Supporting Information

Nanodrawing of Aligned Single Carbon Nanotubes with a Nanopen

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The additional materials in this supporting information are aimed to give the reader a better understanding of the drawing process from different points of view. This includes a chemical analysis of the drawing of complex structures using Raman spectroscopy including the chemical orientation parameter, S, discussed in the main text. In addition, the parameters associated with the actual process of drawing are discussed and illustrated. These include the drawing direction and geometry of the nanopen, the concentration of the dispersion, drawing speed, imposed AFM force, SWCNT concentration associated with line dimension and the washing process.

a. Drawing complex SWCNT structures & their Raman chemical analysis

Using AFM lithography software it was possible to write complex patterns while monitoring the drawing process with the on-line optical microscope. As noted the Nanopen does not obscure the field of view of the optical microscope since only the tip is exposed to the optical axis. Also of importance is that the angle of the bend of the probe tip relative to the cantilever is chosen so that tip apex is not shadowed, by the converging angle of the focused laser beam for the largest numerical aperture lenses used, even those of NA 0.7. In addition, the cantilever is high enough 60-100 μ to be out of focus of the optical microscope lens. This is seen in Figure S1a. Thus, it was possible to record movies of the drawing process (Movie 1). Images seen in this movie are reproduced in Figure S1 and S2.

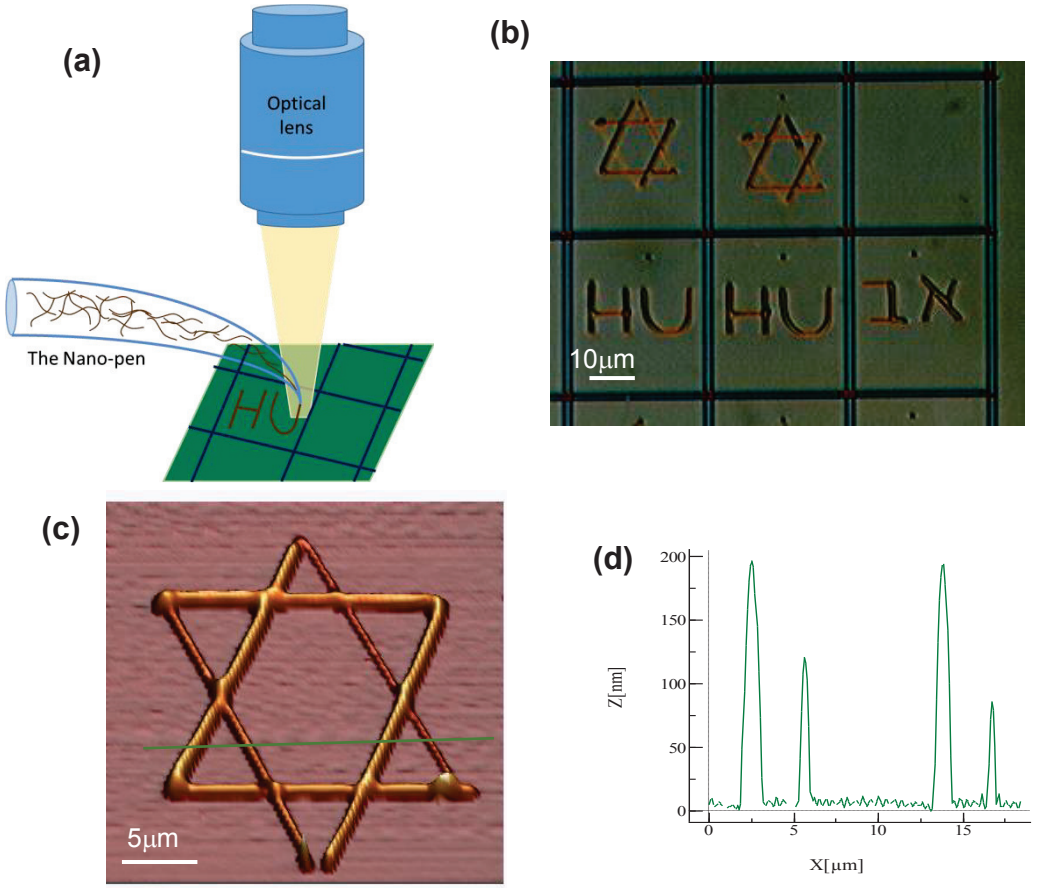


Figure S1. Examples of drawing of complex SWCNT patterns on SiO_2 substrate. (a) Illustration of the nanopen drawing system. Cantilevered glass probes with AFM sensitivity allow for a complete view of the probe tip which permits a direct view of the drawing with a standard upright optical microscope. This permits transparent integration with spectroscopic methodologies such as Raman for chemical characterization of the drawn structures. (b) Drawing of the letters of the Hebrew and English alphabet using NanoChemPlotter™ (Nanonics Imaging Ltd, Jerusalem, Israel). All patterns were drawn with the

same nanopen tip. The structures were drawn at a sufficiently large dimension to be seen through the integrated optical upright microscope for video recording using a CCD camera with x500 magnification. A video of this process is attached (Movie 1). The patterns were written with a 150 nm pipette in contact mode with a writing speed of 5 μm/s. Between the writing of the patterns the nanopen was kept out of contact with the surface at a distance of 0.5 micron. This allows control of when the writing occurs (c) A 3D AFM of the Star of David with (d) an associated AFM line scan. The ability to draw a structure such as the Star of David and the clearly higher regions at the cross points in the 3D AFM show the capability to write add a line to on an already written structure. The optical image associated with this AFM is shown in panel b above (top left image).

