

Supplementary Information

A Phenomenological Model for Selective Growth of Semiconducting Single-Walled Carbon Nanotube Based on Catalyst Deactivation

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1. Measurement and minimization of the background gas level in the furnace

In this study, the background oxidative gases has been minimized mainly by the following three measures. First, the gas exchange chamber (Fig. 3a) was equipped to prevent the contamination of oxygen and water vapor from outside of the furnace. Second, to avoid the generation of carbon monoxide (CO) via the reaction between carbon dirt impurities in the furnace and water vapor during the catalyst conditioning process (water gas reaction: $C + H_2O \rightarrow CO + H_2$), furnace tube and sample holders made of quartz were heated (800 °C, 10 minutes) in an O₂ atmosphere (diluted to about 20% with He) before each CVD process. Using Fourier transform infrared spectroscopy (Thermo scientific, Nicolet6700), we confirmed that CO concentration in the emitted gas from the furnace during CVD processes is less than 0.1 ppm, it reached up to 20 ppm without O₂ cleaning. Third, after O₂ cleaning, the furnace and sample holders were annealed in a hydrogen atmosphere (100%) for 5 minutes to decrease oxygen atoms adsorbed on the furnace. During this hydrogen annealing, water concentration in the exhausted gas typically reached to 100 ppm. By inserting this hydrogen annealing process, the increase in water vapor concentration during the catalyst formation process was less than 2 ppm.

