Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary information

Carbon nanotube columns for flow systems: influence of synthesis parameters

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CNC synthesis

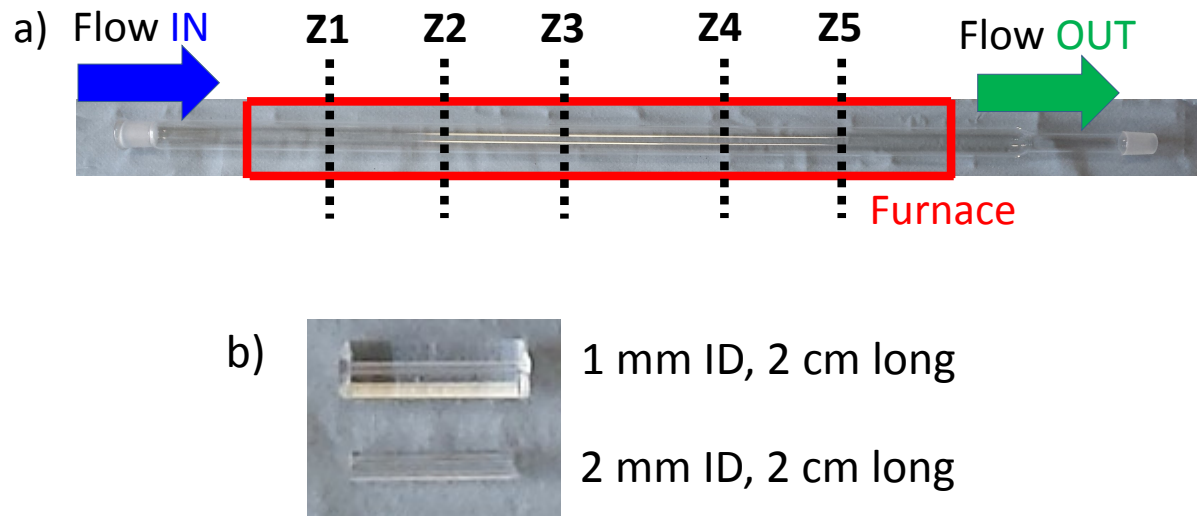


Fig. S1. (a) Schematic representation of the quartz tube (21 mm inner diameter (ID)) used as synthesis reactor. Arrows indicate the direction of the carrier gas flow during the experiment. The quartz tube was divided into 5 zones where quartz column substrates were placed (Z_1=17 cm, Z_2=23 cm, Z_3=29 cm, Z_4=39 cm, Z_5=45 cm, values correspond to position of the entrance of the column relative to the beginning of the furnace). (b) Photograph of quartz-column substrates with 1 or 2 mm ID.

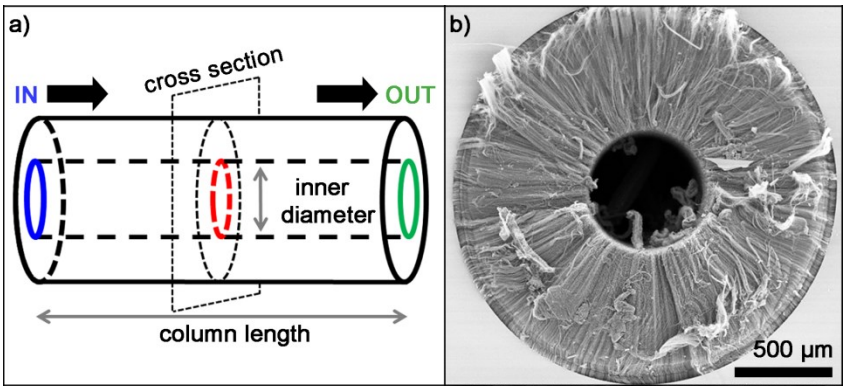


Fig. S2. (a) Schematic representation of a quartz column used as substrate illustrating IN and OUT positions relative to the carrier gas flow during synthesis and a schematic illustration of a cross section across the column. (b) SEM micrograph taken at a CNC cross section. The quartz surface appears as a white background and VA-MWCNTs grown in the inner diameter channel appear in dark grey. The hollow core with partial filling appears as a black disk (without material) in the center of the image.

