Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information for

Supramolecular Nanotubes with High Thermal Stability: A Rigidity Enhanced Structure Transformation Induced by Electron-Beam Irradiation and Heat

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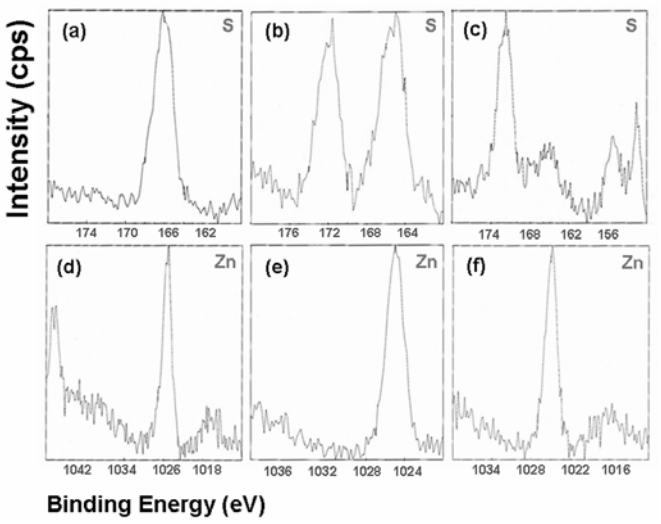

Fig. S1 ESCA spectra acquired at specified binding energy (eV) for Zn and S of precursor zinc hexadecylxanthate (ZnHDX), half-reacted products (HRPs) and as-prepared nanotubes (NTs). (a), (b) and (c) correspond to the S binding-energy region of ZnHDX, HRPs and NTs, respectively; (d), (e) and (f) represent Zn signal of ZnHDX, HRPs and NTs, respectively.

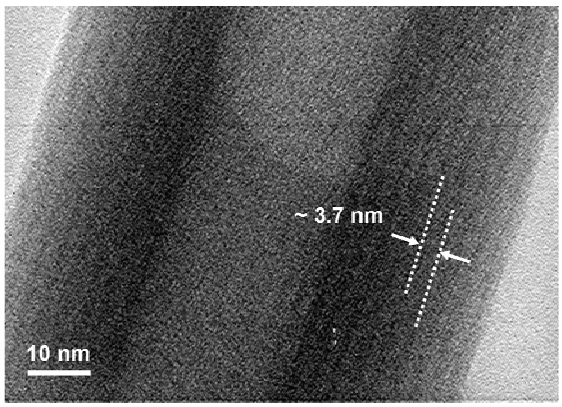

Fig. S2 TEM image of pristine nanotube. The multi-wall structure in the wall region has been characterized to have layer spacing of ~ 3.7 nm.

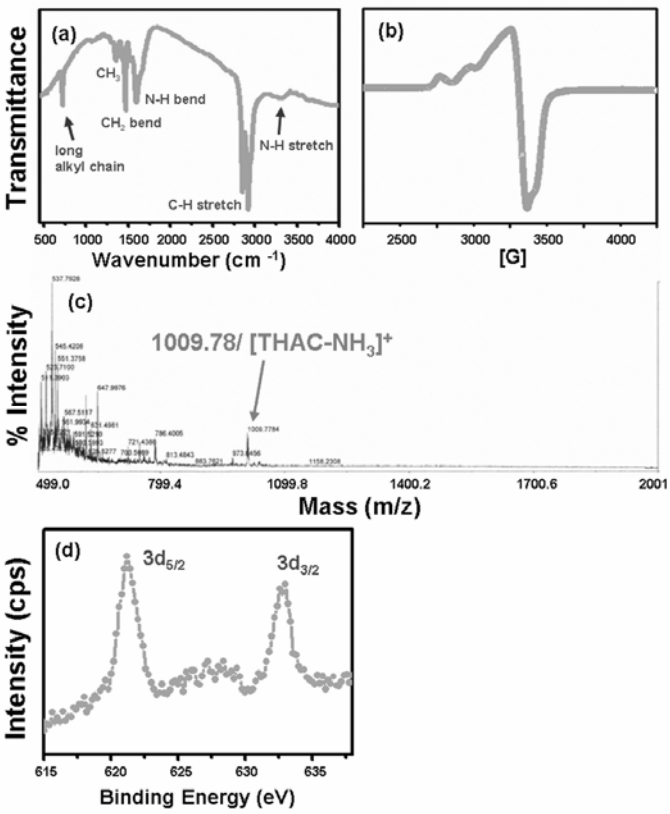

Fig. S3 FTIR, ESR, and MALDI-TOF mass spectra of tetrahexadecylamine copper (II) (THAC)-dioxygen complex. (a) FTIR spectra of THAC complex recorded with KBr medium; (b) Regular axial (frozen, 77K) ESR result of powder form THAC complex; (c) Positive-ion MALDI-Mass spectra with detected fragment ion $[THAC\text{-}NH_3]^+$ at m/z 1009; (d) ESCA result of collected products from the reaction of NaI and THAC-dioxygen complex. Additive shift of iodine $3d_{5/2}$ and $3d_{3/2}$ photoelectron lines stands for the suggested oxidation process.

MALDI-TOF mass spectra (Figs. S2, c) shows fragment ion at m/z 1009, which is considered to present in the form of fragment ion $[THAC\text{-}NH_3]^+$. The active ESR signal (Fig. S2, b) acquired from powder form of resulted complex with calculated spectroscopic g factor of $g_{\parallel}$ (2.28) and $g_{\perp}$ (2.06) implicates an axial environment for the copper (II) ion, i.e., $g_{\parallel} > 2.1$ and $g_{\perp} > 2.0$.[s1] This can be expected for the ground state symmetry of copper (II) d^9 ion is $d_{x^2-y^2}$ and sustained the square-planar geometry of copper (II) ion with HDA molecules. Characteristic FTIR peaks (3260, 2956, 2919(s) 2851, 1596, 1468, 1352 and 721 cm^{-1}) also inform the THAC complex formation (Fig. S2, a).[s2]

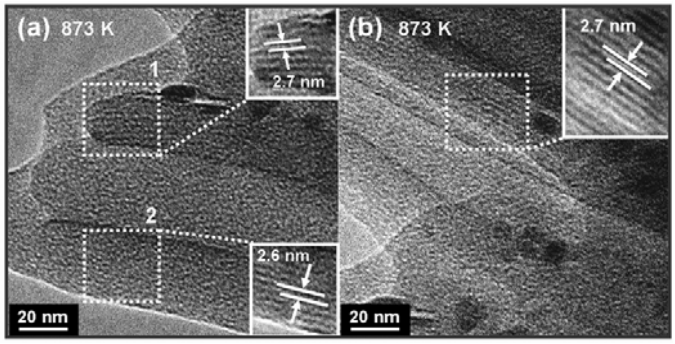

Fig. S4 Multi-wall nanotube structure formed during *in-situ* TEM examination at 873 K. (a) TEM image of multi-layer structured nanotube. Two insets show the fast Fourier-transform (FFT) images of area 1 and 2, respectively. The insets reveal the layer spacing is close to 2.7 nm; (b) Additional TEM and FFT (inset) images taken at 873 K of a nanotube.

References for supplementary information

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(S2) S. Muñoz, G. W. Gokel, *Inorganica Chimica Acta*., 1996, **250**, 59.