Supplementary Information

Atomic force microscope-guided nanoscale 3D patterning for carbon nanofibers with *in situ* Raman spectroscopy

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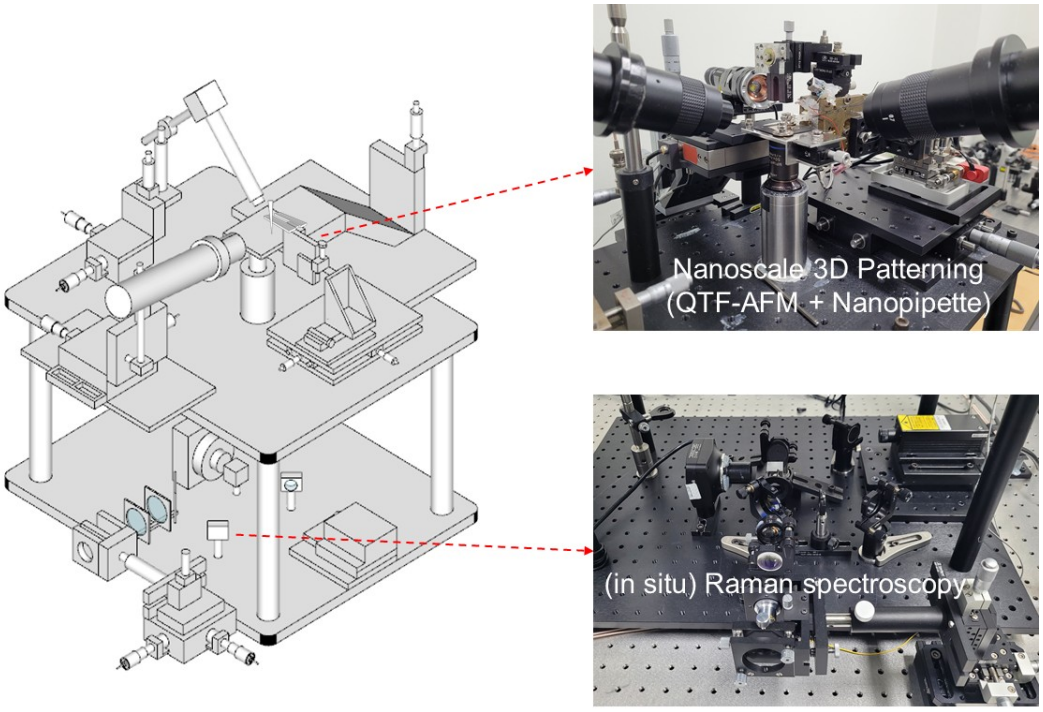

Figure S1. The schematic diagram and actual photographs of the nanoscale 3D patterning and *in situ* Raman measurement devices are presented. In the nanoscale 3D patterning section, the patterning process is performed while observing the sample and the quartz tuning fork (QTF) tip with charge-coupled device (CCD) cameras positioned in two orientations. For *in situ* Raman spectroscopy section, the underside of the sample is monitored with a CCD camera to facilitate the measurement of the Raman spectra.

