

Patterning of [2.2]paracyclophane derivative modified single-walled carbon nanotubes through grid-assisted deposition

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We describe a method to selectively position single-walled carbon nanotubes (SWNTs) modified with a [2.2]paracyclophane derivative (PCP) containing conjugated acetylenic triple bonds in the linear side-chain on fluorine doped tin oxide (FTO)/glass substrates. The method exploits the use of metallic grids as masks put on electrically biased FTO surfaces with PCP moieties positioned in between. The application of the voltage forces the PCP moieties to repel the holes filling the grid bars while PCP modified SWNTs were patterned as the holes.

1. Introduction

Single-walled carbon nanotubes (SWNTs) represent a class of materials with unique physical properties;^{1–4} however their lack of solubility in any solvents has imposed great limitations on their use for possible technological applications. The formation of supramolecular complexes allows nanotubes to be separated into small bundles with proper lengths and functional groups that make them more suitable for their integration into opto-electronic devices.^{5–7}

However for the large scale integration of SWNTs their selective positioning remains a challenge that has to be overcome. In this regard the use of chemical reaction with a substrate has been previously reported.^{8–10} Avouris *et al.* functionalized carbon nanotubes using long-chained aryldiazonium salts end-capped with hydroxamic acid. This allows the selective deposition of the functionalized nanotubes on a metal-oxide substrate.¹¹

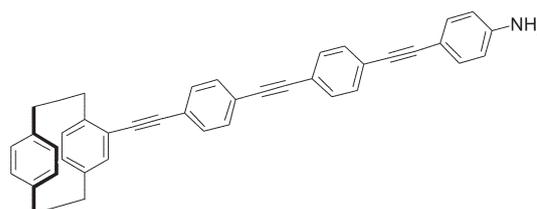
Among all these approaches, assembly based on wet chemistry has received great attention because of the associated mild conditions and the ability to produce well-defined nanostructures. It was demonstrated that wet-chemistry approaches can be used to assemble nanotubes in horizontally ordered arrays on patterned silicon wafer surfaces.¹² Chen *et al.*¹³ report the parallel alignment of nanotubes on solid substrates *via* a solution-based acoustic manipulation technique. More recently Shimoda *et al.*¹⁴ and Russell *et al.*¹⁵ described carbon nanotubes aligned on hydrophilic glass parallel to the solution surface.

As an alternative approach for controlling interfacial properties, it was previously reported that it is possible to fabricate architectures of molecular materials by drop casting of a solution onto a substrate.^{16–20} As the solvent evaporates solid material starts to deposit on the surface with the organisation of the material that is guided by the hydrodynamic flows created by the evaporation process.

The electric field based approaches to control the morphology of thin films, molecules and particles is a research area of growing interest in recent years.^{19–22} In particular Chou and Zhuang²² have demonstrated that when a mask is positioned on the top of the polymer surface with an air gap in between a potential generally arises spontaneously. On some length scales, the polymer melt is unstable under the influence of the electric field and self-assembles into pillar arrays.²² The direct patterning of molecular films obtained in this way can eliminate steps and make the whole lithography process easier, faster and cheaper.

Among the organic molecules with three-dimensional π -electron systems like fullerene and its derivatives, the cyclophanes represent a class of organic semiconductors with outstanding properties. [2.2]Paracyclophanes consist of two aromatic units that are kept in a face-to-face arrangement by ethylene bridges.²³ Due to their optical broadening and low photoreactivity together with high stability against moisture and air, cyclophanes could represent a novel class of semiconductors for the development of electronic active devices.

In this work, we try to control the selective patterning of [2.2]paracyclophane (PCP) **1** (Scheme 1) modified SWNTs through bias voltage assisted dewetting onto fluorine doped-tin-oxide (FTO)/glass substrates covered with metallic grids. Basically, conjugated molecules with the concomitant presence of one electron-acceptor and an electron-donor end group show an internal charge transfer upon excitation that could be of interest for the development of photoresponsive materials.^{24,25} Thus the possibility to combine soluble PCP **1** with a complementary electron acceptor like carbon nanotubes



Scheme 1 [2.2]Paracyclophane derivative 1.