2. Supplemental Raman spectra

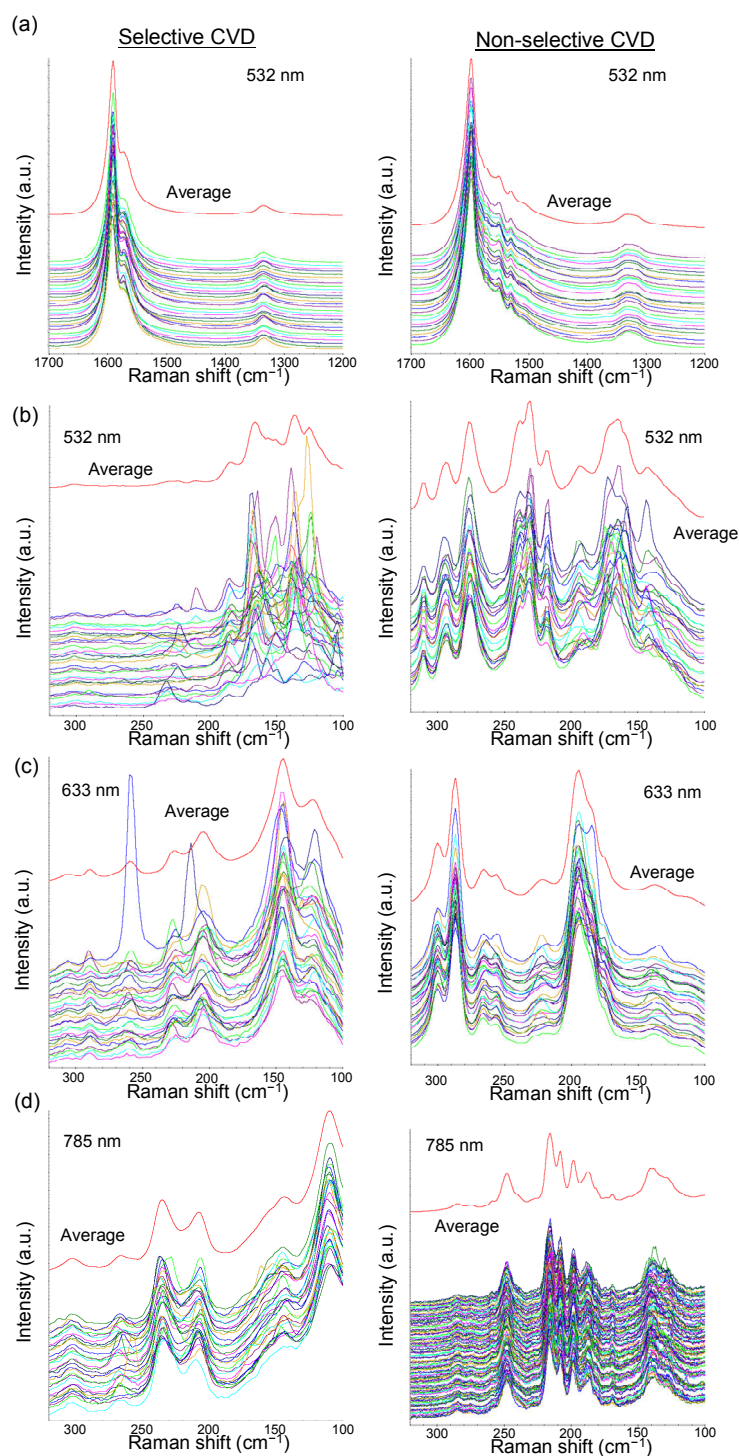


Figure S1. Raman spectra of selective (left) and non-selective CVD (right) collected from more than 25 positions. Red spectra show the average of spectra from all positions. (a) Spectra showing G-band region (excitation wave length: 532 nm). (b) Spectra showing RBM peaks (excitation wave length: 532 nm). (c) Spectra showing RBM peaks (excitation wave length: 633 nm). (d) Spectra showing RBM peaks (excitation wave length: 785 nm).

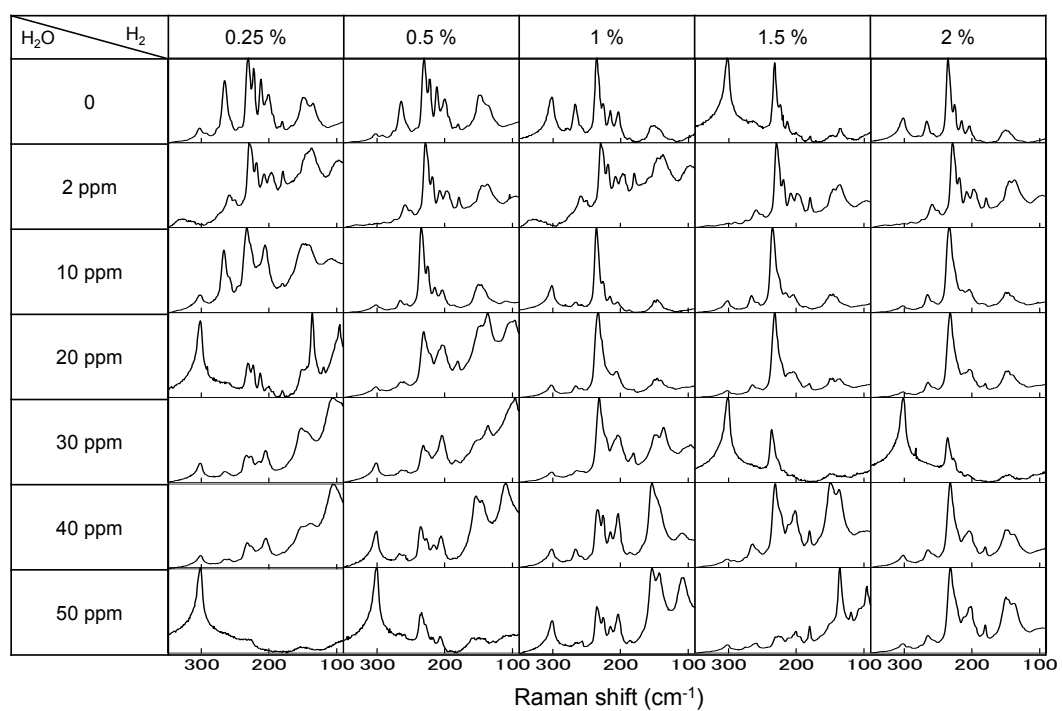
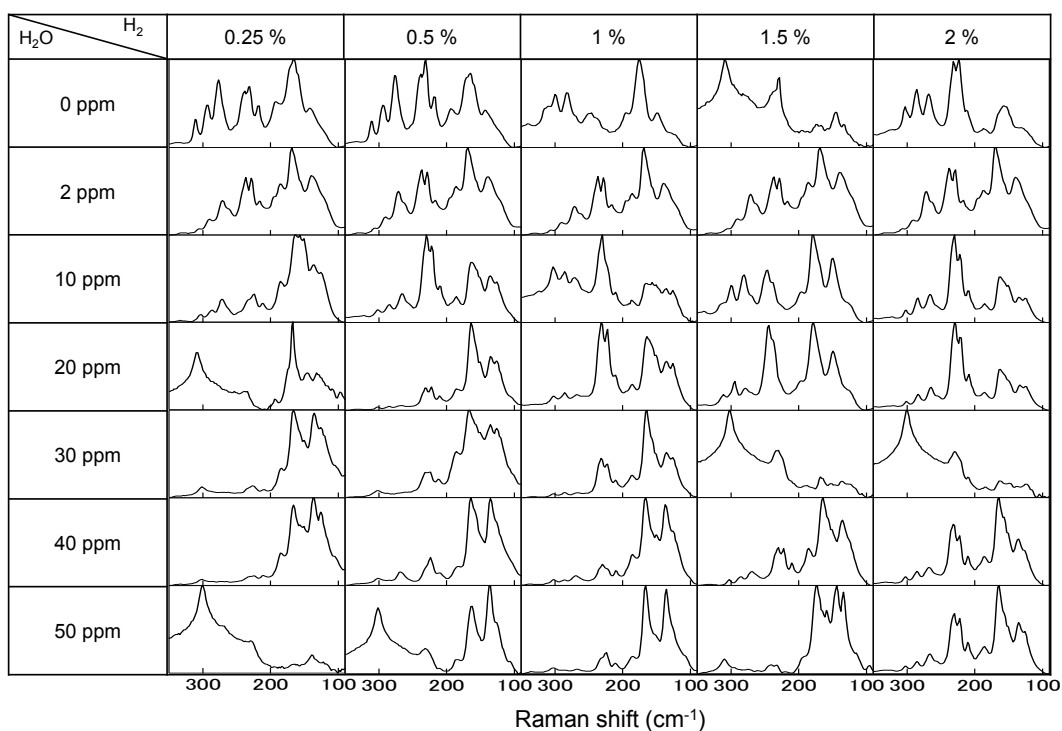