Flow system

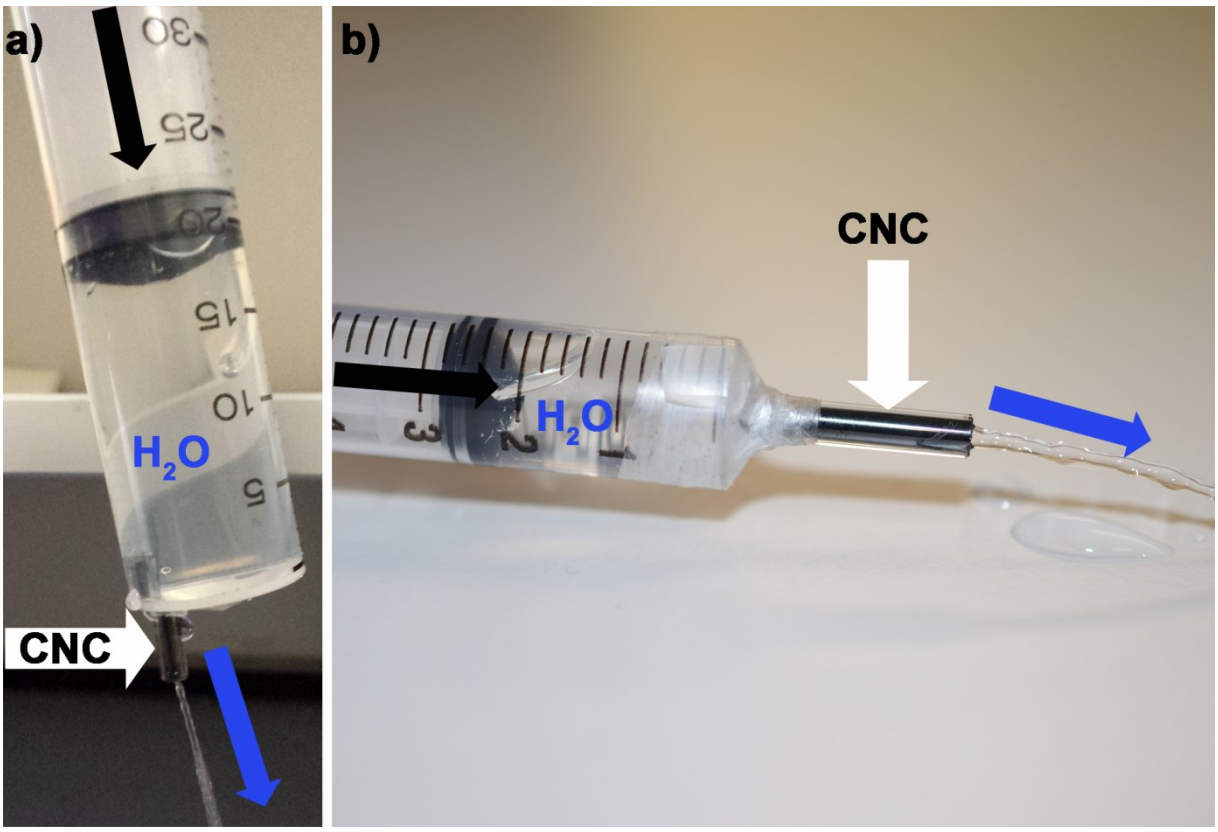


Fig. S3. (a,b) Pictures of a stream of water (highlighted with blue arrows) passing through a CNC. The applied pressure is indicated by a black arrow on the syringe connected to a CNC used as needle (2 mm ID, 2 cm long). Water is passing through the CNC without noticeable loss of the VA-MWCNTs from the CNC.

CNC after synthesis

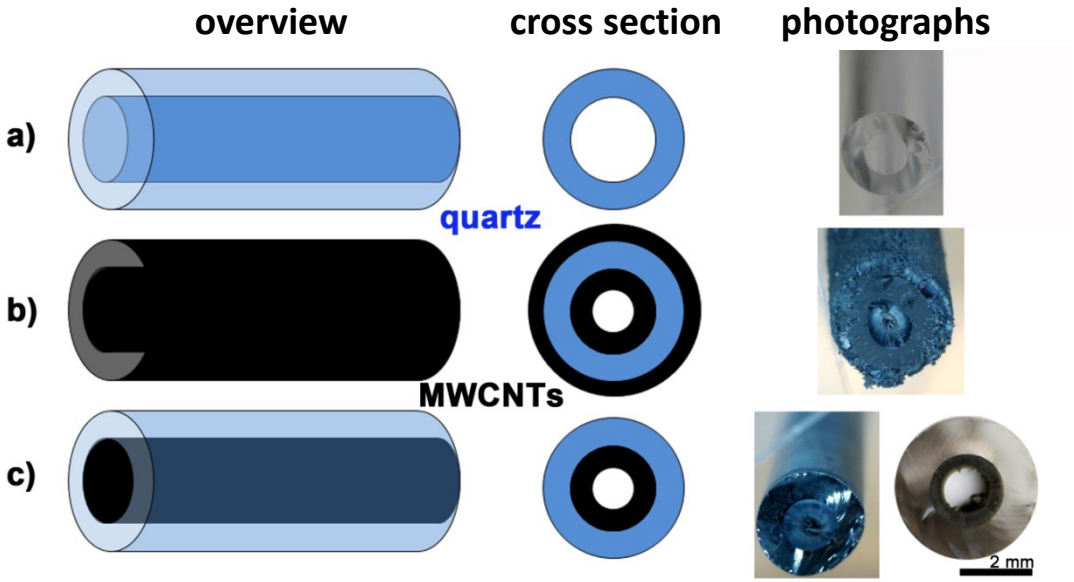


Fig. S4. Schematic representations and related photographs of quartz columns (blue), (a) before synthesis, (b) after VA-MWCNT (black) deposition, and (c) after removing the VA-MWCNTs grown on the outside surface of the columns. All columns in pictures are 2 mm inner diameter and 4 mm outer diameter.

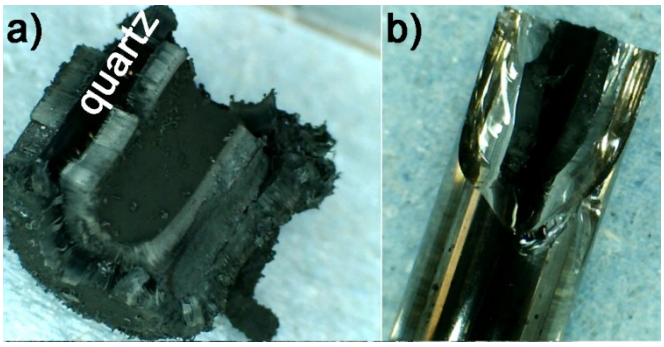


Fig. S5. (a) Optical image of a cross section along a 2 mm ID column axis (longitudinal section) before removing the outer deposits. The picture show VA-MWCNTs grown on the internal and external quartz surfaces of the column. (b) Optical image of a CNC after removal of the VA-MWCNTs grown on the outer surface of the CNC, the photograph shows the growth of VA-MWCNT forests inside the column.