For proving that there are SWCNTs in the drawn structures, Raman was used for chemical analysis. Raman spectra and imaging of the patterns were obtained using a Renishaw inVia Raman microscope at an excitation wavelength of 514 nm with the laser being circularly polarized by a λ/4 waveplate and with a spot size of ~1 μm^2. Integration time was 90s per pixel. By fitting the G+ Mode at 1594 cm^{-1} by a simple Lorentzian model with a linear background we extracted the intensities of the G+ Mode at every point measured. All Raman measurements except the alignment measurement in the next paragraph were done with the same instruments and under the same conditions.

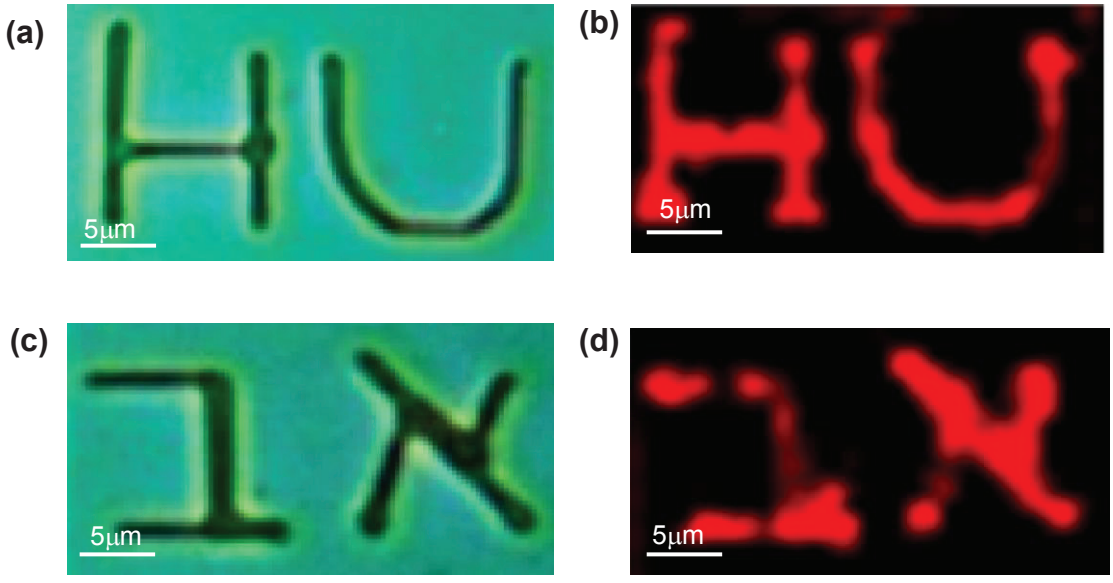


Figure S2. CCD imaging with Raman chemical analysis. (a) CCD image and (b) Raman mapping of the G+ mode of "HU" structure. (c) CCD image and (d) Raman mapping of the G+ mode of the Hebrew alphabet structure.

b. The basis of *S* orientation parameter

For checking the orientation of the tubes on a large area, straight lines have been written as shown in Figure S3. This is shown in the optical image of the lines in Figure S3a. After washing of the lines with distilled water to remove the chemicals in the dispersion (such as surfactants etc) associated with the drawn SWCNTs there appears to be no drawn lines remaining on the surface (see Figure S3b). However the Raman tells a different story. As shown in Figure S3c-e different Raman modes of SWCNTs that were imaged after this drawing and washing process clearly show SWCNT lines where the optical image in Figure S3a had shown that the drawing was performed.

