Supporting information

Reversible positioning at submicrometer scale of carbon nanotubes mediated by pH-sensitive poly(amino-methacrylate patterns

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Figure S5. TM-AFM images of PDMAEMA patterns (100 x 100 µm²; height image) after desanchoring treatment showing the absence of residual CNTs.
Experimental Section

Materials
Films of gold with thicknesses of 950 Å were deposited onto silicon substrates by using an electron beam evaporator manufactured by Si-Mat (Silicon Materials). A 100 Å thick layer of titanium was used to promote adhesion between silicon and the film of gold. 11-mercaptop-1-undecanol (MUD), undecanethiol, copper(I) bromide (CuBr), ethanol absolute, α-bromoisobutyryl bromide, 4-dimethylaminopyridine (DMAP), sodium dodecyl sulphate and triethylamine were purchased from Sigma-Aldrich. 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) was purchased from VWR and filtered through aluminum oxide before use. Methanol was purchased from Acros Organics and filtered through aluminum oxide before use. 2,2-dipyridyl (Bpy) was purchased from Acros Organics. Multiwall carbon nanotubes (thick MWCNTs purified) were supplied by Nanocyl (Belgium). Sonication was performed with a 2210E-MTH BRANDSONIC apparatus.

Atomic Force Microscopy (AFM) analysis
AFM measurements were performed in “tapping-mode” (TM-AFM). The cantilever holding the probe tip oscillates close to the resonance frequency (ca. 300 kHz) above the sample surface so that the tip is in intermittent contact with the surface at the lower end of the oscillation. Simultaneous recording of the phase and the height images provides a map of the local mechanical response. All TM-AFM images were recorded with a Nanoscope V microscope operated at room temperature in air using commercial cantilevers made of silicon with a spring constant of 30 N/m (Veeco). 512x512 pixels images were recorded, and the Nanoscope image processing software was used for image analysis. Unless otherwise stated, image treatment was limited to a “flattening” operation, whereby a first-order surface representing height variations related to a possible tilt of the sample is subtracted from the original image.

Conductive-AFM (C-AFM) measurements were performed under ambient conditions, in contact mode, using the Nanoscope V controller with an extended TUNA module. Si etched probes with Pt/Ir coating (PPPcontPt; Nanosensor) with a spring constant of 0.2 N/m were used. Conducting silver paint was applied on the side of the sample to make electrical connection. The applied voltage was set to 500 mV and the sensitivity to 100 nA/V.

X-Ray Photoelectron Spectroscopy analysis
All reported spectra were recorded at a 90° take-off angle relative to the substrate with a VG ESCALAB 220iXL spectrometer using the monochromatised Al Kα radiation (1486.6 eV).

Synthesis of ATRP initiator
Bis(11-hydroxyundecyl)disulfide 1
An iodine solution (2.5 g, 10 mmol, in 20 ml of ethanol) is added dropwise to a stirring solution of 11-mercaptop-1-undecanol (3.11 g, 15.25 mmol) in 40 ml of ethanol. After addition of the iodine solution, the white crude material is filtered off and washed with ethanol. Then, the residue is recrystallized from ethanol to give the compound 1 in 98% yield.
11,11’-disulfanediylbis(undecane-11,1-diyl) bis(2-bromo-2-methylpropanoate) 2

1 (0.7g, 1.72 mmol) and triethylamine (0.57ml, 4.13 mmol) are stirred at 0°C in 10 ml of dichloromethane. α-Bromoisobutyryl bromide (0.51 ml, 4.13 mmol) is added dropwise followed by DMAP (42 mg, 0.34 mmol) and the mixture is stirred at 40°C for 24 h. Then, the reaction is hydrolyzed with water; the organic layer is washed two times with water and dried over Na₂SO₄. After evaporation of the solvent, the compound 1 is recovered in pure form without further purification in 95% yield.

¹H NMR (300MHz, CDCl₃) δ: 4.17 (t, 4H, CH₂-O), 2.68 (t, 4H, CH₂-S), 1.95 (m, 12H, CH₃) and 1.12-1.79 (m, 36H, CH₂).

Procedure for patterning of gold surface

Some drops of an ethanol solution of 2 (C= 5mM) are spread onto a PDMS stamp. After 5 min, the stamp is dried by a flow of nitrogen and put in contact with the substrate for 30 s.

Typical procedure for surface-initiated polymerization of DMAEMA

A first flask containing 280 mg (2 mmol) of CuBr and 620 mg of Bpy (4 mmol) were submitted to three-time series of evacuation/nitrogen. In a second flask, 15 ml of methanol/water (1:1) was degassed with nitrogen during 15 min and transferred in the first flask containing the catalyst/ligand complex. In a third flask, a mixture of 16.8 ml (0.1 mol) of DMAEMA and 15 ml of methanol/water (1:1), were also degassed with nitrogen. The solution was then transferred to the reactor containing the surface-attached initiator, followed by the transferred of the catalyst/ligand solution. After 1 h, at room temperature, the sample is washed and sonicated, few minutes, in methanol to remove the non-grafted polymer.

Passivation of gold substrate

The substrate, after polymerization of DMAEMA, is immersed in a 2mM ethanol solution of undecanethiol (V = 10 ml) at room temperature for 1h. Then, the surface is washed, sonicated for 1 min in ethanol and dried under a flow of nitrogen.

Typical procedure for the preparation of nanotubes assembly on PDMAEMA patterns

1 mg of CNTs is stirred in 15 ml of water for 10 min. The solution was adjusted at pH 12 by addition of saturated sodium carbonate; acidification (pH 2) was carried out with concentrated HCl. The PDMAEMA patterned substrate is immersed in the stirring solution overnight. Then, the samples were washed and sonicated for 30 s in neutral water.
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