Unconventional nanotubes self-assembled in alumina channels: morphology and surface potential of isolated nanostructures at surfaces

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Synthetic nanographenes have been self-assembled from solution on the surface of nanometric channels of an alumina membrane template. By controlling the interplay between intermolecular and interfacial interactions, the molecules have been adsorbed either ‘face-on’ or ‘edge-on’ on the pore’s surfaces, leading to the formation of columnar stacks in the latter case. Upon thermal treatment at high temperature, the molecular cross-linking of the columns has been triggered, transforming the delicate supramolecular arrangement into robust carbon nanotubes, with the graphitic planes at predetermined orientations with respect to the tube axis. Scanning force microscopy characterization of single nanotubes deposited from suspensions on mica showed that the nanotubes can self-assemble on flat surfaces adopting preferential alignments which reflect the threefold symmetry of the mica substrate. Kelvin probe force microscopy studies revealed that the nanotubes possess a surface potential much smaller than the work function of both graphite and conventional vacuum-processed nanotubes, providing evidence for their more confined electronic structure.

**Keywords:** carbon nanotubes; nanoelectronics; nanomaterials; Kelvin probe force microscopy; \( \pi \)-conjugated molecules; electronic properties of surfaces

1. Introduction

Nanoscience involves the fabrication, characterization and exploitation of nanoscale-confined architectures (Joachim et al. 2000; Maruccio et al. 2004; Rosei 2004). Among nanostructured materials, \( \pi \)-conjugated carbon-based nanoscale architectures have attracted a great interest in (opto)electronics (Friend et al. 1999; Cacialli et al. 2002; Grimsdale & Mülken 2005). The perfect

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One contribution of 12 to a Discussion Meeting Issue ‘Supramolecular nanotechnology for organic electronics’.

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example of $\pi$-type, all-carbon material is graphite. To address the issue of nanoconfinement on the physical properties of matter, the properties of graphite have been compared with those of smaller graphitic-like nanostructures such as fullerenes, nanotubes and polycyclic aromatic hydrocarbons (PAHs; Shiraishi & Ata 2001; Debije et al. 2004).

Since their discovery, carbon nanotubes have been intensely investigated and employed as molecular wires and field emitters. Their chemical structure is similar to that of graphite, although their tubular shape and small size influence their electronic structure deeply.

The work function (WF) of single-walled carbon nanotubes ranges from 4.95 to 4.7 to 4.8 eV (Shiraishi & Ata 2001; Cui et al. 2003; Suzuki et al. 2004), while the WF of multi-walled nanotubes ranges from 5.05 to 5.18 eV (Shiraishi & Ata 2001; Maeda et al. 2003). The WF of metallic carbon nanotubes was found to be larger than that of semiconducting ones by some authors (Okazaki et al. 2003), while other researchers detected no difference (Suzuki et al. 2000). In general, the WF of nanotubes is larger than that of graphite, and increases when the tubes are arranged in bundles (Zhao et al. 2002) or for small nanotube diameters (Rakitin et al. 2003). The latter effect is due to the interaction between $\sigma$ and $\pi$ orbitals, which lowers the Fermi level, as observed when comparing the WF of graphite, nanotubes and fullerenes (Shiraishi & Ata 2001).

A recently revised approach enables the fabrication of unconventional nanotubes via template-assisted thermal reactions of discotic PAHs adsorbed onto alumina porous templates (Zhi et al. 2005a,b). The discotic, liquid crystalline molecules are adsorbed into the alumina pores with mainly edge-on orientation and are then cross-linked at high temperature (Gherghel et al. 2002), yielding nanotubes having graphitic structures, with the graphene layers oriented perpendicular to the tubes’ main axis. The proper choice of the starting molecule makes it possible to produce nanotubes with markedly different mechanical and chemical properties (Zhi et al. 2005a,b), as compared with conventional carbon nanotubes. Moreover, this novel approach allows greater versatility on the tubes’ functionalization, including potential processability from solutions and tunability of a variety of physicochemical properties. To verify whether such architectures are interesting building blocks for nanoelectronics, it is important to unravel their nanoscale electronic properties.