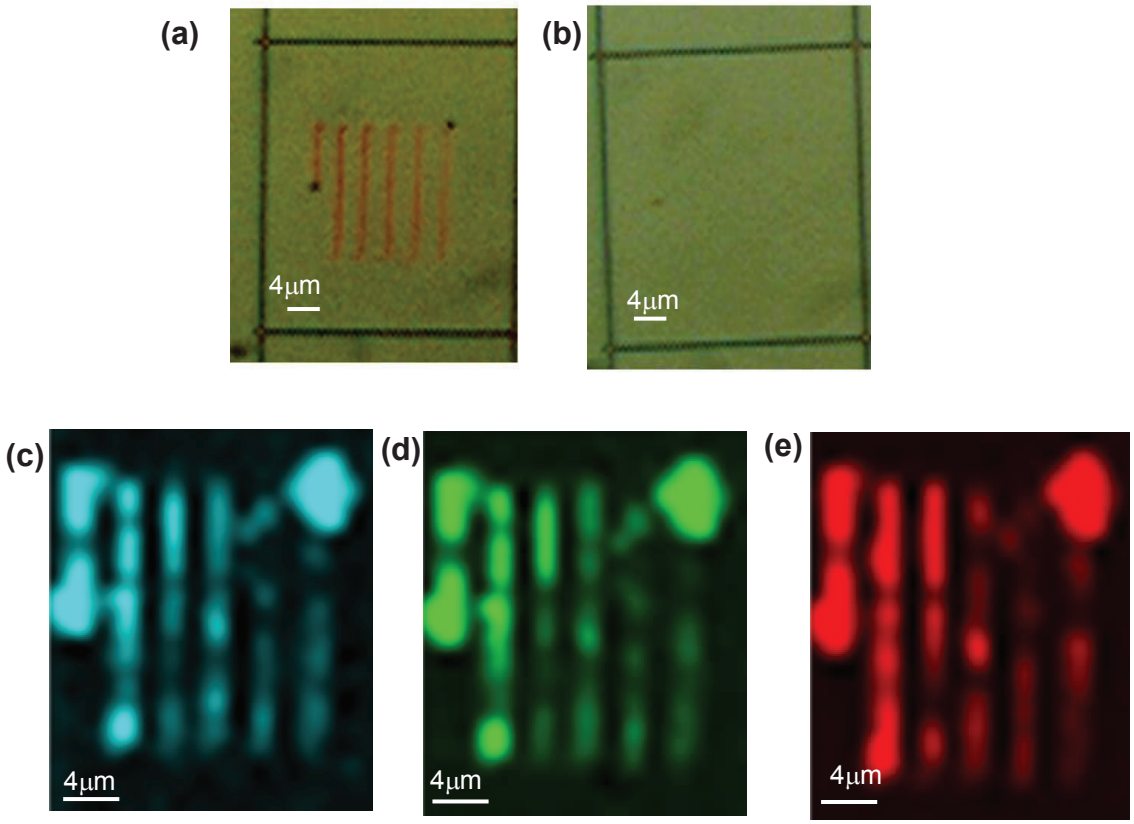


Figure S3. Optical & Raman imaging of drawn SWCNT lines. (a, b) USB camera image with a 500X magnification of the optical microscope, (a) before and (b) after the surface washing procedure. This washing procedure involves simply rolling a drop on the surface and then exposure to a drying operation with nitrogen after waiting 3 hours following the drawing of the structures. (c-e) Raman images of the optical image after the washing operation. Shown is an image of (c) the D mode (d) the G- mode and (e) the G+ mode of the SWCNT Raman spectrum.

The Raman scattering of the structures was used to measure the alignment of the SWCNT's deposited on a surface. As a measure of the alignment we used the order parameter that has been described previously.[31] As noted by Camilo Zamora-Ledezma et al, [31] the order parameter can be written as

(1) $$S = \frac{1}{2} < 3\cos^2\beta - 1 >$$

The angle β is between the tube and the vertical direction in our case, resulting in a parameter range from 1 to -0.5, where 1 implies total vertical alignment (i.e. parallel to the drawing direction) and -0.5 total horizontal alignment (i.e perpendicular to drawing direction). Using (1) we define average angles between 30° (S=-1/8) and 60° (S=5/8) as unaligned.

Assuming a thin, non-absorbing layer of nanotubes and measuring different polarization directions the parameters VV, HH and VH [1] were measured. Here the first letter of the subscript indicates the polarization of the laser and the second the polarization of the analyzer

(2) $$S = \frac{3I_{HH}+3I_{VH}-4I_{VV}}{3I_{HH}+12I_{VH}+8I_{VV}}$$

In order to show the overall alignment of the written CNT's, we performed Raman mapping of the patterned area (see Figure S3a) and recorded the Raman spectrum at each pixel for VV, HH and VH polarizations. The separation between adjacent points was 0.5 µm. For analysis we used the intensity of the G-Mode (See Methods).

In total, SWCNTs with a high vertical alignment were drawn as can be seen in Figure S4b. Red indicates the degree of total alignment. The blue unaligned part comes from the corner points when the tip changed direction and at the very start and end points of the drawing process.

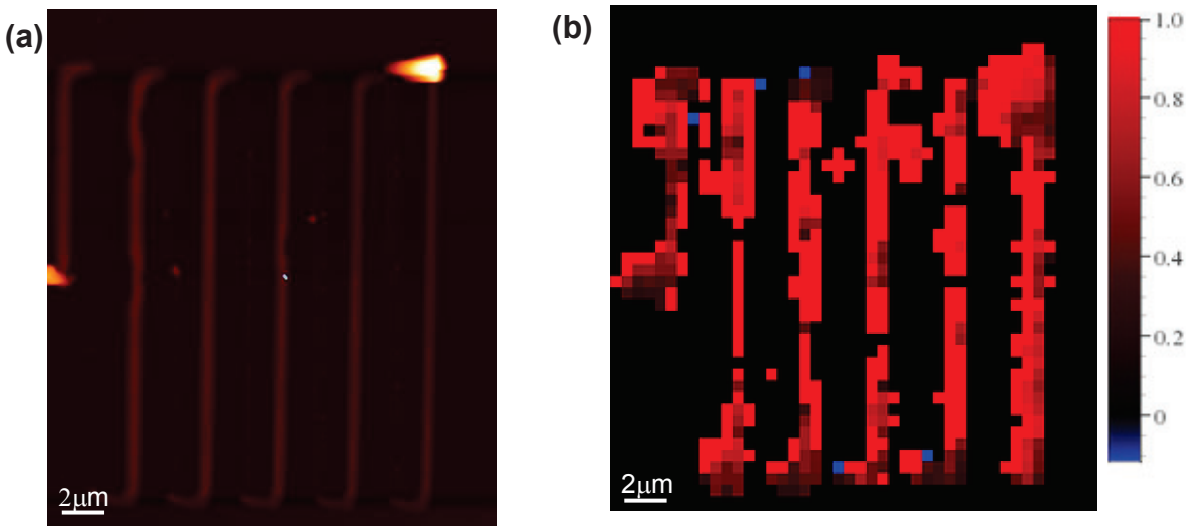


Figure S4. AFM and Raman orientation parameter mapping. (a) The AFM image before washing. (b) The Raman analysis after washing. *S*=1(red) means that the tubes are totally aligned in the vertical direction. *S*=-0.5 (blue) mean total horizontal alignment. The lines of SWCNTs were drawn in a continuous mode where the nanopen changed its direction by 90 degrees at the extremes of each line and as is seen in panel b the *S* parameter was altered in an appropriate way.

