

Nano-assembly of Conjugated Polymer on Carbon Nanotubes: An STM Study

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Introduction

Given the considerable interest in polymer wrapping of nanotubes for organic electronic and nanotechnology applications [1, 2], it is surprising that little systematic investigation with scanning tunnelling microscopy (STM) to directly visualise the polymer conformation on nanotubes has been performed. This is in direct contrast to the abundance of literature that is already available on STM of a variety of molecules absorbing on flat substrates [3]. To the best of our knowledge, the only known attempts to date are the work of McCarthy *et al.* [4] and Czerw *et al.* [5] on poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) and poly(propionylethyl-enimine-co-ethylenimine) (PPEI-EI) organisation on single-walled carbon nanotubes (SWNT) respectively; however the detailed conformation of polymer on SWNT was not discussed. Here, we will report on our latest work on composites of SWNT and the conjugated polymer poly(3hexylthiophene) (P3HT) (Figure 1a). This composite is particularly interesting as SWNT/poly-(alkylthiophene) composites have been actively investigated as materials for organic photovoltaic and optoelectronic memory devices [1, 2].

Experimental

Regioregular P3HT (98% head-to-tail coupling) was obtained from Sigma-Aldrich company. AP (as-prepared) grade SWNT was obtained from Carboxlex Inc. with a quoted purity of around 70%. X-ray photoelectron spectroscopy (XPS) and electron microscopy characterisation of as-received AP-SWNT show that it consists mostly of SWNT with main impurities being amorphous carbon and approximately 5 atom% Ni metal particles. All materials were used without further purification.

A 4mg/ml solution of the polymer was prepared using chloroform as solvent. 5% of AP-SWNT (by weight) were added to the solution and sonicated in an ultrasonic bath for 1 hour following McCarthy *et al.* [1] to promote polymer/nanotube interaction, this step is necessary to dissociate amorphous carbon coating from nanotube surface and allow the polymer to map onto exposed nanotubes. The solutions were allowed to settle for several days. Films were prepared by casting a drop of the supernatant solution onto surface of freshly peeled HOPG (highly oriented pyrolytic graphite). The drop is observed to dry within seconds. STM measurements were conducted on a NT-MDT Solver SPM apparatus. Scanning parameters

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are typical with 0.05nA setpoint, and +800mV bias voltage. The images presented here are raw images without any additional filtering unless otherwise indicated.

Results and Discussion

In striking contrast to images of straight P3HT on HOPG in Figure 1, the composite film shows an abundance of tubular features throughout. As seen in Figure 2, the polymer is assembled on the SWNT in a highly organised manner as corroborated by TEM [1].

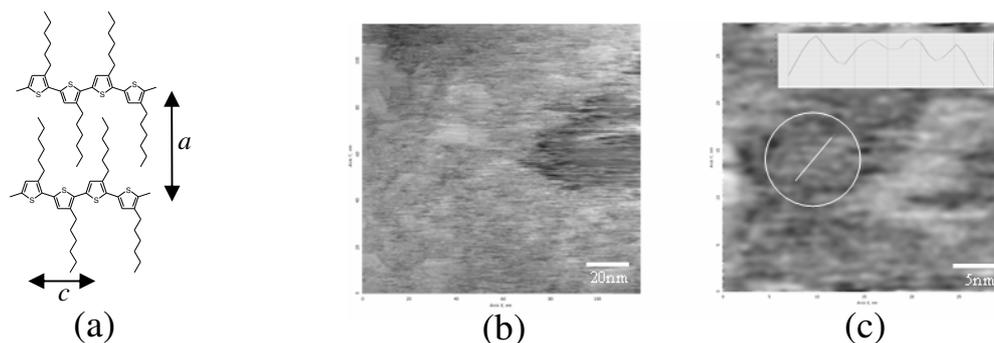


Figure 1: Structure of regioregular head-to-tail (HT) coupled poly(3-hexylthiophene), with c being the repeat distance of a bithiophene unit and a the chain-to-chain distance (a); STM image of straight P3HT on HOPG, more than one monolayer can be seen to form over the first monolayer (b); zoomed and filtered image shows nano-crystalline domains (circled) under the top polymer layers, line profile (inset) shows a of approximately 1.4nm (c).

