

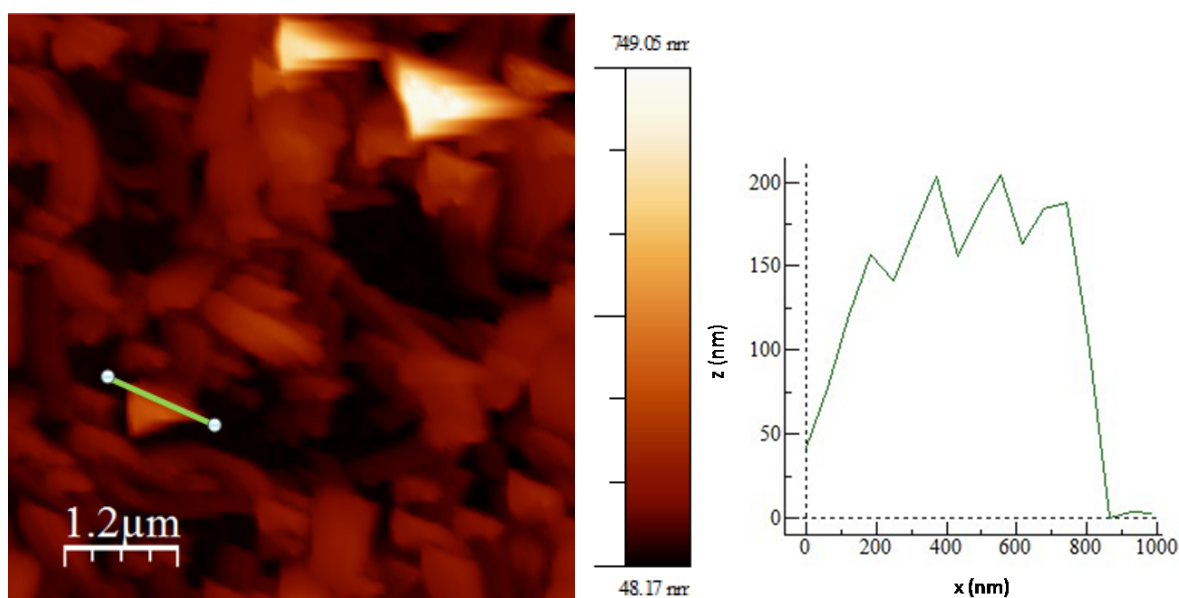
Vertical self-assembly of modified multiwalled carbon nanotubes on gold surfaces induced by chitosan and Tween