The histogram in Figure 2e in the main text is calculated from Figure S4b above.

c. The drawing parameters

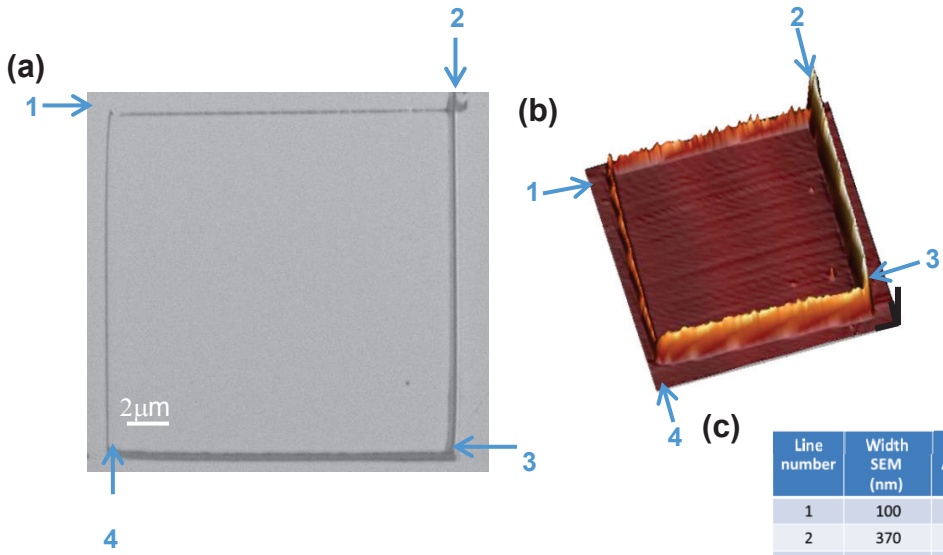
1. The drawing direction and geometry of the nanopen

We found that the angle of the tip of the nanopen relative to the cantilever had considerable influence on the drawing process. The nanopen tip needed to be oriented close to perpendicular to the surface with less than 2 degrees of deviation. The angle was very critical especially in nanopens with aperture sizes that were smaller than 150 nm.

With such mounting it was further noted that the size of the written lines were altered due to changes in the direction of the writing (see Figure S5). This results, as in all fountain pens due to the nature of the pen nib, to changes in the line dimension as a function of the direction of drawing. The advantage with the nanopen is that once this

is appreciated one can choose the drawing direction to get at least two line widths with different heights using the same tip.

Since the AFM image of the lines is a convolution of the AFM tip size with the line dimension we also investigated the structures with SEM which gave more accurate linewidths for the drawn lines. The AFM of course gave accurate values for the height of the line. In the following paragraphs the line widths described were measured using SEM analysis while the line heights were characterized by AFM imaging.



Line number	Width SEM (nm)	Width AFM(nm)	Height (nm)
1	100	360	60
2	370	660	200
3	400	720	120
4	105	420	70

Figure S5. Changing drawing direction. (a) SEM and (b) 3D AFM of the same square. The lines were drawn on n-type silicon with a 100 nm nanopen tip with a speed of 8 μm/s. For this writing process Dispersion II (see Methods) was diluted with distilled water with a ratio of 1:2 in order to get very thin lines. (c) Table summarizing the line widths and heights. As can be seen there are two "kinds" of lines with similar dimensions. The thin lines have the width of the nanopen tip ~ 100 nm.

2. Dispersion concentration

The concentration of the SCWNTs dispersion and its viscosity has a significant influence on the drawing. The higher the concentration - the larger the line dimensions. In addition, the larger the concentration the higher the probability of drawing bundles and pulling such bundles into free air off the surface as a result of retracting the nanopen from the surface. The exact concentration is difficult to define

since it depends on external parameters such as the degree and the time of sonication that influences aggregation. Every attempt was made to use a combination of dilution and sonication that would result in the consistency of writing of continuous lines of carbon nanotubes. Our results suggest that for a particular dispersion such combinations can be optimized.

Figure S6 shows examples of the influence of dispersion concentration. The dispersion included SWCNTs in aqueous solution with an initial concentration of 5 mg/30 ml before sonication and the surfactant sodium cholate (3% by weight). A sonication time of 60 minutes was applied. These conditions led to a very high viscosity of the dispersion and the nanopen pulled a bundle when retracting from the surface (see blue arrow in Figure S6). The bundle was released from the nanopen only when the surface was once again approached at the upper left hand square of the checker board structure. However, after such an operation this nanopen was blocked and could not be applied to further drawing operations.

The other structures in this figure were drawn after dilution with 2 ml distilled water being added to the 3 ml original solution. All the structures in the squares were done with the same 150 nm nanopen and no bundles appeared when retracting. The drawing was done under the same conditions and with the same nanopen orifice size, as was used for the high concentration writing which had previously pulled bundles.

The width of the lines written out of the checker board was ~1 micron, while the written lines in the structures within the checker board were ~250 nm width. Both of these operations were written by nanopens with a 150 nm orifice and the only difference was the concentration.

