Synthesis of subnanometer-diameter vertically aligned single-walled carbon nanotubes with copper-anchored cobalt nanoparticles

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S1 Comparison between Co monometallic catalyst system and Co/Mo bimetallic catalyst system

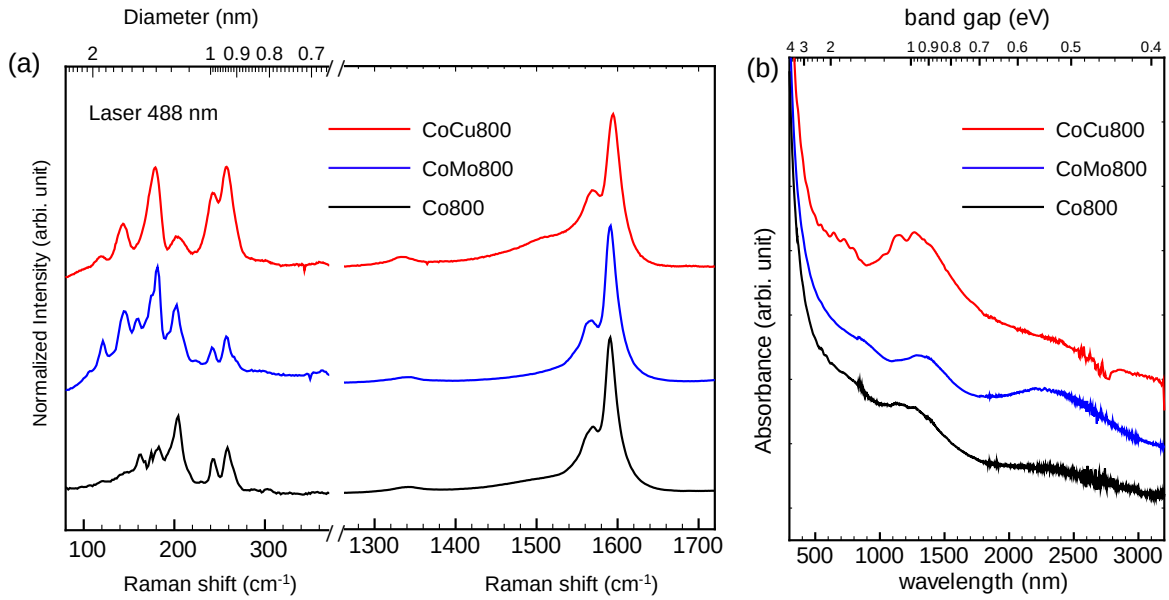

Fig. S1 (a) Raman spectra of as-synthesized CoCu800, CoMo800 and Co800, measured by laser excitation of 488 nm. (b) UV-vis-NIR absorption spectra of CoCu800, CoMo800 and Co800.

As shown by the absorption spectra shown in Fig. S1, at the CVD temperature of 800 ºC, Co monometallic catalyst and Co/Mo bimetallic catalyst systems yielded SWNTs with the similar average diameter (~2.0 nm) and defect level. However, for Co monometallic catalyst system, the yields of SWNTs were very low even at high CVD temperatures (e.g., 750 and 800 ºC). At 650 ºC, the CVD growth of SWNTs became very difficult. The SWNTs synthesized by Co/Mo bimetallic catalyst system have much higher yield and reproducibility than those by Co monometallic catalyst system. Therefore, Co/Mo bimetallic catalyst system was chosen as control group to demonstrate the superiorities of Co/Cu bimetallic catalyst system.

S2 Effect of CVD temperature on the *G*/*D* ratio

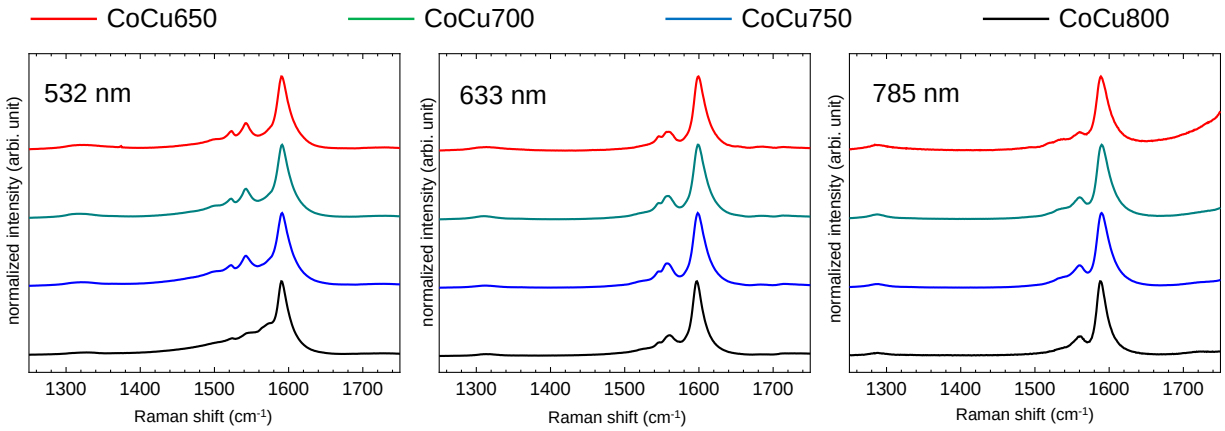

Fig. S2 G band and D band of the Raman spectra of as-synthesized CoCu650, CoCu700, CoCu750 and CoCu800. The laser excitation wavalengths are 532, 633 and 785 nm.