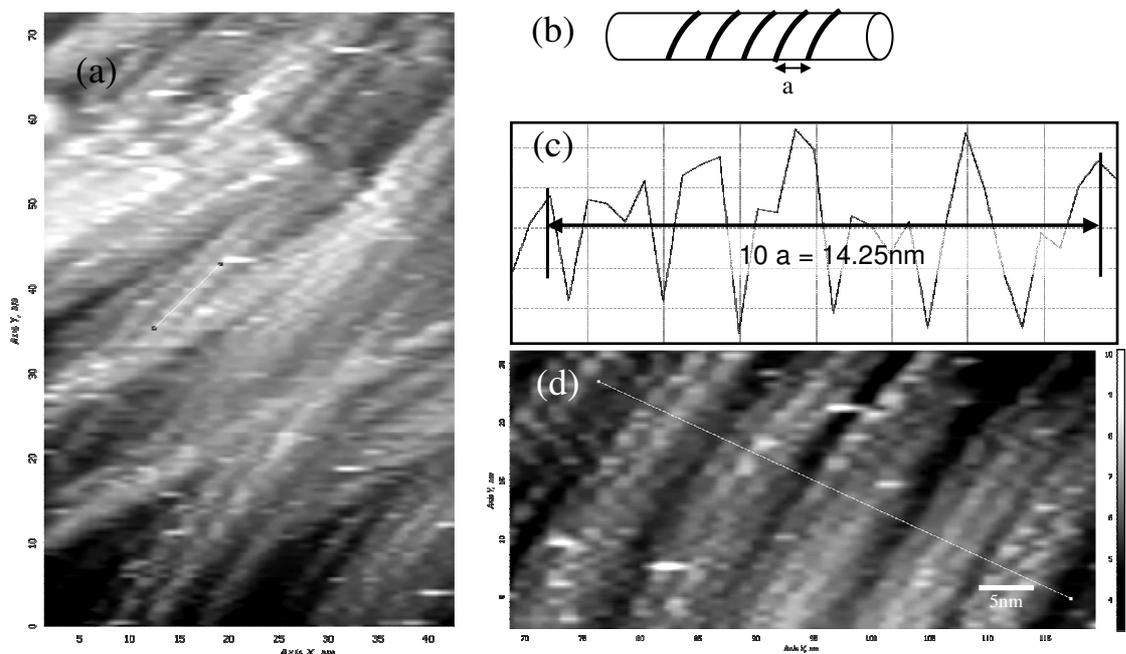


Figure 2: STM of polymer wrapped nanotubes image is taken at an area of polymer/SWNT composite film where bundles are observed to protrude from the film (a); the polymer chain coiling along the axis of a tube is depicted schematically in (b); a high degree of organisation of polymer on SWNT is observed from a line profile along a single polymer wrapped SWNT

backbone, a chain-to-chain distance of about 1.425nm is observed from (c). A bundle of polymer-wrapped SWNTs, the diameter of each tube is about 8 nm from the line profile analysis (d).

Figure 2d shows a bundle of polymer wrapped tube with individual tube diameters of about 8 nm. This suggests that more than one monolayer of polymer is assembled on the tube, since the Carbolex tubes are typically around 1.4nm in diameter [1] and the interstack distance of P3HT is about 3.8Å [8]. It should be noted that determination of the exact diameter of SWNT by STM is difficult since the apparent widths of the tubes are determined by the size of the STM tip rather than the nanotube diameter; this is discussed in more detail in ref. [6, 9]. Topographic profiles along the axes of several polymer-wrapped tubes show a chain-to-chain distance (denoted a) of approximately 1.3 to 2.0 nm. We note that this is in close agreement with a values reported by Grévin *et al.* [7] and as seen from Figure 1c P3HT drop cast on HOPG. While atomic resolution is generally attainable for bare carbon nanotubes, with polymer wrapped tubes, they are not so readily observed. It is however notable that the composite can support electron tunnelling in the voltage window we used, which is testament to the conductivity of the polymer. There have been reports that parallel stacking of polymer chains may increase the conductivity of P3HT by increasing the effective degree of π conjugation [8], this is consistent with the observation that individual rings are unable to be resolved in STM experiments due to increased delocalisation.