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thorough non-covalent modification could represent a novel approach to obtain hybrid photoactive materials.

Moreover, we have previously observed²⁶ that the application of a voltage bias during the evaporation of the solvent influences strongly the architecture of the deposited material. In this case we found that the application of an electrical potential to a conducting surface induces the segregation of the solution toward or away from the field gradient near the metallic grids probably due to the different conductivity of the materials constituting the blend. Thus the material is deposited in confined regions and the overall shape of the three-dimensional architecture is guided by the grid acting as a template.

2. Experimental

The carboxy-functionalized SWNTs (C-SWNTs) were purchased from Aldrich and consisted of ≈ 80 – 90 vol% carbon as SWNTs with a noticeable amount of bundles. [2.2]Paracyclophane derivative **1** (PCP **1**) (Scheme 1) was prepared according to a previously reported procedure.²⁷

The synthesis of the [2.2]paracyclophane derivative **1** was accomplished according to a previous procedure.²⁸ Briefly Pd/Cu catalyzed Sonogashira reaction between 4-ethynyl[2.2]-paracyclophane^{29–31} and *p*-(iodophenylethynyl)trimethylsilane followed by removal of the protecting group using tetrabutylammonium fluoride gave an intermediate aryldiethynyl cyclophane which was then converted into the desired compound **1** by Pd/Cu catalyzed cross-coupling with *p*-(*p*-iodophenyl)ethynylaniline, in 46% overall yield.

A solution of PCP **1** (10 mg) in DMF (10 ml) was prepared by sonication. Carboxy-functionalized SWNTs (0.2 mg) were then added and the resulting mixture was sonicated for 1 h at room temperature.

Infrared spectroscopy (KBr pellets method operating in transmission mode), in the 500 – 4000 cm^{-1} range, was used to check the sidewall modification of the C-SWNTs.

Fig. 1 displays the procedure for creating a molecular pattern by voltage assisted dewetting on a fluorine doped tin oxide (FTO, Tec Glass 15[®], surface resistance $14 \Omega \text{ sq}^{-1}$) covered glass substrate. As template for patterning a copper

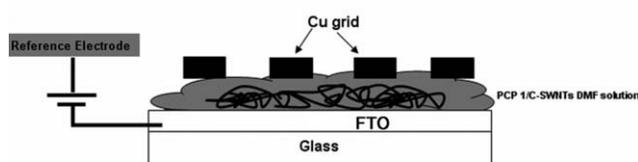


Fig. 1 Schematic illustration of the voltage assisted dewetting procedure used for patterning thin films of PCP **1**/C-SWNTs: as template for patterning a copper grid (400 mesh) with $40 \mu\text{m}$ wide square holes and $10 \mu\text{m}$ wide bars was used. The grids were positioned on the FTO/glass substrate. Samples were prepared by depositing on the grid a drop ($3 \mu\text{l}$) of the solution. During the evaporation of the solvent a fixed electrical potential was applied to the FTO surface by a Keithley 4200 considering its common use as a reference ground electrode. After the complete evaporation of the solvent, the grid was removed in a nitrogen stream.

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The morphology of the molecular patterned structures was characterized by field emission scanning electron microscopy and by AFM (Nanosurf easyScan DFM) in phase contrast tapping mode.

3. Results and discussion

As previously reported^{32–34} the interaction of acid-treated SWNTs with amines yielded stable dispersions of shortened tubes by the formation of zwitterions with the carboxy-functionalities observed on the SWNT ends and on sidewall defects. In this regard scanning electron microscopy was used to obtain direct visualization of our SWNTs.