VA-MWCNT length profiles in CNCs

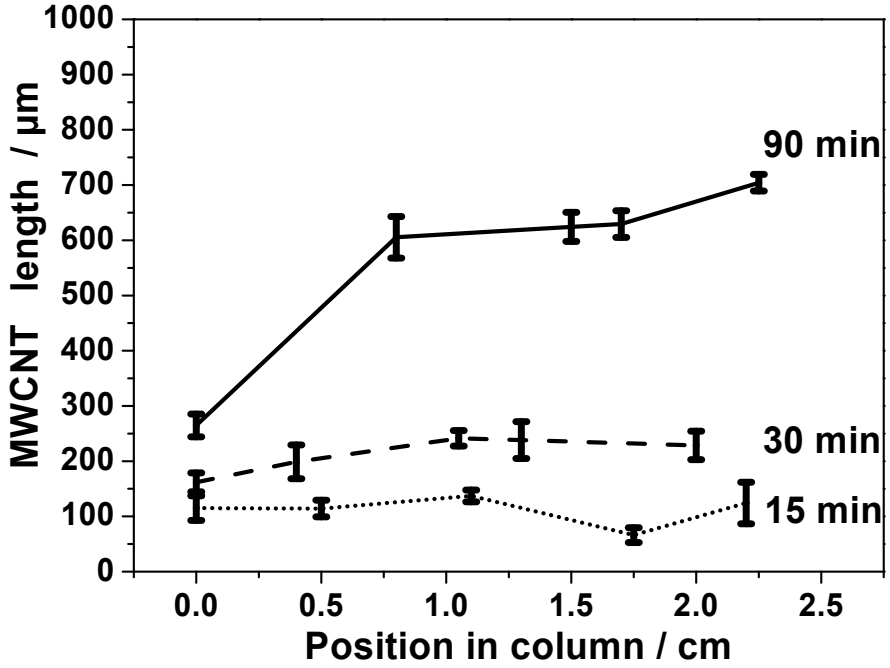


Fig. S6. Length profiles of VA-MWCNTs grown inside 2 cm long columns as a function of the position in the column and as a function of injection time of the hydrocarbon precursor during synthesis. Results were obtained for columns placed 23 cm within the furnace.

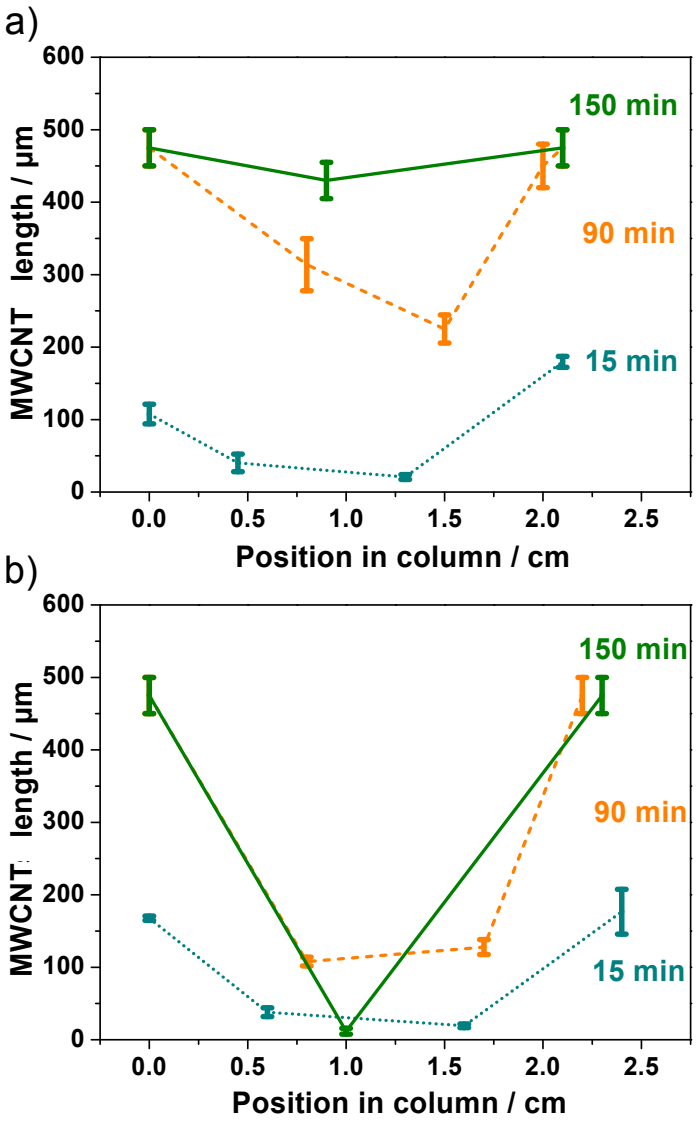


Fig. S7. Length profiles of VA-MWCNTs grown inside a 2 cm long 1 mm ID column as a function of the position in the column and as a function of the duration of the precursor injection. The carrier gas flow rate was 2500 sccm and the column placed (a) 23 cm and (b) 29 cm into the furnace.