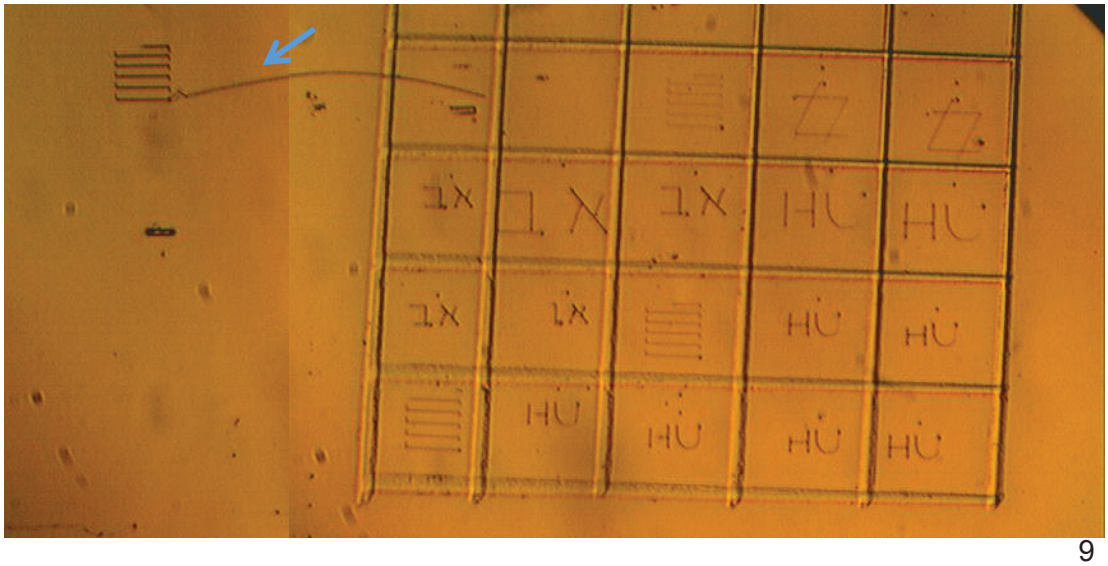


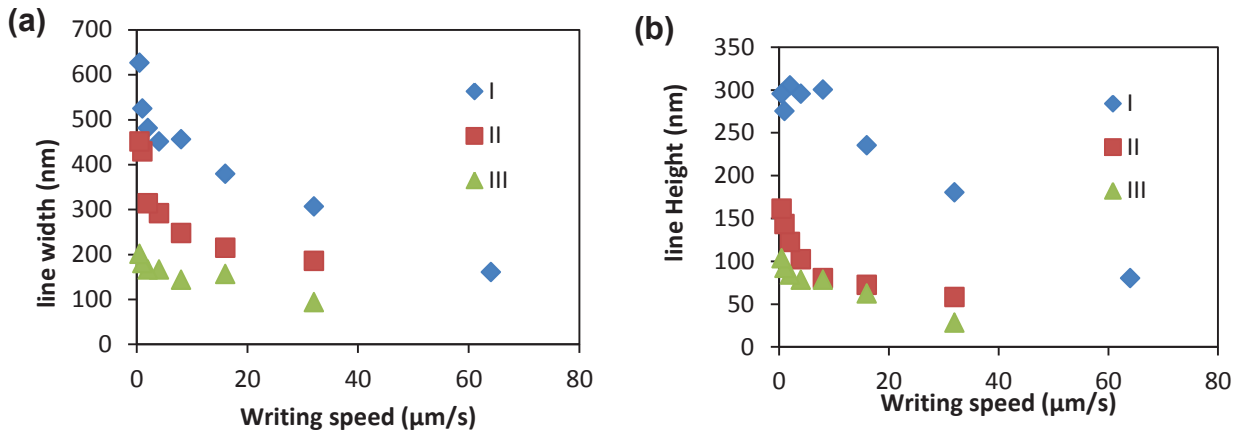
Figure S6. Effect of the SWCNTs concentration on the drawing process. A 150 nm nanopen tip drawn on n-type silicon with a speed of 8 µm/s. The structures were imaged using a USB video camera with a 1280x1008 pixel sensor placed on the output port of the upright microscope (x500 magnification). Each square is 30 µm X 30 µm.

3. Drawing speed

As was mentioned in the paper, the drawing speed affects the dimensions of the drawn lines. For characterizing the effect of speed we chose 3 different nanopens and drew straight lines with different drawing speeds. The pens and dispersions chosen were: Set I – 200 nm nanopen tip with Dispersion II. Set II– 100 nm nanopen tip with Dispersion II. Set III– 100 nm nanopen tip with Dispersion II diluted with distilled water with a 1:2 ratio.

As can be seen in Figure S7, all the nanopens were affected by drawing speed. Faster speed – drew lines with smaller dimensions. The drawing speed was changed from 0.5 to 64 µm/s. When writing 64 µm/s and faster – the lines starts to be non-continuous lines. At speeds between 2-10 µm/s, that were generally used, there are no dramatic influences on the dimension of the lines.

The influence of the diameter of the orifice of the nanopen was also investigated by fabricating nanopens with different apertures. The orifice controls the line dimensions. Also shown is the influence of the functional dependence of two concentrations for different writing speeds.



