Supplementary Information

Template-free hierarchical self-assembly of nanotubes into multi-dimensional and multi-scale structures

Yong Liu, Yuan Gao, Qinghua Lu, Yongfeng Zhou*, and Deyue Yan

School of Chemistry & Chemical Technology, State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200240, China

E-mail: yfzhou@sjtu.edu.cn

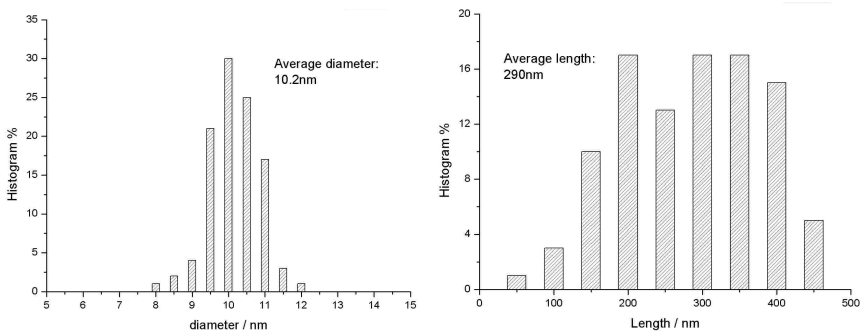

Figure S1 Statistical diagram of size distribution of nanotube diameters and lengths.

Titanate nanotubes have a wide distribution of length and narrow distribution of diameter. About 40 nanotubes was analyzed for the statistic.

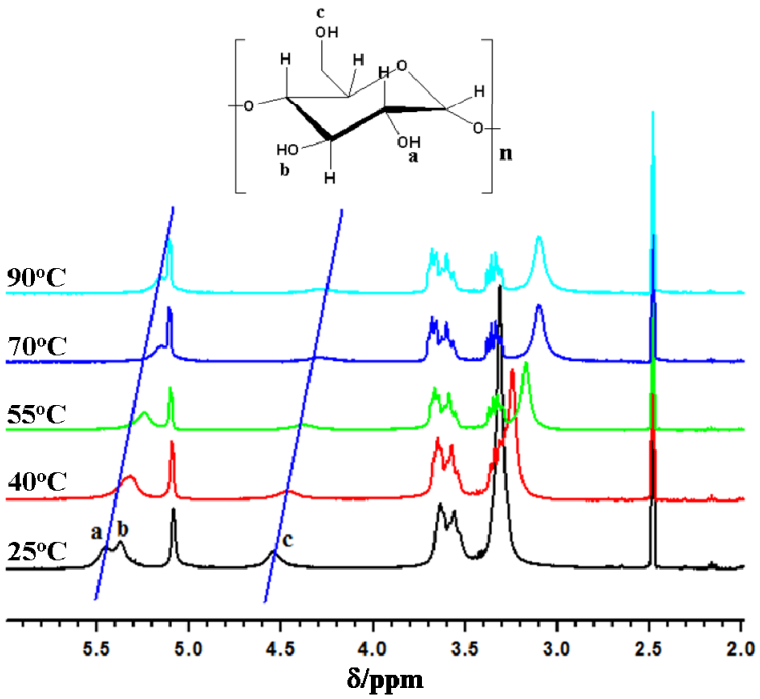

Figure S2. Variable temperature ^{1}H NMR spectra of the A/TNTs and the assignments of the proton signals in amylose. The sample of the A/TNTs was dissolved in dimethylsulfoxide-d_6, and ^{1}H NMR spectra were determined at 25, 40, 55, 70 and 90˚C, respectively. On heating from 25 to 90˚C, the O-H protons shifted upfield from 5.48 and 5.39 (peaks a and b) to ca. 5.10 ppm, and the O-H protons shifted upfield from 4.56 (peak c) to ca 4.10 ppm, respectively. The upfield shifts verified the existing of hydrogen bonds in A/TNTs that were destroyed on heating.

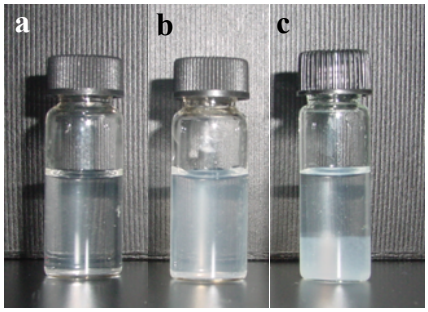

Figure S3. The images of A/TNT aqueous solutions. (a) Fresh A/TNTs aqueous solution with a weight ratio between TNTs and amylose ($R_{T/A}$) of 1%. (b) Fresh A/TNTs aqueous solution with a higher A/TNT content ($R_{T/A}$=2%). (c) A/TNTs aqueous solution ($R_{T/A}$=2%) being kept for 5 days. It was found the aqueous solution of A/TNTs was transparent at lower TNT content ($R_{T/A}$=1%, image **a**), and it became more turbid with increasing the concentration ($R_{T/A}$=2%, image **b**). A sediment phenomenon (image **c**) was observed while keeping the A/TNTs solution ($R_{T/A}$=2%) for 5 days, indicating the aggregation of A/TNTs.