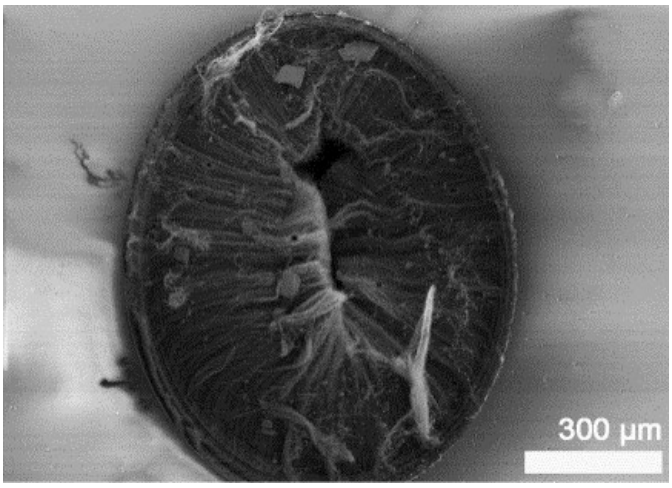
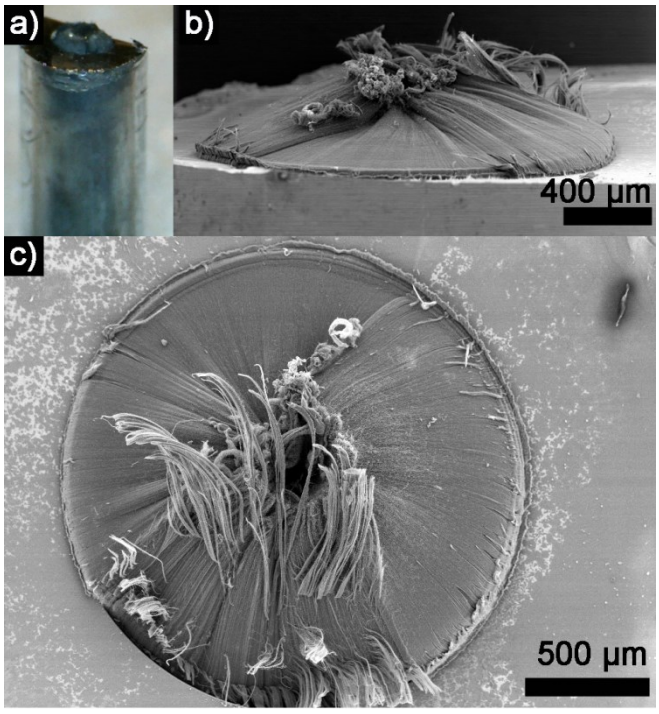


Fig. S8. Scanning electron microscope (SEM) micrograph of a completely blocked 1 mm ID column. It is observed that the as-received 1 mm ID columns do not exhibit a perfectly circular cross section.



1-

2-

Fig. S9. (a) Pictures of VA-MWCNTs protruding at the exit (OUT position) of a CNC with a 2 mm ID and 4 mm outer diameter. (b) and (c) SEM micrographs close-ups of the cross section shown in (a) revealing protruding VA-MWCNTs blocking the core of the column.

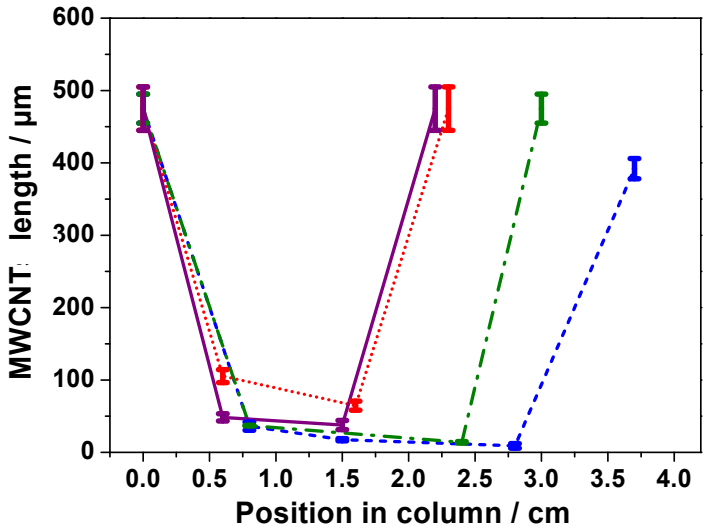


Fig. S10. Length profiles of VA-MWCNTs inside 2, 3 and 4 cm long 1mm ID columns as a function of the position in the column. The carrier gas flow rate was 1000 sccm and the precursor injected for 150 minutes for 2 cm long columns and 90 minutes for 3 and 4 cm long columns. All column-substrates were placed between 23 and 29 cm within the furnace.