From our observation, the C-SWNTs tend to exist as bundles as reported in Fig. 2a. The SEM image shows C-SWNTs within amorphous material entangled with impurities in the form of large submicron aggregates. According to the literature^{32–34} we observed that the treatment of C-SWNTs with an amine based compound like PCP **1** leads to the exfoliation of the majority of the large SWNT ropes into smaller ropes with an enrichment of shorter SWNTs (Fig. 2b).

A typical FTIR spectrum of electrodeposited carboxy-SWCNTs is shown in Fig. 3a. The peak around 1735 cm^{-1} is normally assigned to the C=O-stretch vibration in the COOH group.³² It seems reasonable to assume that the deposited C-SWNTs are PCP **1** modified because of the non-covalent functionalization of the carboxylic groups, both on the basis of the study of Papadimitrakopoulos *et al.*^{33,34} and, also, by the analysis of the IR spectrum of the blend that indicates the presence of carboxylate ion (Fig. 3b, $\nu = 1614 \text{ cm}^{-1}$) and hence the formation of a zwitterion, as previously demonstrated by Haddon *et al.*^{35,36}

Considering the polarizable structure of compound **1** which is a highly π -conjugated system consisting of phenylene rings, acetylenic triple bonds and a [2.2]paracyclophane framework,

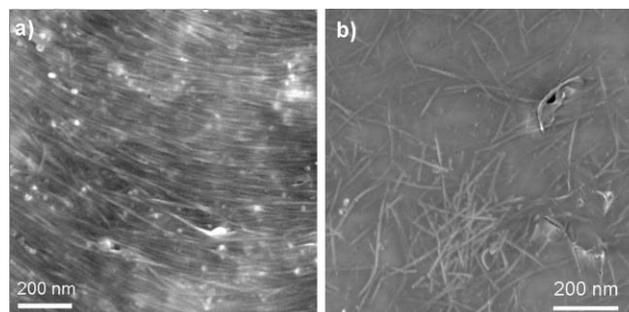


Fig. 2 SEM images of (a) a specimen of pristine C-SWNTs and (b) PCP **1** treated C-SWNTs.

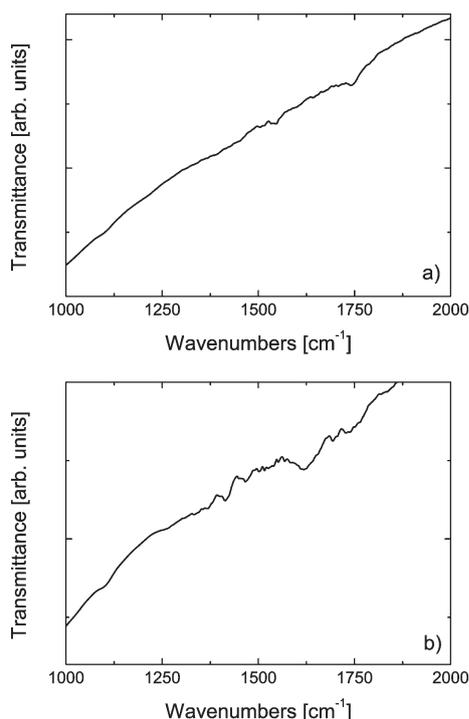


Fig. 3 IR spectra of (a) C-SWNTs and (b) PCP 1 treated C-SWNTs.

the application of an external electric field could lead to changes of the final molecular architecture.

As shown in Fig. 4a the pattern made by the DMF solution of PCP 1/C-SWNTs without the application of the bias reproduces a low quality of the printed patterns as confirmed by the AFM height image reported in the inset of Fig. 4a.

In contrast the application of a voltage (Fig. 4b) of -2 V forces the liquid to repel the holes filling the grid bars even if with an inhomogeneous profile (inset of Fig. 4b). The printed substrate obtained with a bias of $+2$ V (Fig. 4c) consists of about 5 μm wide stripes, which shows that the fabricated patterns are in this case uniform (inset of Fig. 4c). At this stage we speculate that the positive voltage maximizes orientation of the polarizable compound due to a favorable interaction with the electric field lines.