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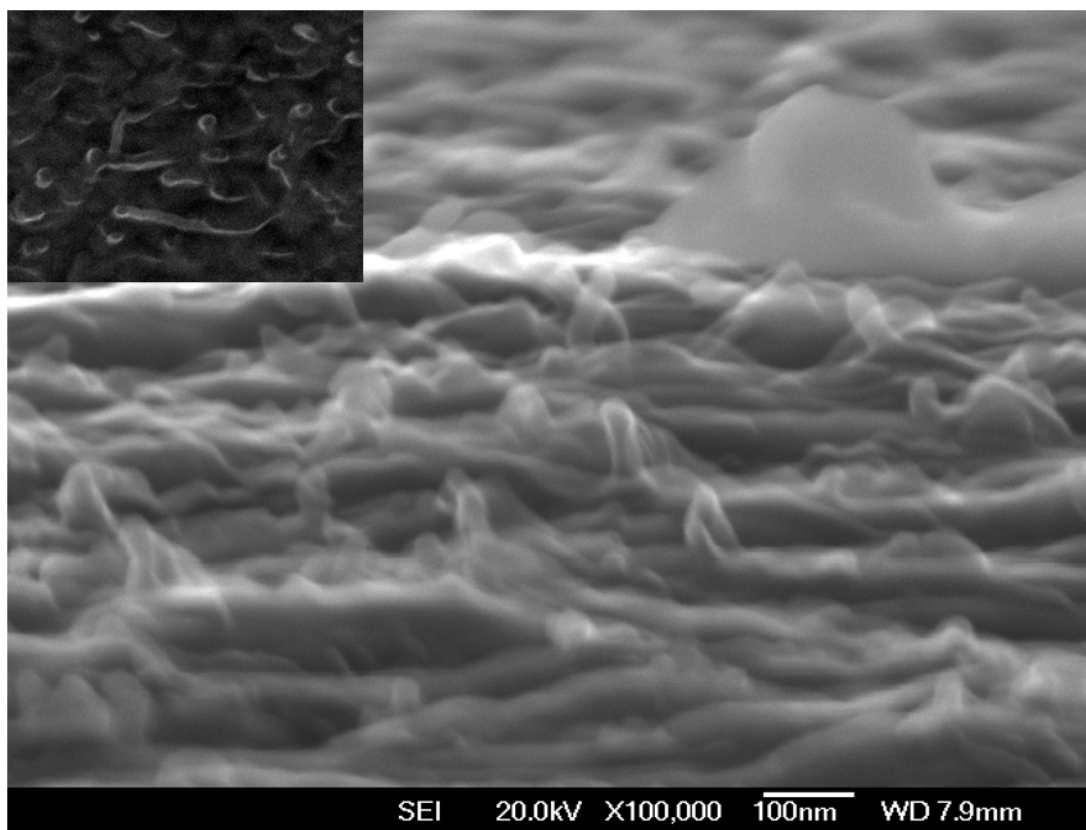
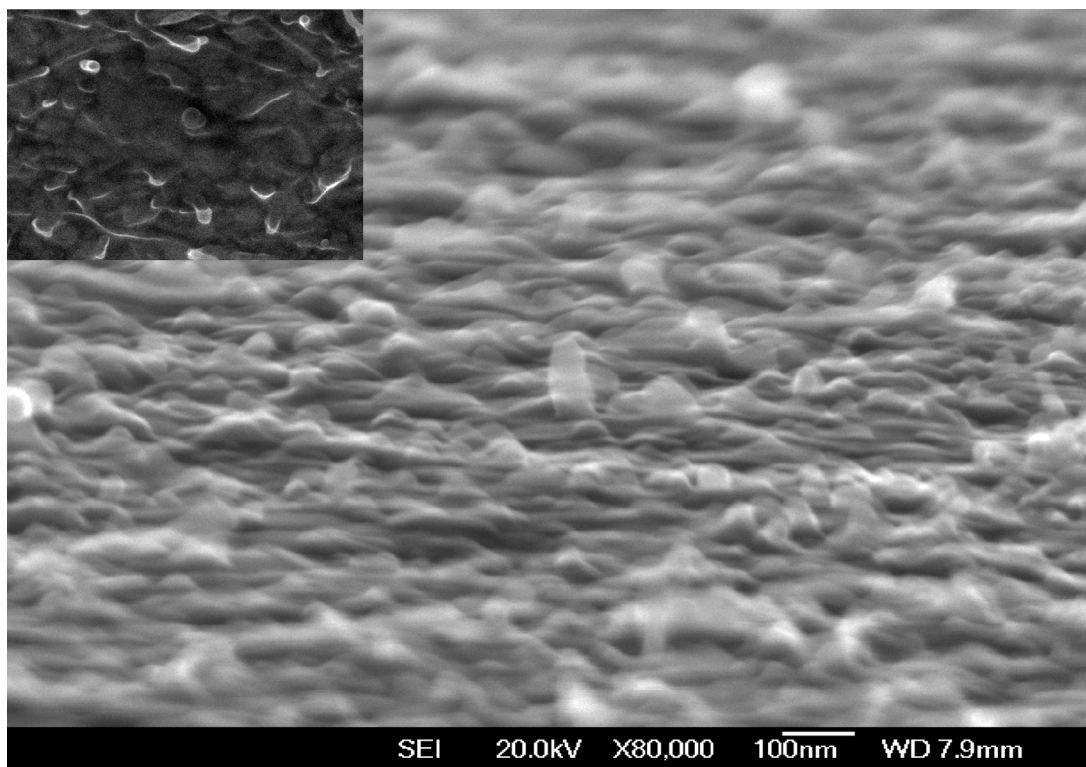
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Supporting Figures