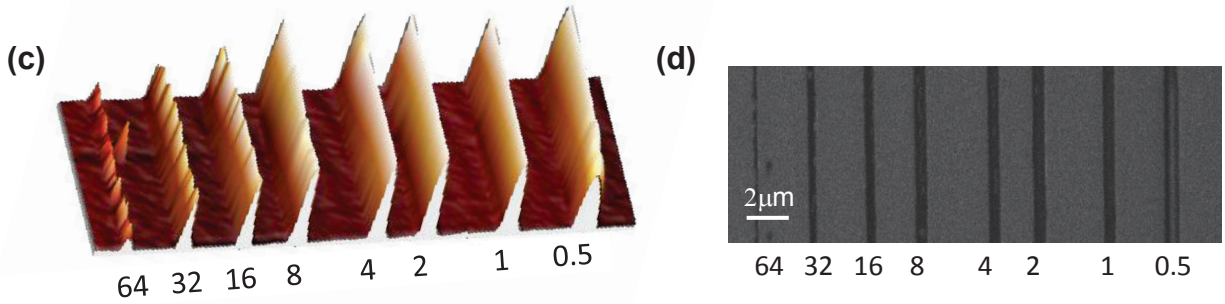


Figure S7. Effect of the drawing speed on the line dimensions. (a) Shows line widths for 3 different sets of conditions, see text for details. (b) Shows line heights for the same 3 sets of conditions. (c) 3-d AFM image and (d) SEM image of set I as an example.

4. Imposed AFM force

The imposed force of an AFM tip on a surface is measured by the set-point in volts which is the difference in voltage of two quadrants of a position sensitive detector.

The set-point used depends on at least two factors: The contact angle of the exiting dispersion with the surface on which the writing is to take place and the resistance of this surface to the pressure of the nanopen. For example, with a gold surface with a smaller contact angle and a low resistance to the pressure of the nanopen a set point of 0.1V was sufficient for writing. More than 0.2 V however caused surface scratching. On the other hand, on silicon with a contact angle with the dispersion that is larger and there is a higher resistance to nanopen pressure a higher value of the set point could be used without damage.

In Figure S8 the influence of much higher set-points on the line dimensions is illustrated.

The same 3 nanopens and dispersions mentioned above were used also for checking the influence of the set-point on the drawing on n-type silicon substrates. It can clearly be seen that the set-point does not change the drawing dimensions until some threshold is reached between 0.7-1.1 V, when the lines became much border. It should also be mentioned that even with such pressures the nanopen tip did not break, and when the set point was returned to values between 0.1-0.3 V the lines became narrow again.

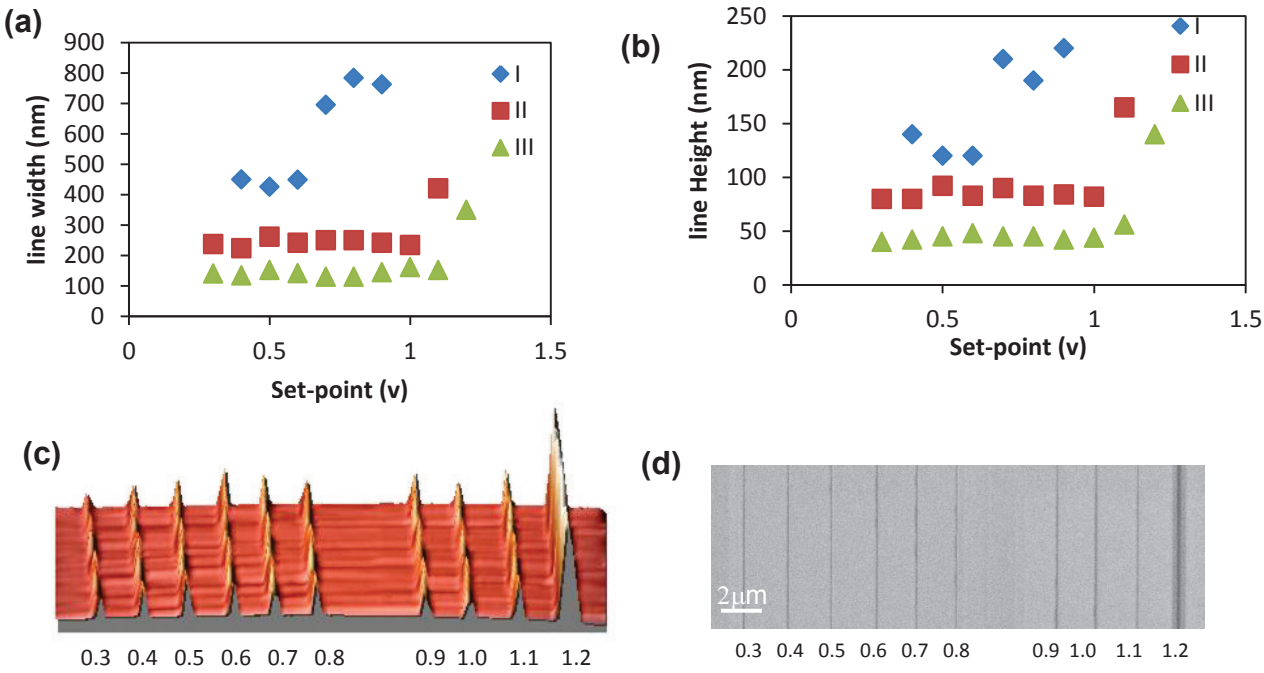


Figure S8. Effect of the AFM setpoint on the line dimensions. (a) Shows line widths for different set points for 3 different sets of orifices and dispersions as noted in the section c3 above. (b) Shows line heights for the structures drawn in panel a. (c) 3-d AFM image and (d) SEM image of Set III noted above as an example.

5. SWCNT concentration associated with line dimension

As mentioned in the main text, SEM or AFM cannot detect whether SWCNTs are present in the drawn lines before they are washed. This is due to the low concentration of SWCNTs in the dispersion that is dominated by other chemicals. Therefore, in order to estimate the amount of SWCNTs in the drawn lines before washing, mapping with Raman scattering was used. Three lines were drawn with the same nano-pen and dispersion, but with different parameters such as writing speed and writing direction. Lines with 3 different dimensions were written. AFM and SEM images were taken for measuring the line dimensions.