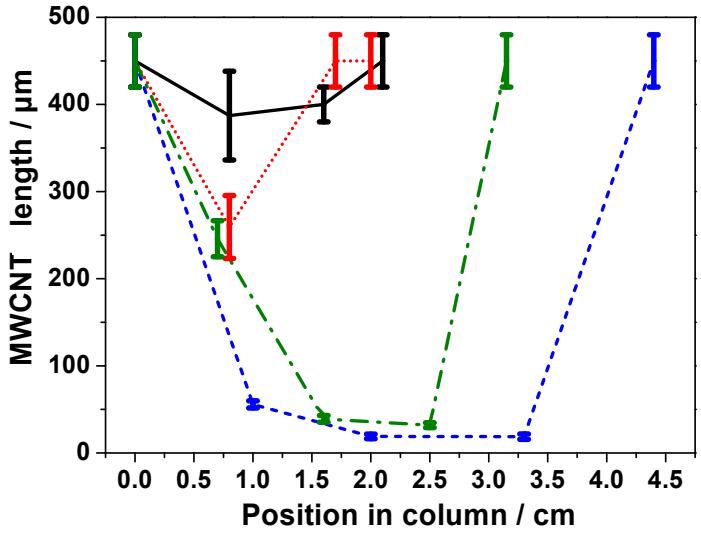


Fig. S11. Length profiles of VA-MWCNTs inside 2, 3, and 4 cm 1 mm ID columns as a function of the position in the column. The carrier gas flow rate was switched from 2500 to 1000 sccm during synthesis. The total precursor injection time was 120 minutes (20 minutes at 2500 sccm and 100 minutes at 1000 sccm) for 2 cm long columns and 90 minutes (15 minutes at 2500 sccm and 75 minutes at 1000 sccm) for 3 and 4 cm long columns. All column-substrates were placed at 23 (black, plain), 27 (blue and green) and 29 (red, dotted) cm within the furnace.

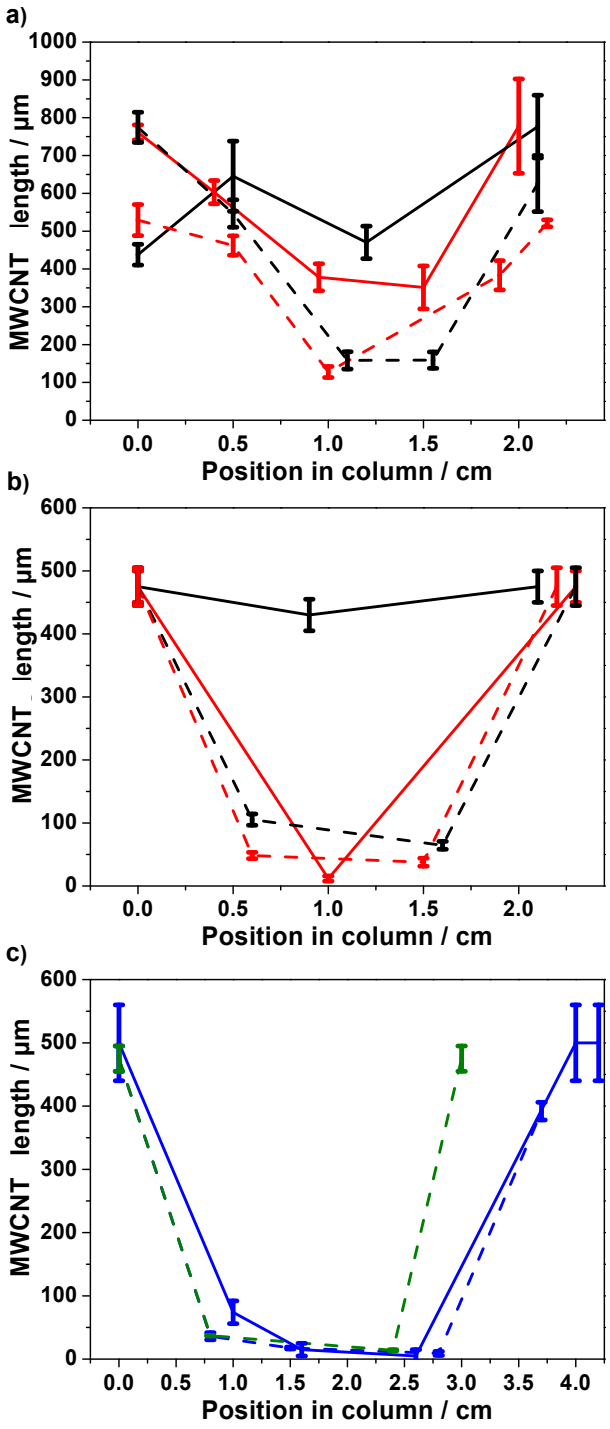


Fig. S12. Length profiles of VA-MWCNTs inside (a) 2 and (b) 1 mm ID columns as a function of the position in the column. The carrier gas flow rate was 1000 sccm (dashed) or 2500 sccm (plain). The column-substrates were placed 23 (black), 27 (green and blue) and 29 cm (red) within the furnace. Experiments were performed with precursor injection times of (a and b) 150 minutes or (c) 90 minutes.