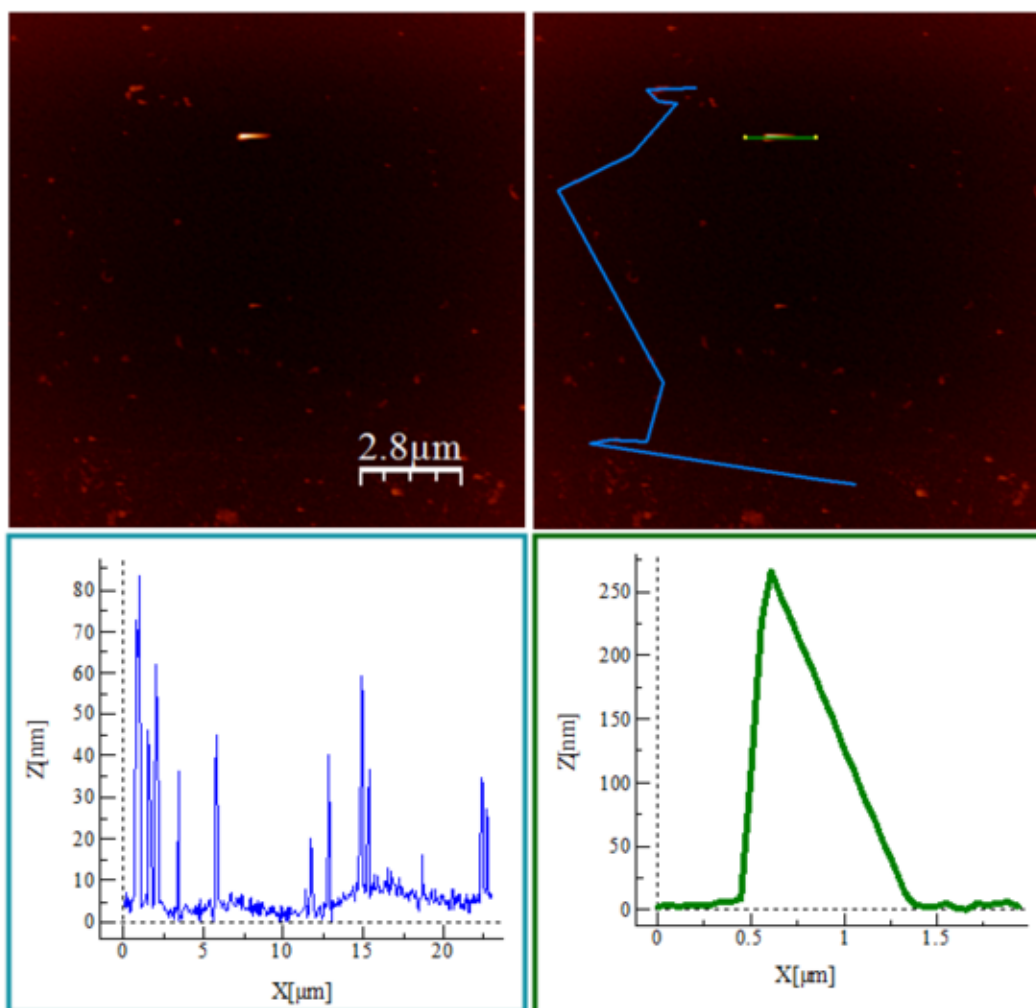


S-1: AFM micrograph of a gold surface modified with MWNT-AET with the assistance of Chit (left), and profile of a selected trajectory (right). In the profile the highest objects do not correspond to a single MWNT-AET but to a bundle of them.



S-2: SEM Images captured with low angle of incidence of the electron beam for MWNT-AET self-assembled on a gold sheet with Tween (up) and Chitosan (down) methods. In each figure an inset is presented which was recorded with an angle of incidence near to the 90°. The inset is not in scale with the bar of the outer image.