For each line, a Raman scattering map was measured with the same parameters (λ=514 nm excitation, integration time (90 s) and a lateral spatial resolution of 0.5 µm in both directions based on the nature of the objective used). In Figure S9, the lines

and their Raman analyses are shown. The first line, with the largest dimension, has G+ peaks intensities of 1000-7000 counts which prove the presence of big bundles of tubes before washing the line. The second line, with a dimension in between the largest and the smallest written line, has G+ peak intensities of 100-700 counts. Thus, this also proves the presence of single or small bundles of tubes. The smallest dimension line has SWCNTs in only one dot at the end of the written line with a weak signal of 50 counts. All the other areas were without any signal. This proves that the line with a 200 nm width contains almost no tubes at the conditions used to record the first and second line.

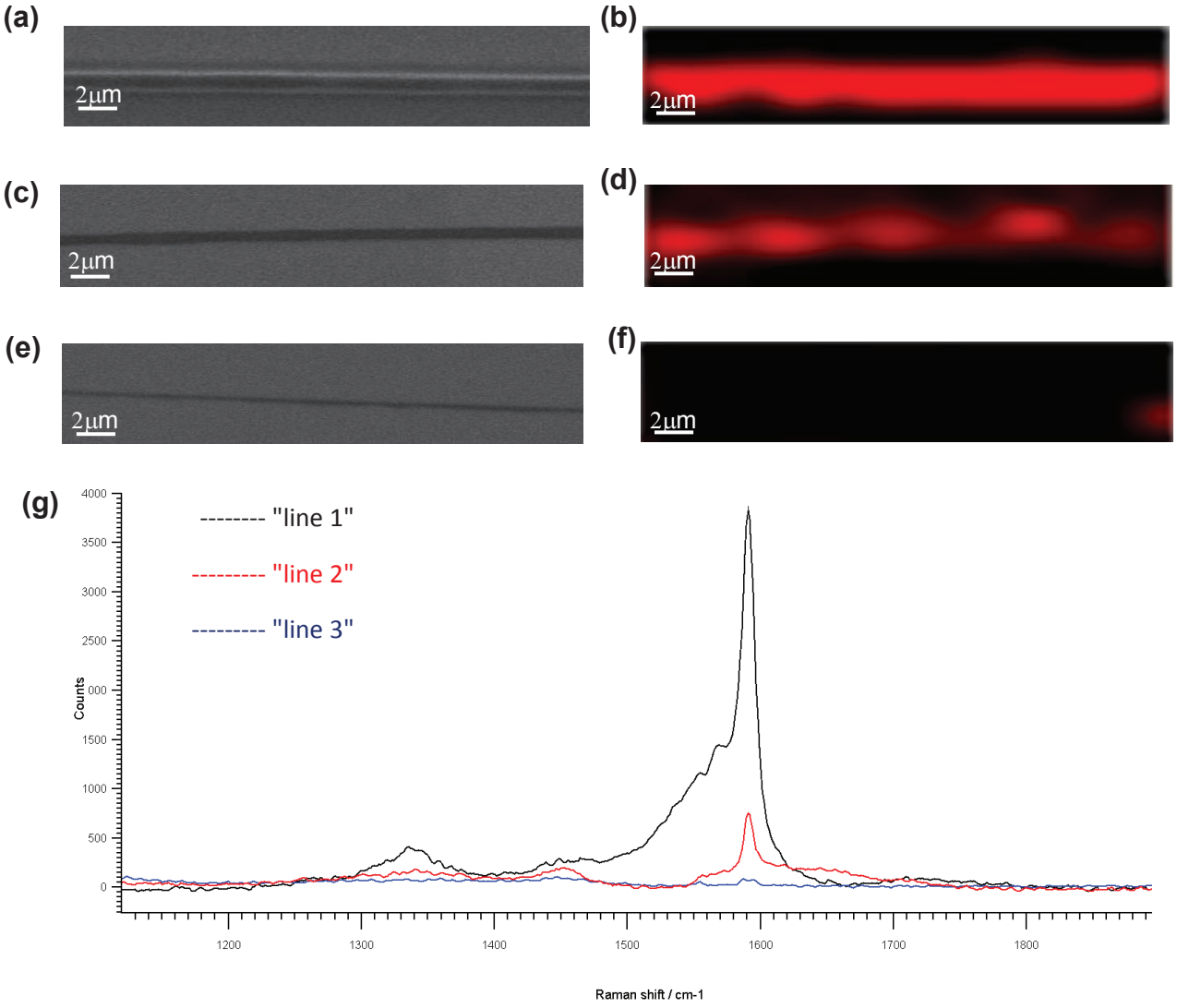


Figure S9. Effect of the lines dimension on the presence of SWCNTs for a dispersion with 0.2% by weight of SWCNTs. (a) SEM image and (b) Raman mapping of "line 1", with 140 nm height and 680

nm width. The peak intensity of the G+ mode at each pixel is 1000-7000 counts. (c) SEM image and (d) Raman mapping of "line 2", with 110 nm height and 420 nm width. The peak intensity of the G+ mode at each pixel is 100-700 counts. (e) SEM image and (f) Raman mapping of "line 3", with 55 nm height and 210 nm width and a weak signal of 50 counts for the G+ mode at one point over the entire Raman map. (g) examples of Raman spectra of each line.