In this work, we study the structure and electronic properties of tubular aggregates obtained from the template-assisted pyrolysis of PAHs and compare them with those of highly oriented pyrolytic graphite (HOPG). Among different PAHs and their precursors (Watson et al. 2001), we have chosen tetraphenyl cyclopentadione (1; Zhi et al. 2005a,b) and two hexa-peri-hexabenzocoronenes symmetrically substituted in the peripheral positions (2, Samorí et al. 2001; 3, Pisula et al. 2005; figure 1). The templates used to drive the nanotube formation were alumina membranes, in which small pores, with diameters as small as 20 nm, were generated by electrochemical etching. Molecule 1 adsorbed with a random orientation on the alumina, giving tubes with a hyperbranched polyphenylene structure at relatively low temperatures, and three-dimensional porous carbon structure at high temperatures (Zhi et al. 2005a,b). Molecule 2 adsorbed edge-on to the alumina, yielding (after pyrolytic cross-link) tubes with the graphitic layer oriented perpendicular to tube axis (figure 1; Zhi et al. 2005a,b). Molecule 3 was expected to be adsorbed face-on to the alumina (Pisula et al. 2005); however, after
high-temperature pyrolysis, only carbon nanotubes with different graphene layer orientations were obtained. We deposited these different nanotubes on an atomically flat substrate from solution and studied their morphology using scanning force microscopy (SFM; Samorì 2005). To explore the effect of chemical structure and order on the electronic properties of the nanotubes, two-dimensional surface potential (SP) maps were obtained by Kelvin probe force microscopy (KPFM; Nonnenmacher et al. 1991; Liscio et al. 2006).

2. Experimental conditions

Compounds 1, 2 and 3 have been synthesized and assembled in nanotubes as described in Zhi et al. (2005a,b). Anodic alumina membranes were purchased from Whatman International Ltd. The average size of the branched pores of the membrane was between 20 and 200 nm (evaluated by scanning electron

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Figure 1. The molecules used to create the nanotubes and a schematic of nanotube assembly through surface adsorption and pyrolitic, high temperature graphitization.
microscopy, SEM) and the thickness was 60 μm. The membranes were washed in ethanol with sonication for 10 min and then dried under vacuum. All compounds were dissolved in dichloromethane (concentration was 5–30 mg ml⁻¹). The solution was then added dropwise onto the membrane surface. The amount of substance loaded in the membrane can be controlled by the concentration and volume of solution applied to the membrane. All heat treatments of the samples were carried out on quartz slides under nitrogen in an electric furnace. All compounds were heated at temperatures ranging from 250 to 1000°C, with intermediate heating stages to promote first the stacking of the molecules into a crystalline phase, and then molecule cross-linking through Diels–Alder reaction or pyrolytic cleavage of side chains (see Zhi et al. (2005a,b) for more details on nanotube formation and Gherghel et al. (2002) for more details on the pyrolysis of PAH molecules). Alumina templates were removed by dissolving them in a solution of NaOH (3 M). The template-free samples were washed with water and ethanol and dried under vacuum. For deposition on substrates, the nanotube suspension was prepared in hot ethanol using sonication and deposited on freshly cleaved muscovite mica by drop casting.

SFM and KPFM made it possible to simultaneously map the morphology and estimate the SP of the nanotubes adsorbed on mica. The SFM studies were executed with an Autoprobe CP from Veeco. The single nanotubes’ diameters were calculated correcting for the tip broadening effect (Butt et al. 1992), assuming a tip radius of 10 nm. KPFM measurements were performed connecting the Autoprobe CP microscope to a lock-in amplifier (Stanford Research Systems, S3830), acquiring topography and SP simultaneously. This technique makes it possible to measure quantitatively the electrical potential on a surface with a lateral resolution on the tens of nanometre scale (for more details, see Jacobs et al. 1999; Palermo et al. 2006).

For the KPFM measurements, a $V_{AC}$ voltage of amplitude 2 V and frequency in the range between 12 and 16 kHz was applied to highly p-doped silicon tips having force constant $k$ of approximately 0.5 N m⁻¹.