In each image the presence of vertical MWNT are observed. In the inset vertical nanotubes can be distinguished as circles on the surface. Both images corroborate the scenario observed by AFM. Like in Fig-1, the presence of a few horizontal MWNT-AET are also observed. It is important to mention that the presence of residual polymer was detected in each SEM image since the modified surface tends to charge and the tubes were observed to move. For the case of the surface modified with Chit this process was very attenuated while with Tween it resulted to be very intense. In the middle of inset of the upper figure (as a dark circle) appears a vertical MWNT-AET that was partially burnt during the focus process.



S-3: AFM micrograph (top left) of a gold surface after immersed for only 2 hours in the suspension of MWNT-AET using Chit as surfactant (rinsed of). As can be observed the surface is scarcely populated with isolated and vertically aligned MWNT-AET. Therefore, we believe that vertically self-assembled MWNT-AET only form bundles (as observed in Fig. 1 or S-1) after the continuous association of isolated tubes. For clarity, this micrograph was repeated (top right) to mark the directions of the selected profiles (bottom, right and left). The color of each trajectory (top right) corresponds to the profiles presented (bottom).

The majority of the isolated self-assembled MWNT-AET found corresponds to the shortest ones (mainly 10-80 nm long). This result is in agreement with previous reports on SWNTs.^{10a} The green profile (bottom right) corresponds to the longest MWNT-AET found (about 250 nm). This latter tube in the fast direction of the scan appeared to be broader (triangle shape). We believe that since this object is very high from the surface and very thin, the process in which the cantilever of the microscope recovers its equilibrium position could be retarded and the vertically self-assembled MWNT-AET appeared as a broader object. This result could give an explanation on previous observations on more populated surfaces such as Fig 1 (main info) and S-1 in which the MWNT-AET could not be perfectly identified, and seem broader than its real size.

Experimental section

All materials and reagents were purchased from Aldrich and were used without previous treatment.

AFM studies were performed on a Nanoscope IIIA from Veeco, with antimony doped silicon tips model TESP-SS (tip rock: 2nm, tip rock max 5nm). Alternative contact mode (tapping) was used at a scanning rate of 0,5 Hz.

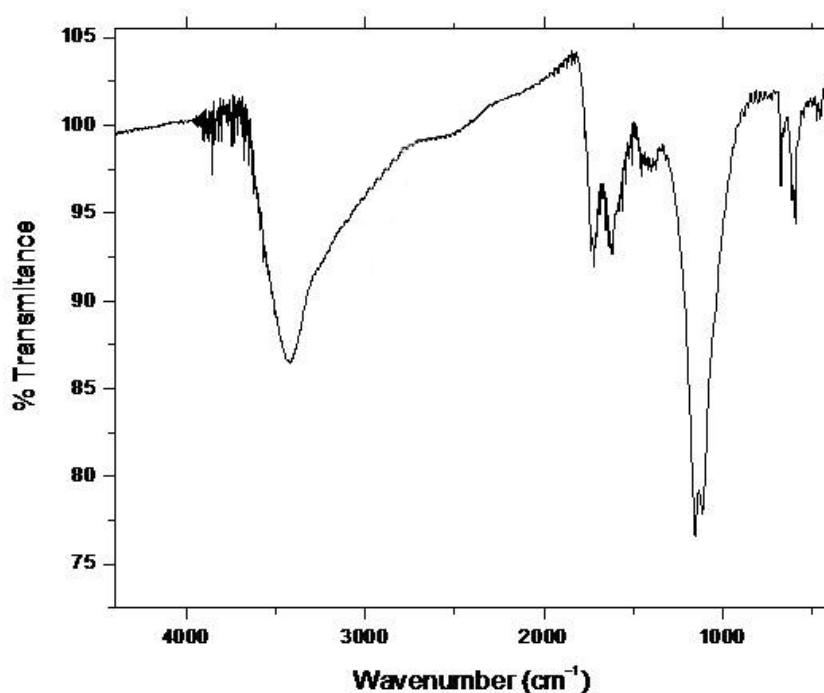
SEM Studies were performed on a Jeol JCM-7000F microscope.