The AFM phase image in tapping mode gives information concerning the loss in energy of the tip upon contact with the surface. In particular, Fig. 5a shows that there are two phases with the intensity of the signal inside the holes that is almost uniform. The AFM analysis performed on the separation zone of the patterning evidences the presence of the tubes filling the hole (Fig. 5b). This result was confirmed by SEM analysis as shown in Fig. 5c and d.

In order to get a comparative result the dewetting behavior of the DMF C-SWNTs solution in the presence of a voltage was also investigated. The pattern made by the DMF C-SWNTs solution without bias reproduces the grid hole (Fig. 6a and b) while when a bias of $+2$ V was applied, a complementary array with the tubes confined under the grid bars was obtained (Fig. 6c and d).

A critical question arises as to the origin of this selective placement of modified C-SWNTs by voltage assisted

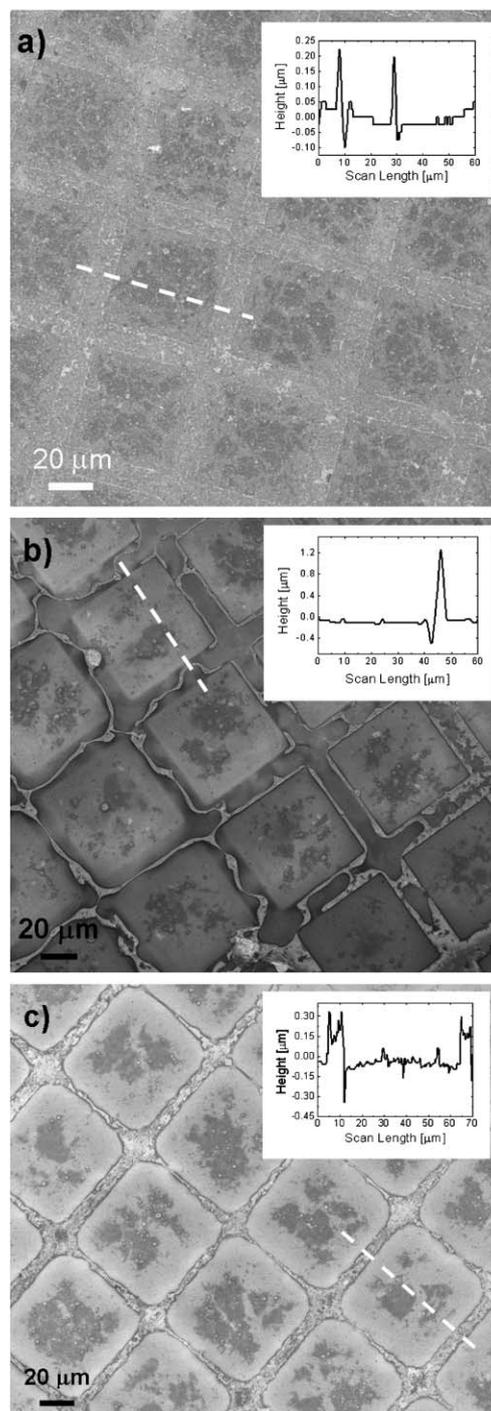


Fig. 4 SEM images of FTO surface patterned using PCP 1/C-SWNTs solution without bias (a) and with a bias of -2 V (b) and $+2$ V (c). The insets show the AFM height images recorded across the white line cross section.

dewetting. A possible mechanism could be related to a significant change of the conductivity of C-SWNTs upon their interaction with PCP 1 compound. It is known^{37–40} that a dielectric particle experiences a force toward or away from the high field gradient near the metallic grids depending upon its conductivity. It is plausible that the nanotube modification disrupts surface conduction caused by the presence of ions on