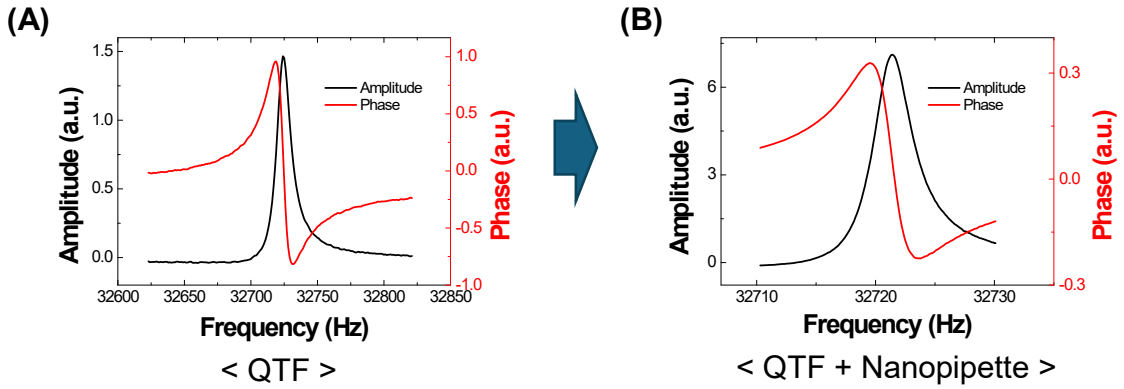

Figure S2. (A) illustrates the amplitude and phase of the QTF itself, presented as a graph. (B) shows the amplitude and phase graphs after the QTF makes contact with the nanopipette. These changes in the resonance frequency of the QTF are used to facilitate the patterning of nanoscale fibers.

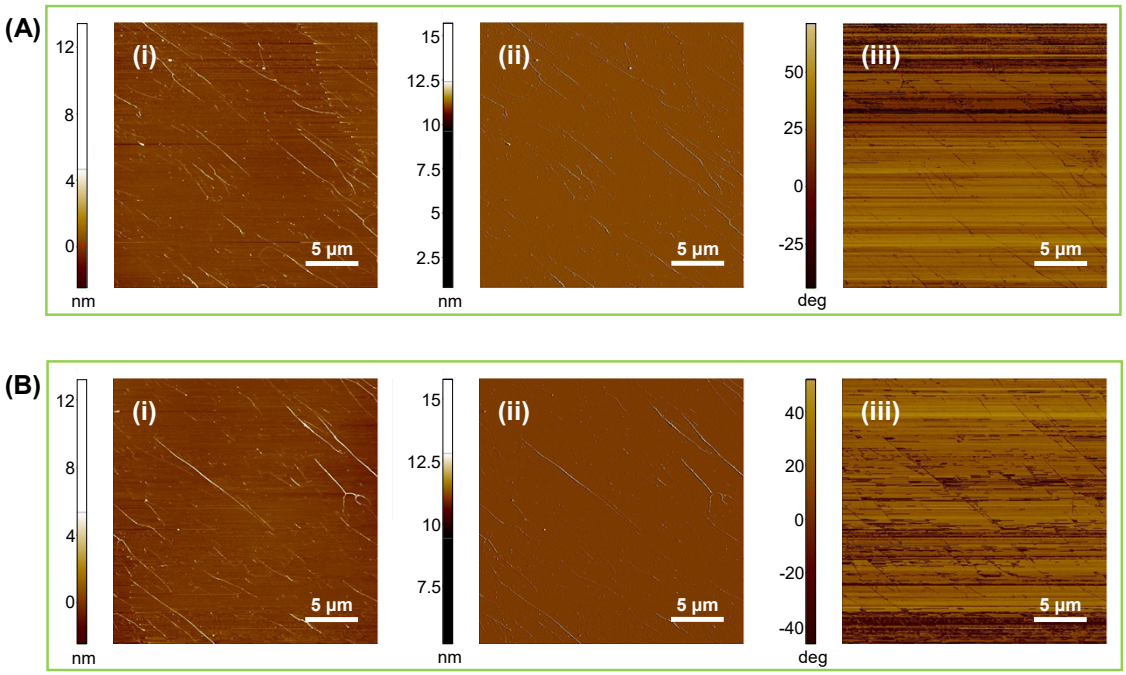

Figure S3. Atomic force microscope (AFM) images of the diluted and evaporated drop of CNT solution. In this experiment, the CNT solution was diluted with deionized water (0.005 wt%) and a drop of the solution was placed on a silicon wafer chip. The average length of the SW-CNTs in the solution was then measured using a commercial AFM system (Park Systems Co., NX-10) in non-contact mode. Measurements were taken at two locations: (A) (i) height information, (ii) amplitude information, (iii) phase information, and (B) (i) height information, (ii) amplitude information, (iii) phase information. A total of 45 different lengths of SW-CNTs were measured, and the average length of the SW-CNTs was approximately 8.15 μm.