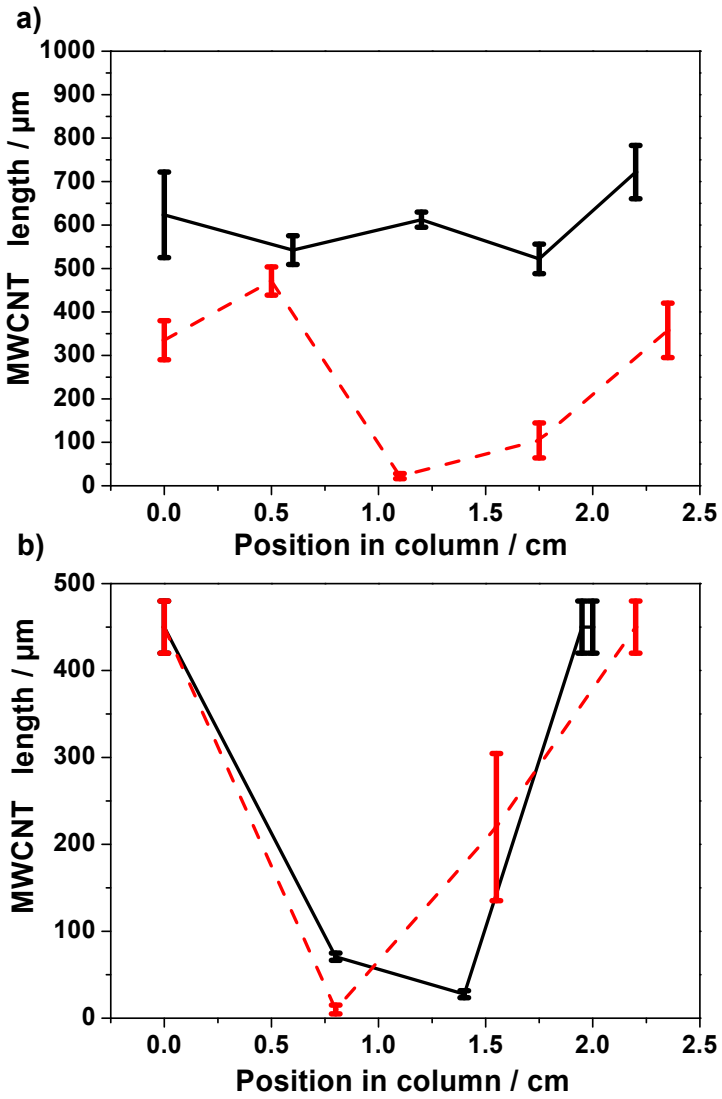


Fig. S13. Length profiles of VA-MWCNTs inside 2 cm long columns with (a) 2 mm ID and (b) 1 mm ID as a function of the position in the column for 2 cm long columns. The carrier gas flow was 5000 sccm and column-substrates were placed 39 (black, plain) and 45 cm (red, dashed) within the reactor. The precursor injection time was 90 minutes.