The SP of carbon nanotubes was compared with that of a freshly cleaved HOPG sample, studied by KPFM after each measurement with the same tip and scan parameters used to observe the nanotubes. The SP of nanotubes is estimated by measuring the SP difference with HOPG. Generally, three terms contribute to the SP of a nanostructure: the WF; the interface barrier between the adsorbate; and the substrate and the polarizability of the sample. Moreover, the effective area size, due to the long-range tip–substrate electrostatic interactions, approaches that of nanotubes and the measured SP is given by the weighted average of both substrate and adsorbate SPs. In the case of macroscopic graphite sample, the measured SP corresponds to the WF. For nanostructures, it is important to define the asymptotic SP as the potential value measured on an ideal infinite and uniform layer of the material under study (Liscio et al. 2006).

3. Results

Figure 2 shows an SFM image of nanotubes obtained from molecule 1 physisorbed on mica. The tubes exhibit an average width of 26 ± 16 nm. The nanotubes form a quite regular continuous network, showing many Y-shaped intersections.
The angles between neighbouring nanotubes amount to multiples of approximately 30°, therefore reflecting the threefold symmetry of the mica substrate (Samorì et al. 1998). The Y-shaped intersections observed are probably due to the branched structure of the alumina template (Meng et al. 2005), as confirmed by the observation of more complex, highly branched geometries adsorbed on the surface (figure 2b). These structures start as a single tube which splits into more tubes, reaching an apparent cross-section of more than 3 µm and fan-like shape typical of anodically etched pores in alumina (Meng et al. 2005).

The apparent thickness of the nanotubes estimated from topographical profiles in SFM images amounts to 2–4 nm, thus almost one order of magnitude lower than their corresponding width, which amounts to 20–30 nm. This difference in the width and height of tubular architectures adsorbed at surfaces visualized by SFM

Figure 2. (a,b) SFM topographical images of nanotubes obtained from molecule 1 deposited on mica. Two different zones of the same sample are reported. In (b), a fan-like structure showing contrast inversion can be observed (see text). The Z-scales are (a) 1.2 nm and (b) 31 nm.
effect has been found to become dramatic when measurements of hydrophobic adsorbates supported on hydrophilic substrates are performed in an atmosphere characterized by a high relative humidity (Ji et al. 1998; Zhuang et al. 2005). Moreover, additional roles can be ascribed to the indentation of the nanotube by the probing SFM tip (Prokhorova et al. 1998) and the adhesion of the SFM tip to the surface (VanNoort et al. 1997; Samorì et al. 2002). In some cases, an inversion of contrast in the topographic images was observed on these branched structures. This artefact in SFM imaging is known to occur when the tip passes from an attractive to a repulsive regime during its swing (Garcia & San Paulo 1999).

The length of the structures shown in figure 2b is approximately 5 μm, thus much smaller than the total thickness of the alumina template (60 μm). This suggests that only the pores closer to the membrane side, where anodic etch was initiated, possess this fan-like structure. The rest of the bulk alumina consists of regular parallel pores, which lead to straight nanotubes observed by SEM (Zhi et al. 2005a, b). The ability of nanotube production to follow template shape even in forming these complex branched structures is relevant and will be discussed in more detail later.

KPFM studies enabled us to resolve by SP mapping the single nanotubes prepared from compound 1 adsorbed on mica, although the signal-to-noise ratio was quite low. Nevertheless, it was possible to estimate the SP of the nanotubes which amounts to SP = 3.8 ± 0.2 eV.

A similar morphology was obtained for tubes of compound 2, despite the different precursor used to generate the tube (figure 3a). TEM measurements revealed that the nanotubes obtained from molecule 2 have the graphitic layer perpendicular to tube axis (as shown in figure 3b). However, the average width of the tube in this case is slightly smaller, i.e. 19 ± 6 nm, although the same Y-shaped pattern is observed, with multiples of 30° angles reflecting again the mica substrate symmetry. The SP measured on the type 2 carbon nanotubes amounts to 3.8 ± 0.3 eV, again lower than that of conventional carbon nanotubes, suggesting significantly different electronic properties. One of the reasons could be due to different orientation of the π orbitals with respect to the nanotube’s main axis. This can be probably explained also in view of the lower crystallinity of these nanotubes, assembled by chemical approaches, when compared with the conventional ones, which are instead grown under harsher conditions.