Figure S4. The changes in the z-axis position and the amplitude of the QTF during the 3D patterning process using the proposed system are shown. The approach graph represents the moment when the sample is approached, while the retraction graph illustrates the moment when the sample moves away, resulting in the formation of the CNT fiber. The starting point of the retraction graph corresponds to the moment when the sample makes contact with the pipette, and the length on the x-axis indicates the length of the formed fiber.

Figure S5. Evidence of controlled CNT fiber length fabrication. After vertically patterned the CNT fiber on the glass surface placed between the Au-coated glass, the fiber was laid horizontally by touching it with the same pipette tip, and its length (~14 μm) was subsequently observed by using the SEM.

Figure S6. *In situ* Raman spectroscopy immediately after the 3D patterning process. Figure (A) shows an optical microscopy image of the patterned CNT fiber on the glass surface placed between the Au-coated glass (shown in Figure 3). This image makes it possible to precisely identify of the location where the laser is being focused during Raman spectroscopy measurements. In the optical image, the CNT fiber appears to be tilted due to the angle of light incidence, but is actually perfectly perpendicular to the sample [S1]. This was further confirmed using a commercial optical microscope. (C) illustrates the use of a 532 nm laser to measure the Raman spectrum of the CNT fibers located within the red and green boxes in (A), respectively.

Figure S7. Several examples of the CNT nanofibers fabricated by using the vertical patterning method (A-C). Especially, (B) and (C) show the samples observed by optical microscope after being tilted slightly after patterning on the Au-coated glass surface. This method made it possible to observe the vertical structures more clearly.

Figure S8. Several examples of the CNT nanofibers fabricated by using the horizontal patterning on the Au-coated glass surface and the glass surface placed between the Au-coated glass (A-D). The CNT nanofibers are fabricated by the drawing method, and their morphology were observed by optical microscopy (OM). Especially, we fabricated CNT nanofiber with a diameter of approximately 100 nm by reducing the size of the nanopipette holes to about 100 nm on the Au surface (D), and the fabricated CNT fiber is then measured as ~100 nm diameter by using scanning electron microscopy to define the diameter (SEM).

Figure S9. Comparison of the CNT Raman peaks on a glass surface and different thicknesses of Ag-coated surfaces with a droplet of SW-CNT solution to define the optimal Ag thickness for the Raman intensity of the fabricated CNT nanofiber in (A). The samples were coated by using the sputtering machine for 0 seconds, 40 seconds (~7.4 nm thickness), 80 seconds (~14.6 nm thickness), and 120 seconds (~22.1 nm thickness) with a current of 9 mA by using a sputtering machine (COXEM Co., SPT-20), and a drop of CNT solution was placed on each. For example, (B) used a profilometer (Bruker Co., DETEK) to measure the exact thickness between points 1 and 4 indicated by the white dotted lines in (A), which was approximately 22.1 nm.