Infrared spectra were carried out in a Rayleigh WQF-510 FT-IR spectrophotometer. Each spectrum was the average of 32 scans collected at a resolution of 2 cm⁻¹. Samples were prepared as of KBr pellets containing approximately 2 wt % of the sample material.

Cyclic voltammetric determinations were recorded with a 384B EG&G Princeton Applied Research Polarographic Analyzer Model controlled by home-built software. Each modified gold electrode was used as working electrode, Ag/AgCl (sat) as reference and a platinum one as counter electrode. The cyclic voltammograms were recorded in a K₃[Fe(CN)₆] solution (0.01 M) containing Na₂SO₄ (0.1 M), at a scan rate of 0,1 V/s.

S-4 Oxidation of MWNT

MWNTs (10 mg) were introduced into a mixture $\text{H}_2\text{SO}_4/\text{HNO}_3$ (10ml) (V/V 2/1) and dispersed for 5 min in a sonication bath. Passed that time they were introduced in a boiling water bath with magnetic stirring for 20 minutes. Both processes (sonication and heating with magnetic stirring) were alternated repeatedly for 2 h. The obtained black dispersion was then centrifuged at 3000 rpm for 20 min. The precipitate was thoroughly washed with distilled water until pH 7, and then washed with ethanol and ether.



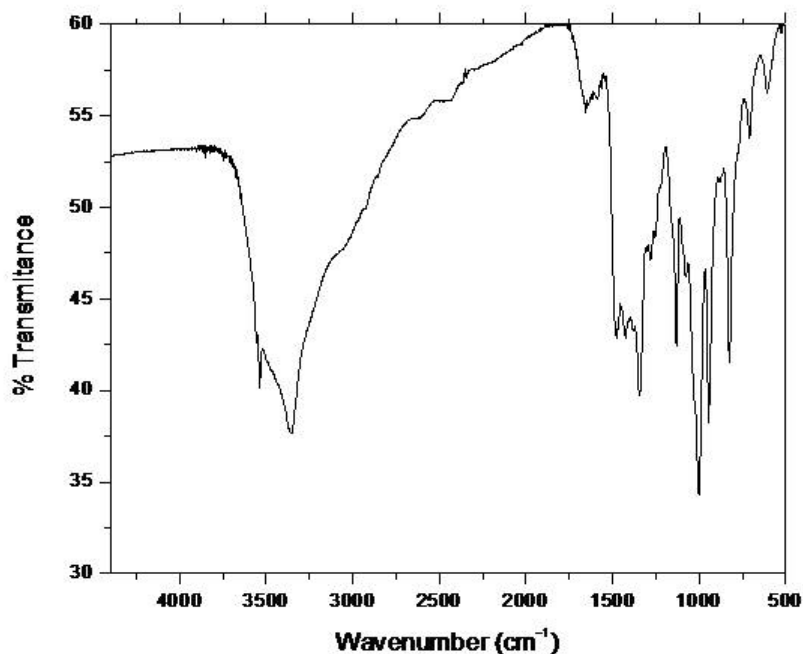
S-4: FT-IR spectra of oxidized MWNTs

Table 1: Assignment of signals in the FT-IR spectrum of oxidized MWNTs

Signal (cm ⁻¹)	Assignment
3421	ν O-H (carboxylic acid+phenols)
1720	ν C=O (carboxylic acid)
1620	ν C=C aromatic rings
1157,1400	ν C-O + δ OH

S-5 Condensation of 2-aminoethanethiol on oxidized MWNT

Oxidized MWNTs (9 mg) were introduced in an eppendorf with dry DMF (2 mL) and AET (50 mg) was added. The mixture was sonicated for 5 min followed by 20 min of magnetic stirring and this sequence was repeated three times. 50 mg of dicyclohexyl carbodiimide were added and the mentioned sonication-magnetic stirring sequential process was repeated three more times. The mixture was then set to react overnight with magnetic stirring and under nitrogen atmosphere. After the condensation process the obtained MWNT-AET were separated from the reactant solution by centrifugation at 4000 rpm for 20 min and washed 7-10 times with ethanol and 3 times with ether. Each washing process implied 5 min of sonication and centrifugation.