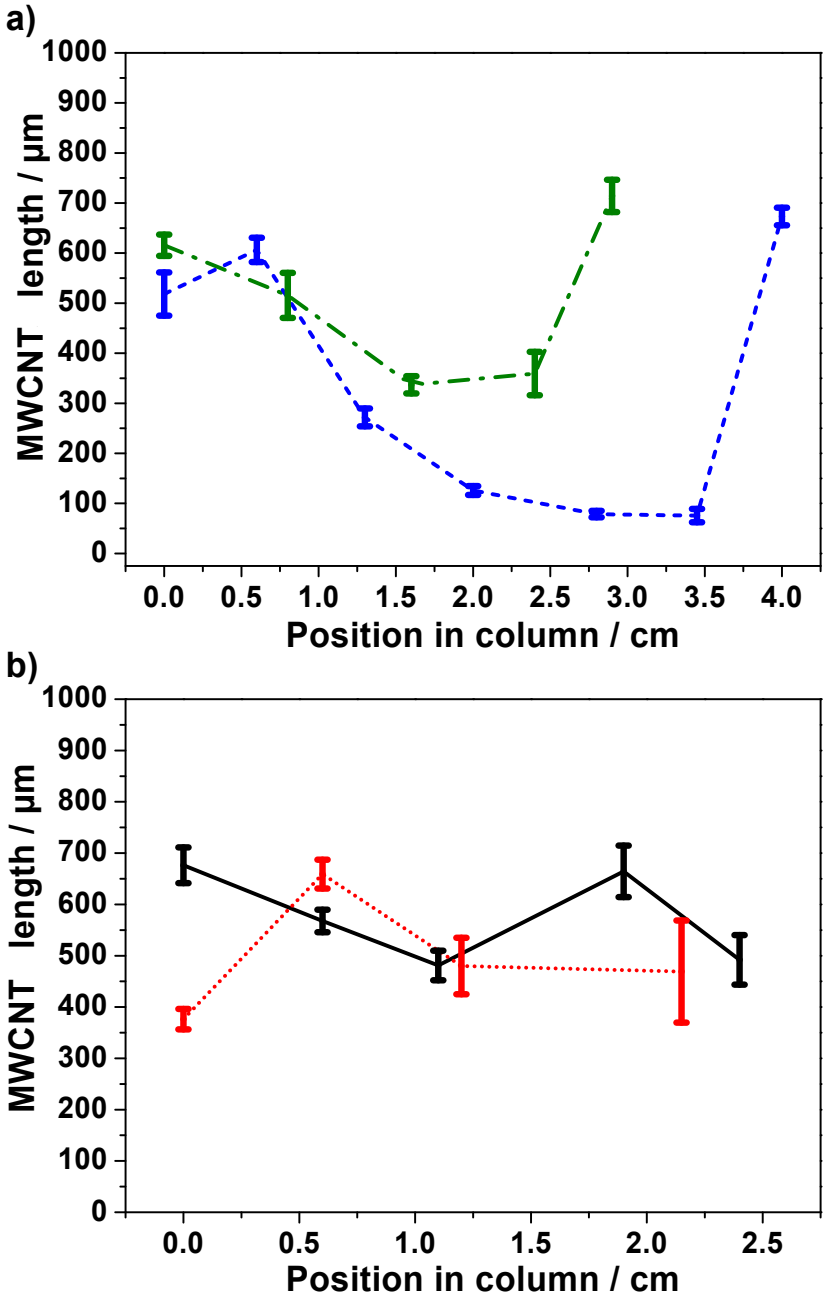


Fig. S14. Length profiles of VA-MWCNTs inside 2 mm ID columns as a function of the position in the column. A change of the carrier gas flow rate was performed during synthesis and the precursor injection time was (a) 15 minutes at 2500 sccm and then 75 minutes at 1000 sccm. Samples were placed at 27 (blue and green) cm into the furnace. The reproducibility of the results displayed in Fig. 5a is reported here in (b) where samples were placed 23 cm (red) or 29 cm (red) into the furnace.

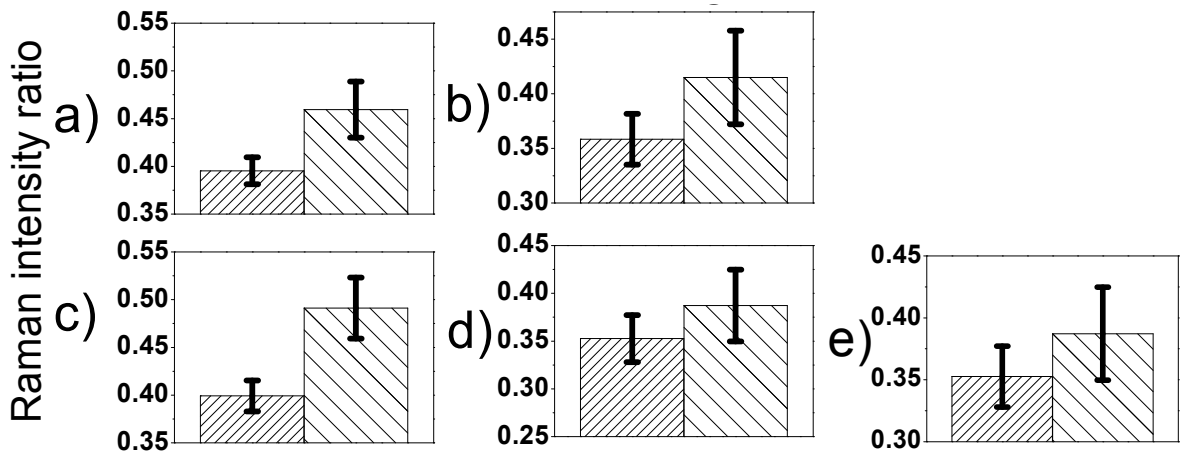


Fig. S15. Raman intensity ratios of VA-MWCNTs grown at the entrance (IN, dense stripes) and exit (OUT, sparse stripes) of a column with inner diameter (a, b and e) 2 mm and (c and d) 1 mm with length (a and c) 2 cm (b) 3 cm and (d and e) 4 cm. The carrier gas flow rate was 1000 sccm and the precursor injected for (a and c) 150 minutes (b, d and e) 90 minutes. Substrates were placed between 23 and 29 cm into the furnace. In contrast to the other flow rates the I_D/I_G ratio is now slightly higher at the exit rather than the entrance of the tubes, correlating with the longer MWCNTs observed at the IN position rather than OUT.