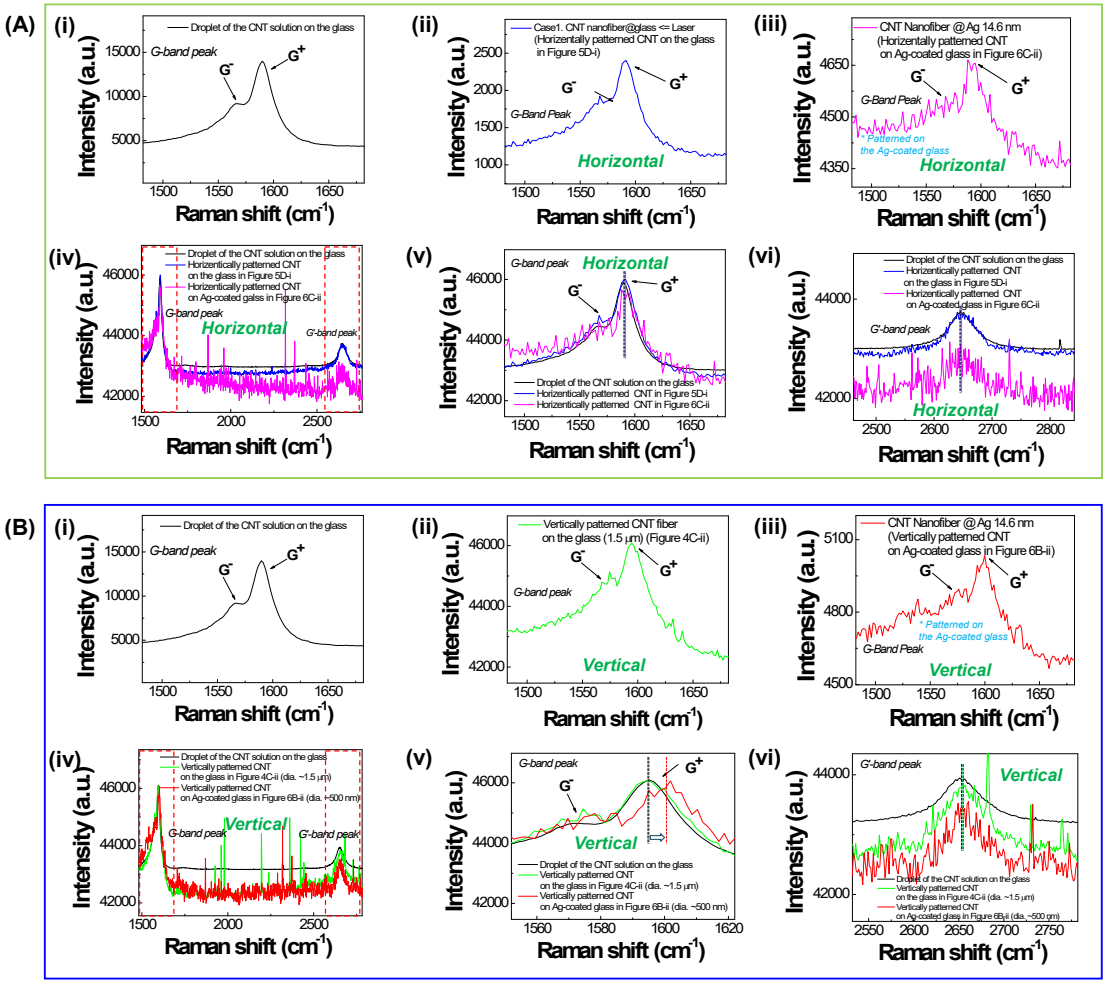

Figure S10. Raman analysis of the fabricated CNT nanofibers by using the proposed system both case of vertical patterning & drawing method. (A) shows the horizontally patterned CNT fibers on glass (A-ii, from Figure 5D-i) and those on Ag-coated glass (A-iii, from Figure 6C-ii) of the context comparing with the droplet of the bare CNT solution as the reference signal (A-i). As shown, no significant band peak shifts were observed (A-iv, v, vi). Meanwhile, (B) shows the vertically patterned CNT on glass (B-ii, from Figure 4C-ii) and those on Ag-coated glass (B-iii, from Figure 6B-ii) of the context. A slight blue shift of ~7 cm^{-1} was observed in CNT nanofibers with a diameter of 500 nm, while the 1.5 μm diameter CNT nanofiber shows almost identical peak position (B-iv, v, vi) comparing with droplet of the bare CNT solution (B-i). This indicates the 1.5 um diameter CNT nanofiber still behave as bulk matter. This phenomenon is thought to be due to the pressure exerted on the CNTs as a result of the surface tension and interfacial pressure between the liquid and air acting isotopically around the circumference of the CNTs when ejected through a nanopipette for the case of nanoscale diameter under 1 μm. Smaller diameters are predicted to experience greater pressure, resulting in a more pronounced blue shift. In the case of horizontally patterned CNT nanofibers, one side is attached to the substrate, reducing the interfacial pressure around the circumference. This may explain the relatively smaller blue shift observed under these conditions.

References

[S1] S. An, B. Sung, H. Noh, C. Stambaugh, S. Kwon, K. Lee, B. Kim, Q. Kim & W. Jhe, Position-resolved Surface Characterization and Nanofabrication Using an Optical Microscope Combined with a Nanopipette/Quartz Tuning Fork Atomic Force Microscope, *Nano-Micro Lett.* **6**(1), 70-79 (2014).