At elevated CVD temperature, the catalytic activity of Co is much higher than that of lower temperature. Moreover, the reaction dynamics of ethanol increase significantly with temperature.[S2] Therefore, with the increase of CVD temperature, the quality of as-synthesized SWNTs are improved. The *G*/*D* ratios of CoCu650, CoCu700, CoCu750 and CoCu800 are 24, 27, 30 and 35, respectively. The *G*/*D* ratio is the average value calculated from the Raman spectra of the three laser excitation wavelengths.

S3 Effect of Ethanol Partial Pressure on Morphology, Diameter and Quality of SWNT Films

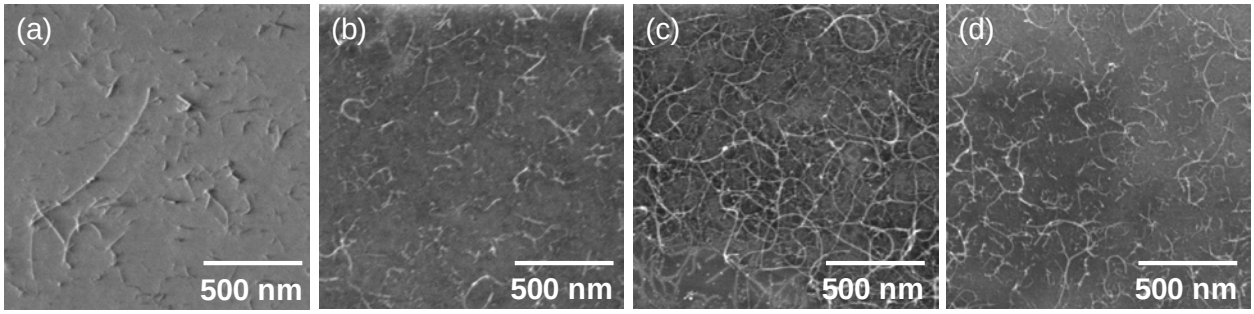

Fig. S3-1. SEM images of as-grown SWNT film by CoCu650 under different ethanol partial pressure. (a) 140 Pa. (b) 90 Pa. (c) 67 Pa. (d) 45 Pa.

From the perspective of device applications, it is of great interest to tune the length of the SWNTs (or SWNT bundles) and the film density while maintaining the subnanometer diameter of SWNTs. By elongating the CVD growth time, we did not observe significant changes in the density of CoCu650 film, with the length of SWNTs (or SWNT bundles) kept at several hundred nanometers. It may be attributed to that the growth of SWNTs was terminated during the increase of the pressure from vacuum (system vacuum is 20 Pa) to 1.3 kPa. At a low CVD temperature of 650 ˚C, the catalysts activity is limited. If the adsorption of carbon stock is much faster than its precipitation into SWNTs, excessive supply of ethanol may become an overdose of carbon and poisons the catalysts. Therefore, the key to improve the yield of SWNTs at a low CVD temperature is to find the appropriate partial pressure of carbon stock which favors SWNT growth the most.

Here, the carbon stock was diluted with Ar with the total pressure kept as 1.3 kPa. The SEM images of the SWNTs synthesized using Co/Cu bimetallic catalyst system at 650 ˚C under different ethanol partial pressures of 140, 90, 67, 45 Pa are shown in Figure S3-1. It can be clearly observed that the yield and density of SWNTs on the substrate increased when the

ethanol partial pressure decreased from 140 Pa to 67 Pa. Further decrease of the total pressure resulted in the decreased growth speed, which may be attributed to the insufficient carbon supply. The SWNT samples synthesized under different ethanol partial pressures were also characterized by Raman spectra under the laser excitation of 532, 633 and 785 nm, as shown in Figure S3-2. There were almost no changes in the *G*-band, *G*/*D* ratio or RBM region, which means that the ethanol partial pressure has little impact on the diameter and quality of CoCu650.