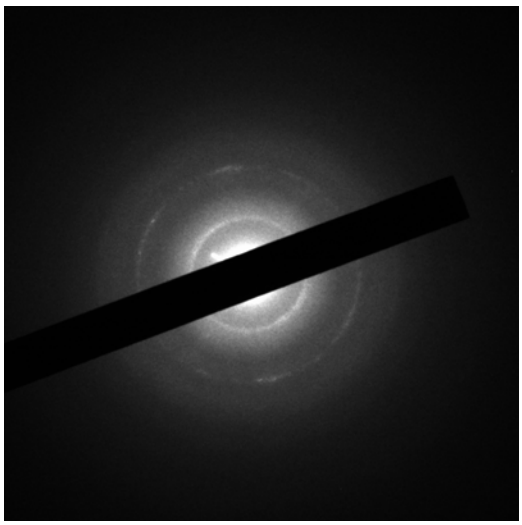

Figure S4. SAED pattern of pristine TNTs. The selected area is about 1 μm in diameter and contains many nanotubes. Only diffraction rings are observed, which indicates the pristine TNTs are polycrystalline.

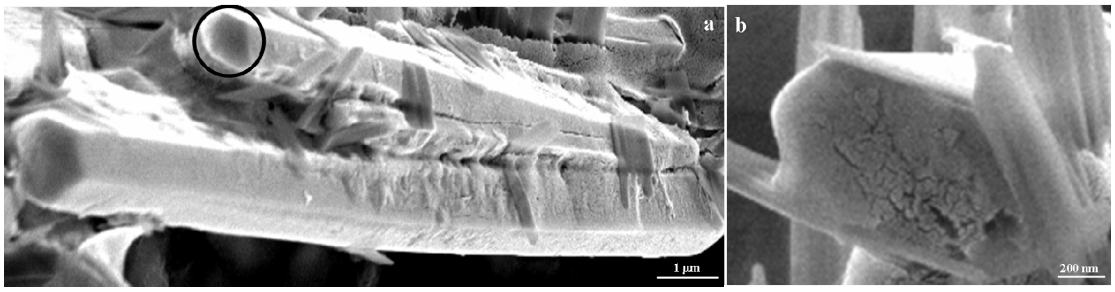

Figure S5. *H*r-SEM image of the 3D nanotube crystals. (a) Hexahedron crystal. (b) The magnified end of the hexahedron crystal as indicated by the black circle in image a.

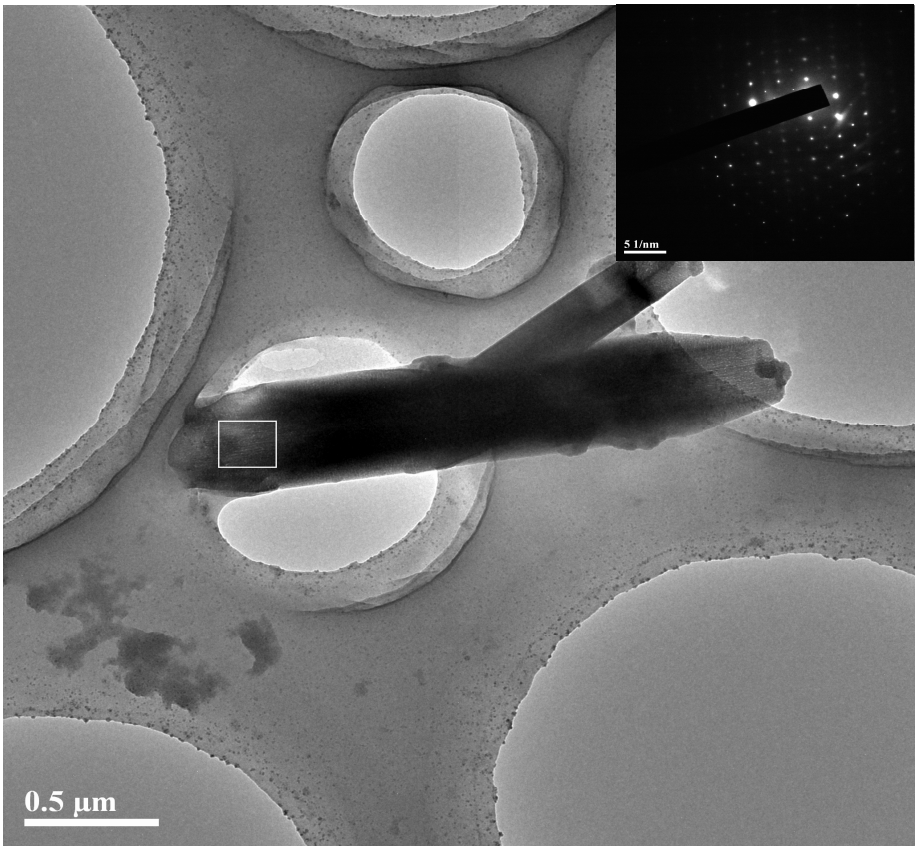

Figure S6. TEM image of the hexahedral rod with perfect crystal facets and the corresponding SAED pattern (inset). The highly-aligned nanotubes can be discerned at the end of the rod. The SAED pattern indicates the formation of perfect crystals with hexagonal unit cells along the crystal facet.