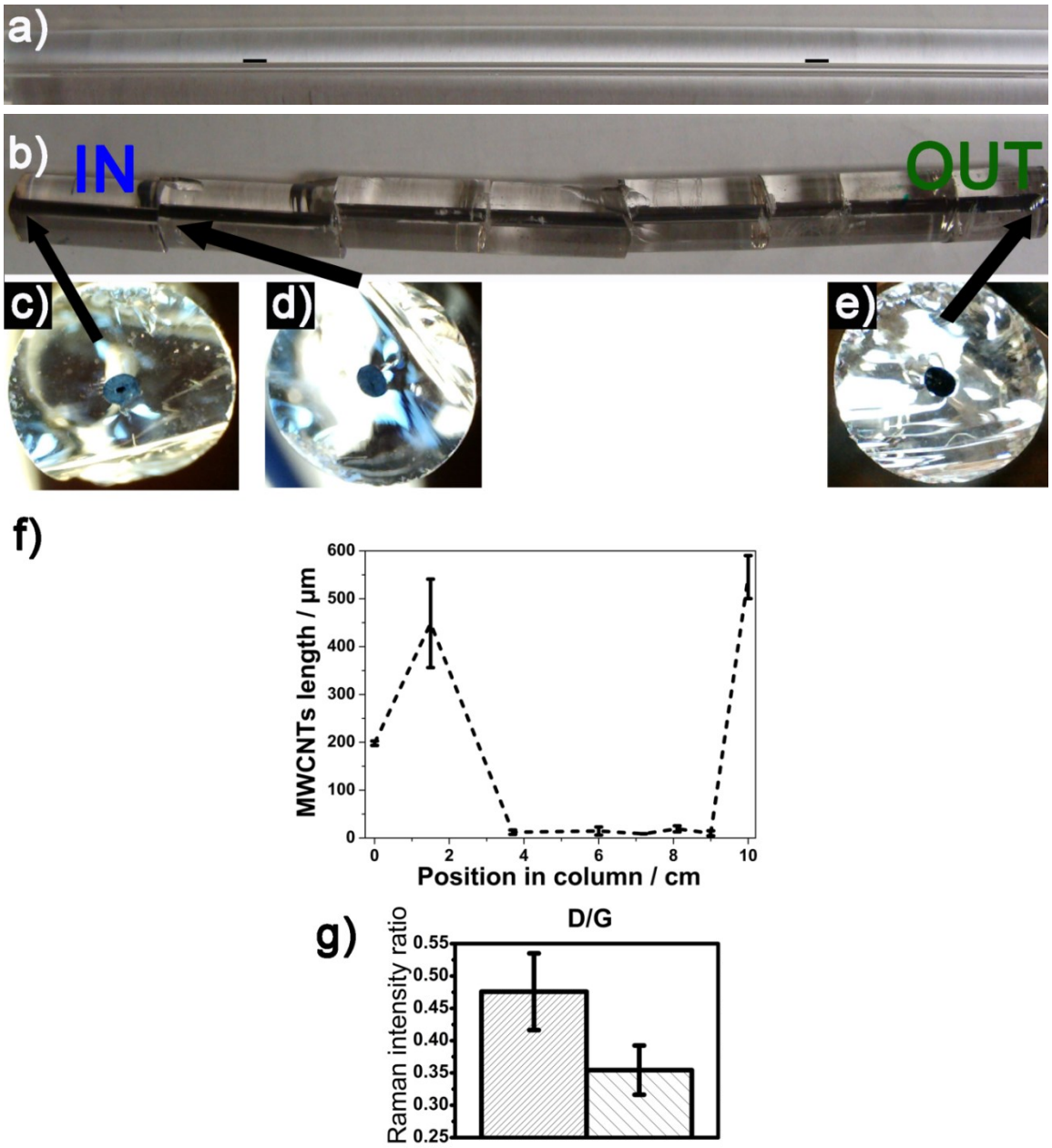


Fig. S16. Photographs of (a) 1mm ID column before synthesis. (b) 10 cm long 1 mm ID column after synthesis and after cross sectioning in order to measure the MWCNT length profile in the CNC. Associated cross section photographs (c) at the entrance of the column, (d) at 1.5 cm within the column, and (e) at the exit of the column. The carrier gas flow rate was 2500 sccm and the duration of the precursor injection was 90 minutes. Substrates were positioned 27 cm into the furnace. (f) VA-MWCNTs length profiles for MWCNTs grown in the same column as a function of the position in the column. (g) Raman intensity ratios comparing values obtained at the IN and OUT positions.

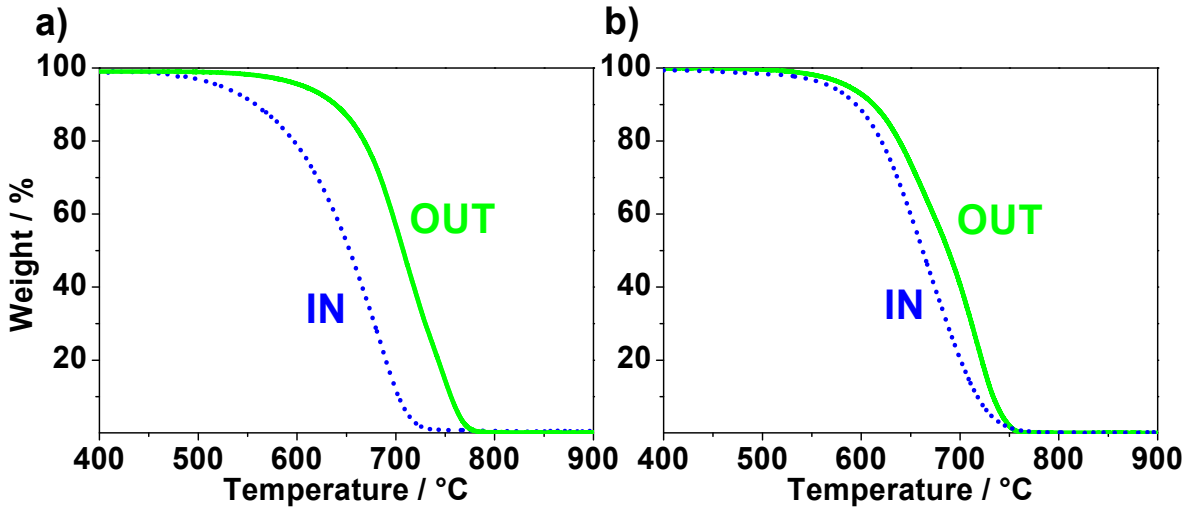


Fig. S17. Thermogravimetric analysis of MWCNTs collected at the IN and OUT positions of two 2 mm ID CNCs. A carrier gas flow rate of 2500 sccm was used for the synthesis of both CNS. The precursor injection time was (a) 90 minutes and (b) 150 minutes.

The oxidation resistance of MWCNTs grown at the exit (OUT) of the column is higher than for MWCNTs grown at the entrance (IN) since the temperature at which oxidation and mass loss happens is higher for the OUT (green, plain) than the IN (blue, dashed) curve. These results suggest a difference in quality of MWCNTs to be correlated with the difference of length and in Raman spectra observed. Different growth conditions at the two ends of the column probably account for this observation. Measurements were performed with a Perkin Elmer Pyris Thermogravimetric Analyser from 100 °C to 900 °C at 10 °C min^{-1} and samples dried overnight at 200 °C under nitrogen.