Electronic Supplementary Information for

A sweet spot for highly efficient growth of vertically aligned single-walled carbon nanotube forests enabling their unique structures and properties

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Detailed experimental processes for each catalyst preparation method and CNT synthesis process

The detailed experimental processes are described in the following according to the different catalyst preparation methods:

Standard Super-Growth (water-assisted) CVD: Catalyst Fe film (~1.8 nm) was sputtered onto Si/(~40 nm) Al_2O_3 substrate. The substrate was inserted into a 1″ diameter quartz tube furnace and the temperature was raised to 750 °C in 90% H_2 with He as carrier gas at a total gas flow rate of 1000 sccm. Then the water vapor (~100-150 ppm) was introduced into the furnace. After ~6 min, H_2 gas was switched off and C_2H_4 carbon source (~10% in He) was switched on to perform the growth for ~10 min. Once the growth was finished, the furnace was cooled down to room temperature in He.

Aluminum-capped Fe: ~5 nm aluminum film was sputtered onto Si/SiO_2 substrate, followed by an oxygen plasma treatment (3 min at 100 W). Then, catalyst Fe film (0.5-2.5 nm) and capping aluminum film (0.5-2.0 nm) were separately sputtered to form the trilayer structure. The formation phase was carried out at different formation temperatures (550-750 °C) in 90% H_2 with He as carrier gas at a total gas flow rate of 1000 sccm, followed by a growth phase at 750 °C with 1% C_2H_4 in He for various durations.

Arc plasma deposition of catalyst: Catalyst nanoparticles were deposited in a high vacuum chamber (~4×10^{-4} Pa) onto Si/(~40 nm) Al_2O_3 substrates by arc plasma deposition. Voltage, determining arc current, was increased to increase nanoparticle size and ranged from 80–180 V at a fixed capacitance of 720 μF. The density of deposited nanoparticles was determined by the number of arc pulses, which ranged from 100 to 170. The substrate was inserted into a preheated CVD system at 750 °C to reduce the metallic nanoparticles (90% H_2 in He at a total flow rate of 1000 sccm) for 1 min, immediately followed by a growth phase for 6 min using 1% C_2H_4 as the carbon source and He as the carrier gas at 1000 sccm total flow rate.

Fe film thickness (1.8-5 nm): Fe thin films with thicknesses of 1.8-5.5 nm were sputtered onto Si/(~40 nm) Al_2O_3 substrates. The catalysts was inserted into a 3″ furnace and the temperature was increased to ~800 °C in H_2/He (90%/10%) ambient. CNTs were synthesized with a diluted

C_2H_2 (10% C_2H_2 in He) as carbon source at ~800 °C with optimized C_2H_2 of 30–60 sccm and water vapor concentration of 100–270 ppm for ~10 min.

Thin Fe film (0.9-1.8 nm): Fe thin films with thicknesses of 0.9-1.8 nm were sputtered onto Si/(~40 nm) Al_2O_3 substrates. The substrates were inserted into a 1″ furnace preheated at 750 °C for ~6 min in H_2/He (90%/10%) ambient and followed another ~6 min with introducing water vapor of ~100-200 ppm. CNTs were synthesized with C_2H_4 (70 sccm) as carbon source, He as carrier gas and water vapor of ~100–200 ppm for ~10 min at a total gas flow rate of 1000 sccm.

$FeCl_3$ catalyst by wet chemistry: $FeCl_3$ (iron chloride) was dissolved into organic solvents and coated onto Si/(~40 nm) Al_2O_3 substrate to form the catalyst. The catalyst was introduced into the furnace and exposed to H_2/He (40%/60%) ambient at 750 °C. Subsequently, CNTs were synthesized by water-assisted CVD with C_2H_4 (10%) and water vapor of 100−150 ppm at 750 °C for 10 min.

Total gas flow (500-4000 sccm) & Annealing temperature (500-950 °C): Fe catalyst (1.5 nm) was sputtered onto Si/(~30 nm) Al_2O_3 substrate. The substrate was inserted into the furnace and exposed to H_2 with different flow rates (total gas flow rate: 500-4000 sccm) and H_2 concentrations (10-90% with He as carrier gas) and ramped to the annealing temperature (in the range of 500-950 °C) in 15 min and ramped within an additional 3 minutes to the fixed growth temperature of 840 °C. Water-assisted CVD was carried out immediately at a fixed growth condition (50 sccm C_2H_4, 950 sccm He, and ~100 ppm water for 10 min at 840 °C).

Annealing time (1-11 min): Fe catalyst (~1.8 nm) was sputtered onto Si/(~40 nm) Al_2O_3 substrate. The catalyst was inserted into a 1″ furnace preheated at 750 °C and annealed for ~1-11 min in H_2/He (40%/60%) ambient. CNTs were synthesized using Super-Growth CVD with 70 sccm C_2H_4 as carbon source and He as carrier gas for 10 min.

Annealing time (1-30 min) for thin Fe film: Thin Fe catalysts (~0.9-1.2 nm) were sputtered onto Si/(~40 nm) Al_2O_3 substrate. The catalysts were inserted into a 1″ furnace preheated at 750 °C and annealed for ~1-30 min in H_2/He (40%/60%) ambient with water vapor of ~200-300 ppm. CNTs were synthesized using Super-Growth CVD with 70 sccm C_2H_4 as carbon source and He as carrier gas for 10 min.

Annealing temperature (750-900 °C) for thin Fe film: Thin Fe catalysts (~1.2-1.8 nm) were sputtered onto Si/(~40 nm) Al_2O_3 substrate. The catalysts were inserted into a 1″ furnace preheated at 750-900 °C and annealed for ~6 min in H_2/He (40%/60%) ambient. CNTs were synthesized using Super-Growth CVD with 70 sccm C_2H_4 as carbon source and He as carrier gas for 10 min.

Adding H_2O during annealing (4.5-18%): Fe catalyst (~1.8 nm) was sputtered onto Si/(~40 nm) Al_2O_3 substrate. The catalyst was inserted into a 1″ furnace preheated at 750 °C and annealed for ~6 min in H_2/He (40%/60%) ambient with various water vapor concentrations (He (with water vapor) gas flow rate: 45-180 sccm, real water vapor concentration was ~300-1200 ppm). CNTs were synthesized using Super-Growth CVD with 70 sccm C_2H_4 as carbon source and He as carrier gas for 10 min.

Air exposure time (6-60 sec): Fe catalyst (~1.6 nm) was sputtered onto Si/(~40 nm) Al_2O_3 substrate. The catalyst was inserted into a 1″ furnace preheated at 75 °C and annealed for ~6 min in H_2/He (90%/10%) ambient. Then the catalysts were took out and exposed to an ambient environment for 6-60 sec. A growth stage was immediately carried out using Super-Growth CVD with 75 sccm C_2H_4 as carbon source, He as carrier gas, and ~75 ppm water vapor for 9-12 min.

Reactive ion etching (10-35 W, 5-35 min): Fe catalyst (~1.6 nm) was sputtered onto Si/(~40 nm) Al_2O_3 substrate and then treated by reactive ion etching under various conditions (10-35 W, 5-35 min). The treated catalyst was inserted into the furnace preheated at 750 and annealed for ~6 min in H_2/He (90%/10%) ambient. CNTs were synthesized using Super-Growth CVD with 75 sccm C_2H_4 as carbon source, He as carrier gas, and ~75 ppm water vapor for 10-13 min.