The third molecule (3) investigated self-assembles on alumina similar to molecule 2, leading to graphitic nanotubes as well. The main difference relies on the presence of oxygen atoms in the side chains, which should promote a face-on adsorption of the molecular discs on the alumina. The stacking orientation of hexa-peri-hexabenzocoronenes can therefore be expected to be different when compared with molecule 2, ultimately influencing both graphene layer orientation and electronic structure of the nanotube. Figure 4 shows that, in this case, very long and structurally defined tubes are obtained. The width of single nanotubes was found to be 34 ± 9 nm. Aggregation forming larger bundles composed of many single nanotubes was observed. As previously described, an influence of the mica substrate on nanotube orientation is observed, as reflected by multiples of 30° angles between different tube segments (see arrows).

The nanotube bundles appear evident also in the KPFM images (figure 4c). The measured SP = 4.0 ± 0.3 eV is slightly higher than that of the tubes obtained from molecules 1 and 2, and slowly approaches the WF of HOPG (4.65 eV; Palermo et al. 2005), although the difference is still very large. While in topographic images smaller
branches of the larger bundle have been visualized, they were not resolved in the KPFM images. This is due to the large size of the effective area in the SP mapping by KPFM, which relies on long-range electrostatic interactions, leading to a decrease in the lateral resolution. This effect is also reflected in the simulated KPFM image.

Figure 3. (a) SFM image of nanotubes obtained from molecule 2 deposited on mica. The Z-scale is 12 nm. (b) TEM image of one of the nanotubes, showing the orientation of graphitic layers perpendicular to tube axis. In the inset, a zoom in of the nanotube structure is shown.
Such an image type is calculated using a two-dimensional convolution procedure (Liscio et al. 2006) between the effective area and the KPFM image, which is reconstructed with infinitesimal lateral resolution by assigning to each point of the topographic image the asymptotical SP value of either mica or nanotube. The effective area is well described by a two-dimensional Voigt curve calculated as proportional to the perpendicular electric field of the tip along the sample surface, in which the analytical expression was calculated by Lyuksyutov et al. (2004).

4. Discussion

The SFM analysis revealed nanotubes having a well-defined anisotropic structural motif characterized by a nearly constant cross-section. The nanotube cross-section is dictated by the alumina used as template, and thus only subtle
differences between the different nanotube types (1–3) have been observed. While their sizes are similar, their tendency to form intertube aggregates is markedly different. Nanotubes 1 exhibited a scarce propensity to aggregate and a tendency to form extended networks on the surface. Within the network, single nanotubes are oriented along preferential directions reflecting the threefold symmetry of the mica substrate. Their SPs, as measured with KPFM, are approximately 3.8 eV, i.e. approximately 0.85 eV lower than that of HOPG. The small SP can be ascribed to factors determined in first instance by the presence of chemical and structural defects, such as the unreacted C=O and C≡C groups in nanotubes of molecule 1 (Zhi et al. 2005a,b).