Figure S2. Raman spectra showing RBM peaks of SWCNTs synthesized with different water and hydrogen amounts during catalyst conditioning process. Upper: excitation wavelength of 532 nm, lower: 785 nm.

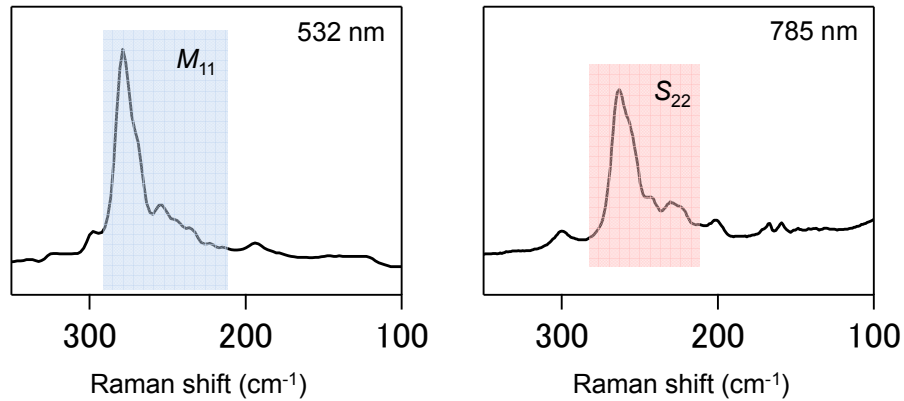


Figure S3. Raman spectra of HiPco. Left: 532 nm excitation wavelength, right: 785 nm.

3. Reference experiment feeding water vapor during SWCNT growth process

To exclude the possibility that the selective etching of m-SWCNT, previously reported mechanism of selective growth, worked mainly in the current work, a reference SWCNT growth experiment was conducted by the following process. Catalyst formation process was conducted as same as described in the manuscript. Then, without catalyst conditioning process, water vapor (50 ppm) and hydrogen (0.25%) was introduced into the furnace during SWCNT growth process with ethylene flow (0.25%). Raman spectra (Figure S4) shows a significant RBM peaks corresponding to m-SWCNT, resulting in a greatly decreased selectivity of $P_{\text{small}} = 53\%$ from CVD process with catalyst conditioning process using same amount of water and hydrogen.

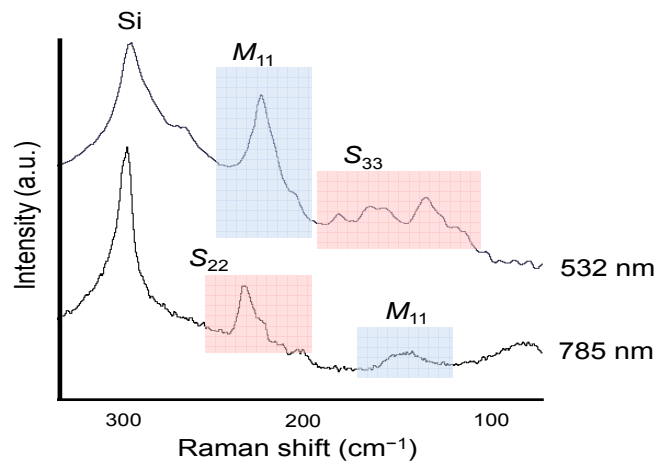


Figure S4. Raman spectra of SWCNTs synthesized in the reference experiment. Upper: 532 nm excitation wavelength, lower: 785 nm. Raman shift regions indicated by red and blue squares represent the signals from m-SWCNT and sc-SWCNT, respectively.