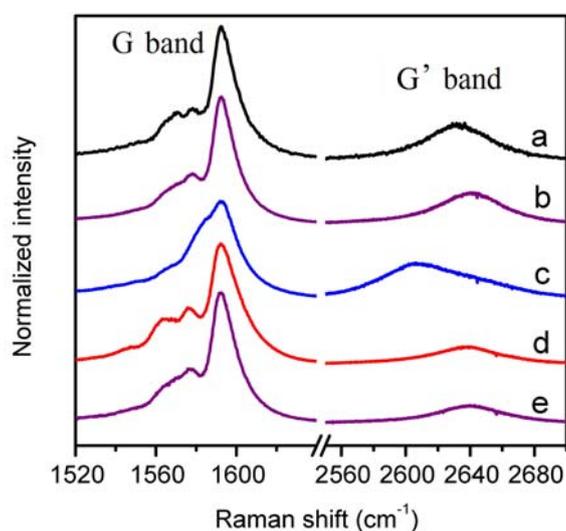


Fig. S5 Raman spectra of the pristine SWNT (a), bmimBr/C₆₀@SWNT (b), bmimBr/C₆₀@SWNT annealed at 1200 °C for 30 h (c), C₆₀@SWNT (d) and C₆₀@SWNT annealed at 1200 °C for 30 h (e). The spectra were obtained by using a He-Ne laser at 1.96 eV. All spectra were normalized to the G band of the outer tube at around 1592 cm⁻¹.

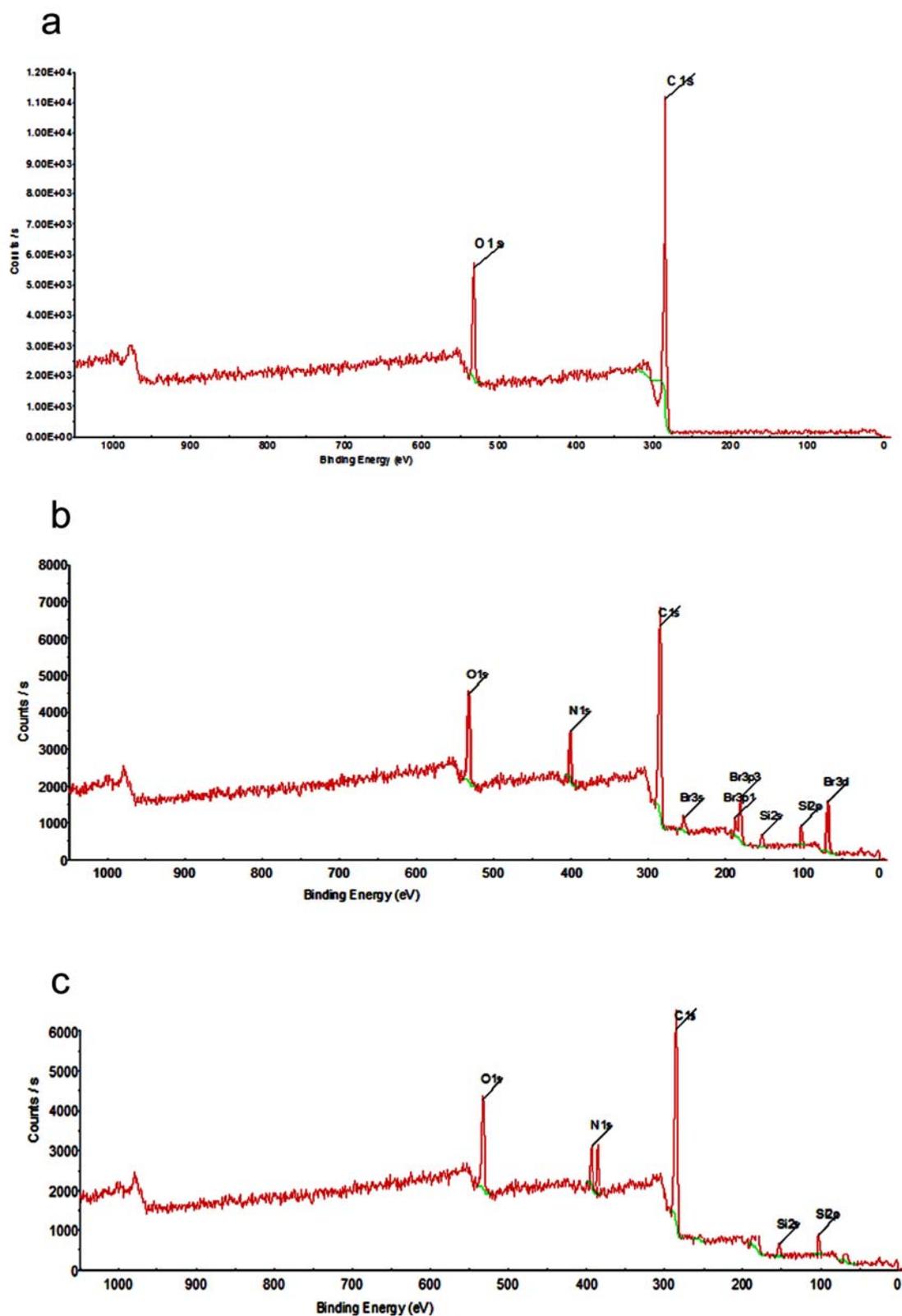


Fig. S6 XPS spectra of the pristine SWNT (a), bmimBr/C₆₀@SWNT (b), and bmimBr/C₆₀@SWNT annealed at 1200 °C for 30 h (c).

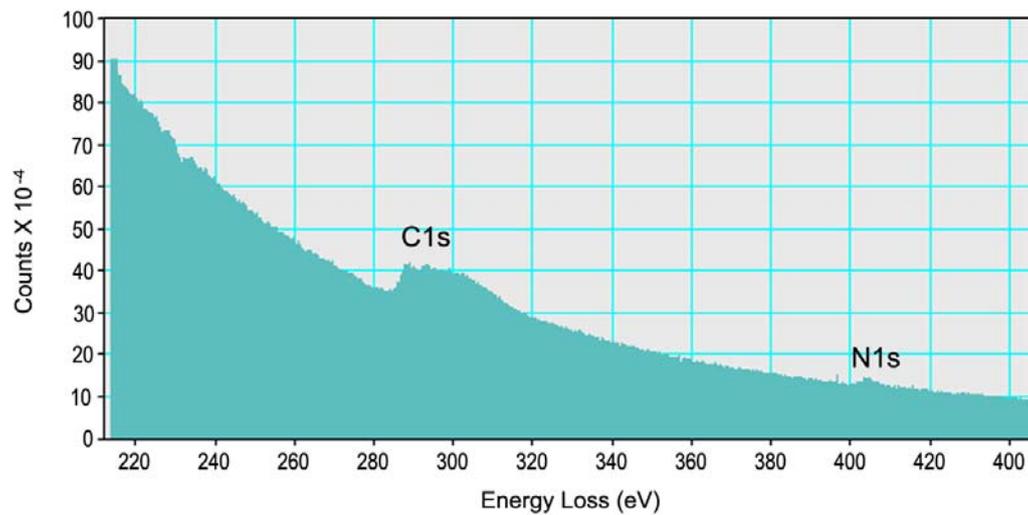


Fig. S7 Representative EELS spectrum taken for the final products obtained by annealing bmimBr/C₆₀@SWNTs at 1200 °C for 30 h. The C and N K-edges around 285 and 401 eV are seen.