The comparison of nanotubes obtained from 2 and 3 is interesting. Both of the tubes are graphitic nanotubes. Graphene layers in tube 2 are oriented perpendicular to the tube axis, and in tube 3 are oriented along different directions. The SP estimated for nanotubes of type 2 amounted to 3.8 eV, while it was found to be slightly larger (i.e. 4.0 eV) for nanotubes of kind 3. All measured SPs are notably smaller than the WF of graphite and also differ from those of conventional nanotubes that are known to exhibit a WF higher than graphite. The higher WF of conventional nanotubes has been justified with the mixing of σ and π valence states, due to the bending of the graphitic layer (Shiraishi & Ata 2001). Differently, in the present case of unconventional nanotubes, the fabrication process employed, based on the self-assembly of discotic molecules followed by thermal annealing which drives polymerization from a liquid-crystalline phase (Zhi et al. 2005a,b), is likely to remove most of the mechanical stress due to small molecular discs and relatively large nanotube diameter, especially in the case of nanotubes with the graphitic structure perpendicular to the tube axis. When compared with type 2 tube, where all the graphene layers are oriented along the same directions perpendicular to the tube axis, a large number of the graphene layers in type 3 tube are oriented parallel to the tube axis, and are thus similar to those in conventional carbon tubes. This determines the larger shape persistence and the higher SP of type 3 tube when compared with the type 2 tubes. The small SP could also be ascribed to other factors such as chemical and structural defects in the nanotubes, which can be foreseen to possess a relatively higher density of active sites on the surface when compared with conventional nanotubes (Zhi et al. 2005a,b).

The difference in SP and aggregation behaviour between nanotubes 2 and 3 indicates that the graphitic layer orientation represents the prime but not the only critical factor affecting nanotube electronic structure, since the stacking of the nanographenes before the pyrolysis plays a pivotal role, in agreement with the previous observations (Zhi et al. 2005a,b).

Our results reveal that through fine tuning of (i) the molecules’ orientation on a templating non-planar alumina surface, (ii) the intermolecular stacking, and (iii) chemical side functionalizations, a wide range of architectures with similar SPs can be tailored.

Although our nanotubes are more easily processed from dispersion obtained by sonication when compared with conventional nanotubes, their easy processability into ultra-pure yet ordered architectures at surfaces remains a major challenge (Räder et al. 2006). The deposition process hardly led to homogeneous films, and large variations in nanotube density were obtained on each sample location. The measured diameters of the nanotubes were much smaller than
those estimated from SEM images (Zhi et al. 2005a, b), suggesting that the employed sonication treatment was successful in solubilizing, thus depositing on the mica mostly the smaller and consequently more soluble nanotubes.

Given the branched structure of the alumina pores (Meng et al. 2005), nanotubes with different diameters can be formed at different depths into the template, as confirmed by the observation of highly branched fan-shaped nanotubes (figure 2b). The results described here demonstrate that large PAHs can penetrate into the template for depths of several micrometres and are able to generate nanotubes mimicking even complex shapes. The KPFM measurements showed that these nanotubes possess relatively low SP, and thus can be of potential interest as hole-collecting nano-objects. This, together with the good charge mobility shown by such polyaromatic molecule stacks (Debije et al. 2004), suggests intriguing perspectives for the bottom-up fabrication of highly branched three-dimensional structures of hole-collecting nanotubes. Once such structures are grown, the alumina template can be dissolved and replaced with an electron-acceptor material, leading to bi-component phase-segregated architectures for photovoltaic applications.

5. Conclusions

Three different PAHs have been self-assembled on the non-planar surface of nanometric channels electrochemically fabricated inside an alumina template. The discotic molecules, which could be adsorbed either edge-on or face-on on the alumina surface, undergo pyrolytic carbonization upon heating at high temperature, leading to the formation of carbon nanotubes made from covalently linked synthetic nanographenes. Depending on the molecule employed, nanotubes with the graphitic layer oriented either parallel or perpendicular to tube axis can be tailored. These nanotubes are highly stable, i.e. they can be deposited from dispersion on a solid substrate and readily characterized by scanning probe microscopies. The preferential orientation of the nanotubes according to the threefold symmetry of the mica surface suggests strong interfacial interactions. The SPs of all different nanotube types are much smaller than that of graphite, and depend to a large extent on the stacking capability of the molecules employed.

We are grateful to Matteo Palma for enlightening discussions. This work was supported by the EU through the project ForceTool (NMP4-CT-2004-013684) and Marie Curie EST project SUPER (MEST-CT-2004-008128), by the ESF-SONS-BIONICS, by the Regione Emilia-Romagna PRITT Nanofaber Net-Lab as well as by the bilateral programme CNR-CNRS. Dr Zhi and Prof. Müllen thank the financial support of ENERCHEM project through the Max Planck Society.

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