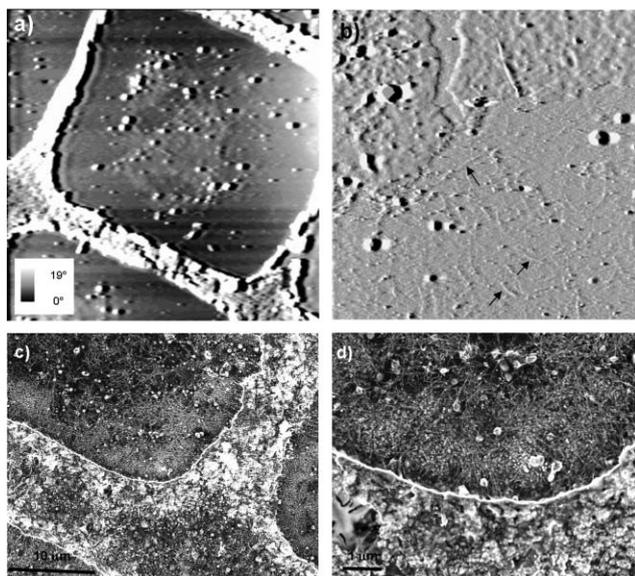


Fig. 5 (a) Phase image in tapping mode AFM ($70 \mu\text{m} \times 70 \mu\text{m}$) of the PCP I/C-SWNTs patterned onto a FTO/glass substrate with a bias of +2 V. (b) AFM image in tapping mode ($20 \mu\text{m} \times 20 \mu\text{m}$) of the PCP I/C-SWNTs patterned onto a FTO/glass substrate with a bias of +2 V. (c) SEM image of FTO surface patterned using PCP I/C-SWNTs solution with a bias of +2 V. (d) Higher resolution SEM image of (c).

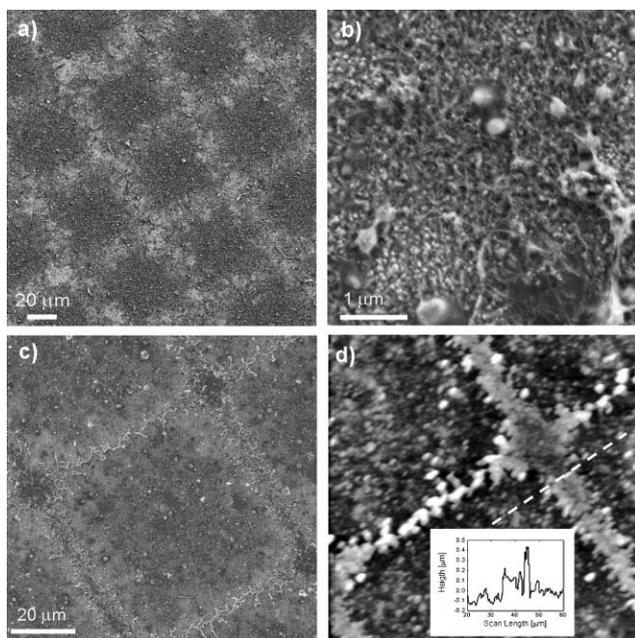


Fig. 6 (a) SEM image of the patterned C-SWNTs on a FTO/glass substrate without bias. (b) High magnification view of (a) showing C-SWNTs confined to the grid holes when no bias was applied to the FTO/glass substrate. (c) SEM image of the patterned C-SWNTs on a FTO/glass substrate with a bias of +2 V. (d) AFM image in tapping mode ($70 \mu\text{m} \times 70 \mu\text{m}$) of the C-SWNTs pattern on a FTO/glass substrate with a bias of +2 V. The inset shows the AFM height image recorded along the white line cross-section.

its sidewalls. A more detailed investigation of the causes of this is currently under way.

4. Conclusions

In summary, we have shown that selective placement of [2.2]paracyclophane modified nanotubes on indium-tin-oxide/glass substrates can be achieved using a voltage assisted dewetting approach. It was observed that when a metallic grid, used as mask, is positioned on an electrically biased FTO surface, the PCP 1 moiety positioned in between fills the grid bars while PCP 1 modified SWNTs are patterned as the holes suggesting that the PCP greatly affects the dielectric function of the nanotubes.

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