As was mentioned in the main text, in lines that were less than 200 nm wide no SWCNTs were deposited after washing. The Raman data prove that before washing there were no detectable tubes in these lines and thus no chance of detecting any remaining tubes after washing. It is possible to increase the concentration of SWCNTs and then there will be a high probability of bundle formation, making it very challenging to write individual tubes.

d. Washing process

The washing process also influences the amount of remaining SWCNTs on the surface. The main influence is the time that is given for the SWCNTs to settle on the surface before washing. A time of 1-3 hours is the minimum for getting single tubes with good statistics. However if the time between drawing and washing is longer for example 1 day or more bigger bundles will be deposited.

The washing process was performed by placing a drop of water on the drawing, and rolling it from the surface .Also the direction of the washing has significant influence. If a big drop of water is placed on the whole sample and the waiting time is a few minutes no SWCNTs will be placed on the surface. However, if we roll a drop very quickly on the drawn area the probability to get tubes on the sample – became very high. The direction of the washing is also important, when this is done in a direction parallel to the direction of the drawing there is a higher probability of effectively placing SWCNTs. The alignment of the SWCNTs was not affected by the washing process.

After the first wash, when the SWCNTs have made a strong connection with the surface, other washing steps, like putting a drop on the whole sample, will not decrease the amount of SWCNTs that already had been connected.

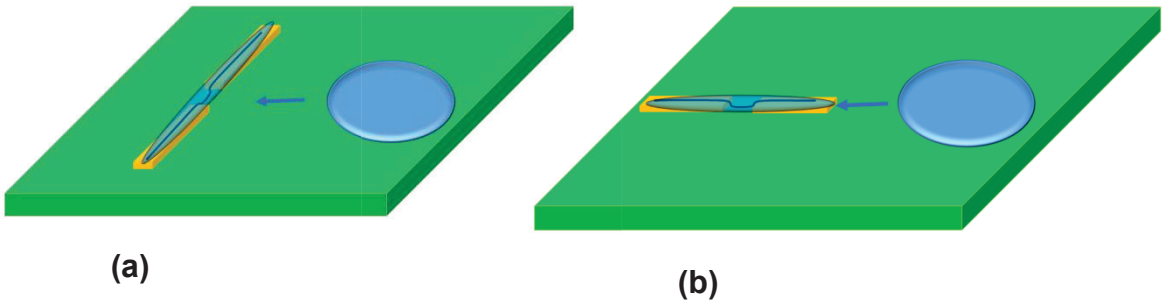


Figure S10. Washing options after the drawing process. (a) The washing operation by rolling a drop of distilled water in a direction perpendicular to the drawn line. (b) The washing by rolling a drop in the parallel direction of the drawn line. The "rolling" needs to be fast (<1 sec for short settling times) in order to get good placement of the SWCNTs. The parallel direction gives better results.

Examples of placing long lines with single and aligned SWCNTs across gold electrodes and over a gap are shown in figure S11. The SWCNT placement was done by rolling a drop of distilled water in a direction parallel to the drawn lines, 2 hours after the drawing process. A movie of drawing the SWCNT interconnections over the gold electrodes is also attached (Movie 2).

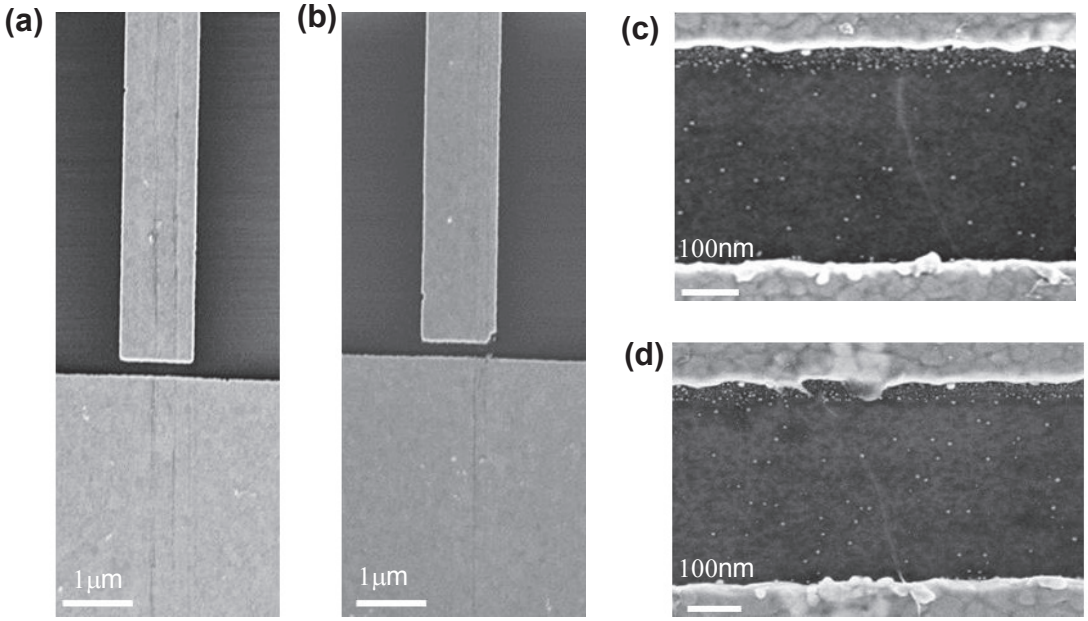


Figure S11. Drawing single and aligned SWCNTs on a pre-patterned chip. (a,b) SEM images of the thin lines of SWCNTs over electrodes of 1.2 micron width. (c,d) High resolution SEM images of single SWCNTs over a 500 nm gap between two gold micro-pads.