Supporting Information

Selective Synthesis of Diameter- and Interlayer-Controlled Carbon Nitride Nanotubes with Hydrogen Ensnaring Nanopores
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Experimental Procedures

Synthetic procedure of templates: The organic silica mesoporous template was synthesized from a mixture with 1,4-bis(triethoxysilyl)benzene (BTEB) precursor, Aldrich, in the presence of Octadecyltrimethylammonium chloride (ODTMA) surfactant, TCI. Ionic surfactant ODTMA (6.666g, 47.88mmol) was dissolved in a mixture of ionic-exchanged water (200ml) and 6M sodium hydroxide (NaOH) aqueous solution (16ml, 200mmol NaOH) at 50~60°C. BTEB (8ml, 49.67mmol) was added to the transparent mixture solution in which ODTMA was dissolved completely under the vigorous stirring at room temperature. The solution was treated ultrasonically for 20 min and stirred for 20 hrs at room temperature. After stirring, the mixture was kept in a 95°C oven for 20 hrs under static condition. The resulting white precipitate was collected by filtration and dried to yield as-synthesized organic silica mesoporous materials. Surfactants embedded in pores were removed by stirring 1.0g of as-made materials in 250ml of ethanol with 9ml of 36% HCl aqueous solution at 70°C for 8 hrs to yield an organic silica mesoporous template.1
The preparation of catalyst particles: The catalyst precursors doped in the mesoporous template were metal salts of iron(II) acetate, Aldrich. The catalyst precursors were deposited onto the template by the microwave-assisted hydrothermal method. 5wt% of iron(II) acetate was added in 100mg of as-synthesized template and 50ml of N,N-Dimethylformamide (DMF) was poured in the mixture. The mixed solution was treated ultrasonically for 5 min, and the solution was radiated for 90 sec by microwaves 2.45Ghz, 700W. After the treatment, the solution was filtrated and dried overnight in the oven to yield brown materials that metal precursors doped in the template. To reduce the metal salt on the template, hydrogen gas flew in chamber conditions of 300°C, 400torr at 200sccm for 2 hrs. Finally, the dark brown powder was removed from the chamber at ambient temperature.

CNNT growth by PECVD method: 15mg of the resulting powder was mixed in 3ml of the acetone, and then the solution was coated on the substrate (SiO₂). After the coated substrate was completely dried in the oven, metal particle impregnated templates were inserted into a PECVD apparatus. The temperature was raised to 300°C, and nitrogen gas was injected into the chamber at 85sccm. When the chamber kept the pressure at 20torr, the plasma was applied to the substrate at 850W for 1 min without a carbon source. Then the temperature was increased to 600°C, and methane gas flew in situ at 15sccm. The pressure of the chamber was sustained for 10 min at 23torr. The composite products after the growth turned black due to the carbon deposition.
Comparison between conventional process and new plasma-assisted process: Fig. S1 shows the conventional and new plasma-assisted process for synthesis of CNNT from organic silica mesoporous template. Conventional method forms metal catalyst on outer surface (Fig. S1 (c)), which results in large diameter and interlayer distribution of CNNT. (Fig. S1 (e)) However, in case of new plasma-assisted method, the catalyst on the outer surface is removed by plasma treatment (Fig. S1 (d)), so that the CNNTs grown after this treatment have been found to have the uniform diameter of 3.4 nm and mainly 3 interlayers. (Fig. S1 (f))

**Fig. S1.** Conventional (left) and our new plasma-assisted (right) processes to grow nanotubes. (a) the template doped with 5wt% iron(II) acetate; the inset shows the iron component in the template by EDS analysis, (b) the thermally reduced template after doping 5wt% iron(II) acetate, (c) the template treated with plasma for 1 min after doping, (d) the template treated with plasma for 1 min after doping and reducing, (e) CNNTs grown from the plasma-treated template after doping metal precursors, and (f)
CNNTs grown from a plasma-treated template after doping metal precursors and reducing the doped template.

*The deterioration of CNNTs’ crystallinity:* To induce the change of CNNTs’ graphitization, the specimen was treated with the aqueous sodium hydroxide (NaOH) solution of 1M at 80°C for 24 hr.

*Characterization:* The Raman spectroscopy RFS-100, Bruker with 1064nm of Nd-YAG radiation and 4cm⁻¹ resolution was performed to analyze the graphitization of CNNTs. FT-IR (FT-IR 4100, JASCO) was performed in the range of 400cm⁻¹~4000cm⁻¹. The BET analysis utilizing nitrogen gas in 77K was used to analyze the pore width and the pore width was measured by HK method.

*Temperature Programmed Desorption (TPD) analysis:* The weight of the specimen, which were CNNTs grown from the organic silica mesoporous template, was 20mg, including the template. The specimen was outgassed at 300°C for 5hr before the charging of hydrogen in CNNTs and hydrogen of 50 bars was charged in the specimen at 100°C for 3hr. In order to trap the hydrogen in the specimen, the reactor was quenched into the liquid nitrogen of 77K. The desorbed hydrogen was analyzed in the gas chromatograph (HP 5890) as the temperature was increased in the speed of 3K/min from 77K to 573K.
Fig. S2. The spectra of FT-IR on the surface of CNNTs.

Fig. S3. The RBM graphs of the Raman spectroscope, where the single-walled carbon nitride nanotube included in the template-CNNT was disappeared after the base treatment.

REFERENCES