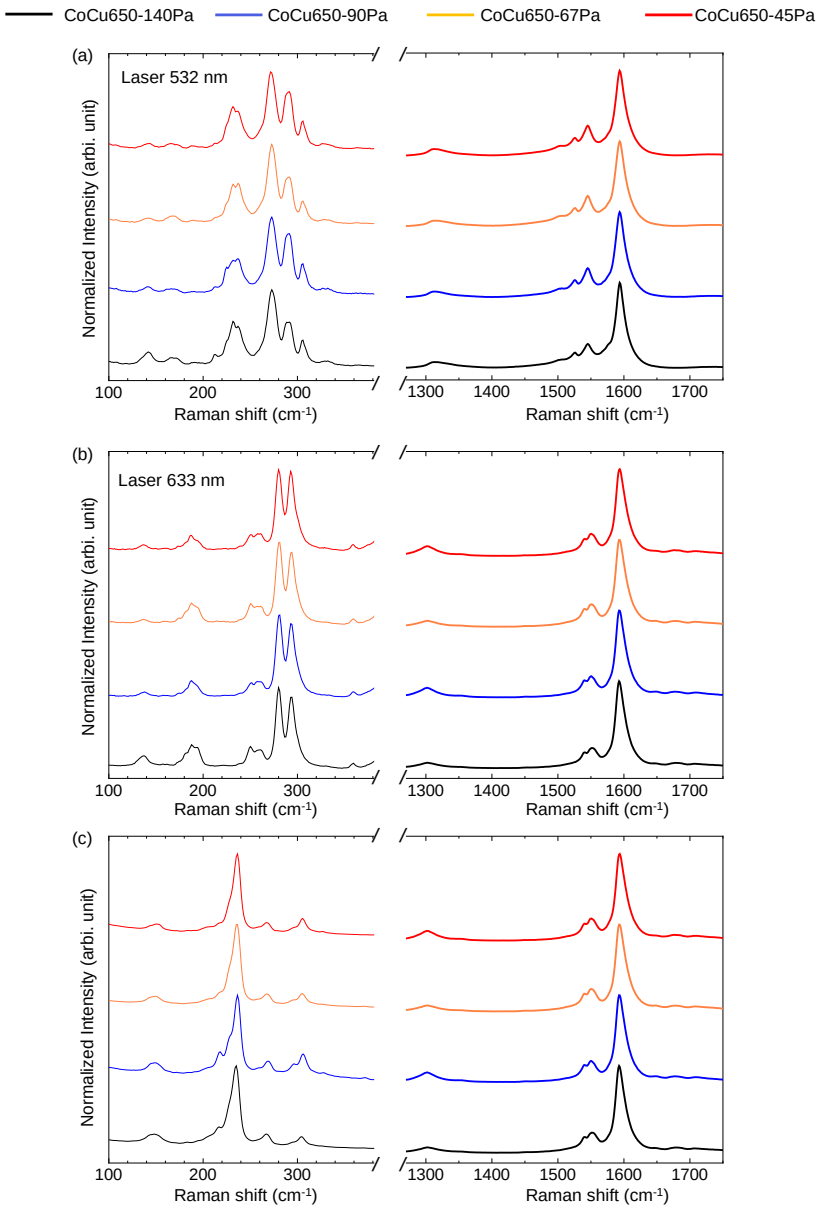

Fig. S3-2 Raman spectra of SWNT films synthesized using Co/Mo bimetallic catalyst system at 650 ˚C under different ethanol partial pressures. (a) 140 Pa. (b) 90 Pa. (c) 67 Pa. (d) 45 Pa.

S4 Raman spectra of Si/SiO_2 substrate

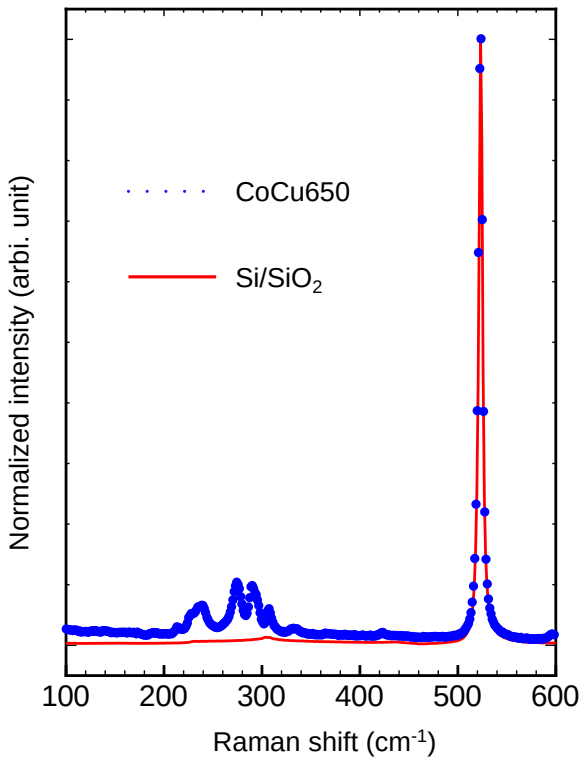

Figure S4 Raman spectra of as-synthesized CoCu650 and Si, measured by laser excitation of 532 nm.

Reference

S1. V. Jourdain, C. Bichara, *Carbon* 2013, **58**, 2.