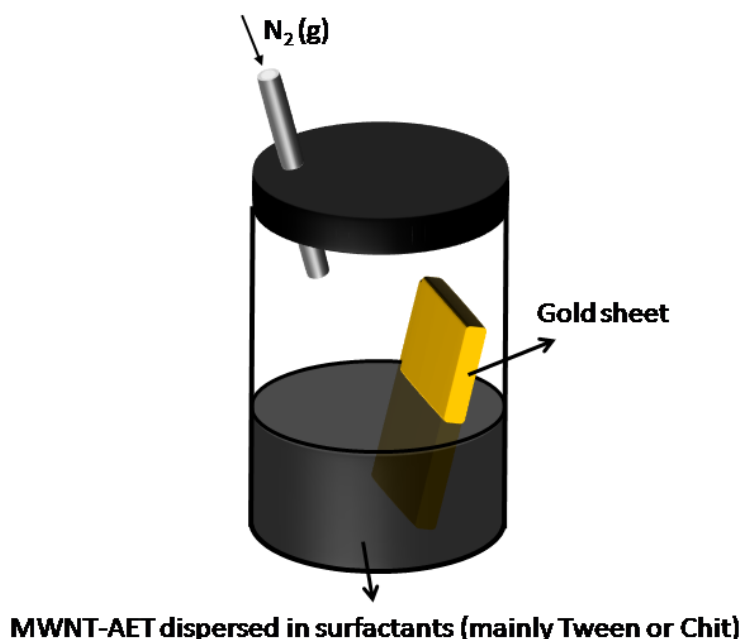
S-5: FT-IR spectrum of MWNT-AET

Table 2: Assignment of signals in the FT-IR spectrum of MWNT-AET

Signal(cm^{-1})	Assignment
3564	ν N-H (secondary amide)
3353	ν O-H (phenols+acids)
2925,2896	ν C ^{AS} _{sp3} -H and ν C ^S _{sp3} -H
2609	ν S-H

1664	ν C=O (amide)
1473	δ^S (-CH ₂ shears)

S-6 Self-assembly of MWNT-AET on gold surfaces using the three different surfactants



MWNT-AET (8.1 mg) were dispersed in 0.3 mL of solution of SDS (10% wt), Tween-80 (0.35% wt) or chitosan (1% wt) with sonication for 10 min. The gold surface was immersed in each of these suspensions (as in the scheme) for approximately 17 h under nitrogen atmosphere. Then each surfactant was rinsed off. For Tween 80 the modified surface was introduced into hot DMSO (at 80 °C) and magnetically stirring for 6 h. Chitosan was removed by introducing the gold piece in acetic acid 2-3 % (V/V) for only 2 h at room temperature. SDS was removed by a simple rinse with bidistilled water.

Previous to the MWNT-AET self-assembly the gold sheets were immersed in piranha mixture H₂O₂:H₂SO₄ 1:1 for 12-24 h and rinsed with bidistilled water. After this process the gold sheets were immersed and stored in HCl (1 M) until the moment of the self-assembly of MWNT-AET. The minimum time for the hydrochloric acid treatment was 15 min. The HCl was removed by copious rinse with bidistilled water previous to the immersion in the MWNT-AET suspension. The gold electrodes were submitted to an electrochemical oxidation process in HClO₄ (0.1 M) at a fixed potential of 2.33 V. The electrode was maintained in such conditions until it becomes red (formation of Au₂O₃) typically for 10-15 min. The gold oxide is then removed also by immersing the electrode

in HCl 1M for approximately 20 min. After this period the electrode is rinsed with bidistilled water and immersed in the MWNT-AET dispersion.

Note: It is important to remove any type of gold oxide from the surface that will be submitted to modification using the hydrochloric acid treatment. Otherwise we had observed that the polymers tend to interact strongly with the surface and the dispersed MWNT-AET do not self-assemble on the gold surface.