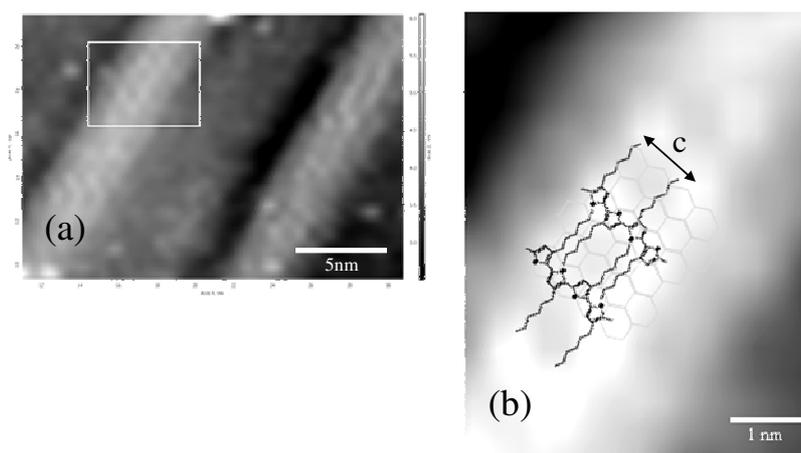


Figure 3: Twin nanotubes of 4nm diameter (a); zoomed and filtered image of single tube (boxed region in (a)) (b).

Figure 3a shows a pair of tubes about 4 nm in diameter. Taking into account tip dependent effects on the diameters of nanotube [6], and the substrate compression effect where single shelled nanotubes are more easily compressed than multishelled (in this case multi-polymer layer coated tubes constitute multishelled tubes) [9], we believe that there is only monolayer coverage on these tubes. In Figure 3b, a high resolution zoom of the boxed area, a repeat distance c of approx. 8 Å is observed; this corresponds to the model of Mena-Osteritz *et al.* [8] in which the molecular orbitals of every second thiophene ring matches a similar electronic environment on the underlying graphene surface, thereby giving rise to extensive electron tunnelling. The wrapping on this high resolution image seems to be at an angle to the tube axis, which we measured to be approx. 4° . This corresponds to a (12,9) chiral SWNT similar to that observed by Venema *et al.* for a 1.4nm diameter SWNT [6]. The hexagonal lattice is drawn in to clarify. We propose that the bithiophene units map onto an underlying benzene

ring through $\pi - \pi$ stacking, as illustrated by the overlaid schematic, resulting in increased delocalisation. Electron tunnelling occurs predominantly through these delocalised states. We further observed that the a distance in these high resolution sections are approx. 1nm, considerably shorter than those observed on the wider tubes in Figure 2c (1.3 – 2 nm). We propose that this is due to epitaxial effect of the first one or two monolayers in contact with the SWNT due to compression of the intra-chain distance as thiophene backbone disrupt the interaction between nanotubes by close packing along their length. This is however a thermodynamically less favourable conformation for the polymer due to high strains that the polymer chain will experience [10]. Therefore, at subsequent layers, the polymer relaxed into the interdigitated conformation through side-chain crystallisation with minimal influence from the substrate. An inorganic semiconductor analogue for this picture is found in the heteroepitaxy of lattice mismatched semiconductors [11].

Based on these observations, we argue that the primary wrapping mechanism for monolayer formation is main chain crystallisation templated by the underlying nanotube. That is, the chain wraps around the tube following its chirality, resulting in the compression of a distance, with thiophene backbone interaction with the nanotube lattice dominating the crystallisation as it seeks to eliminate interactions between adjacent tubes by close packing on the tube surface. A secondary mechanism occurs at subsequent layers where side chain crystallisation dominates. In this case, thiophene backbones lies flat through $\pi - \pi$ interaction with the delocalised π system of the nanotube-monolayer, and the alkyl side chains adopt interdigitated conformation, causing the polymer chain to wrap around the tube in a helical fashion [10]. Molecular mechanics modelling is currently underway in order to establish a theoretical framework for the wrapping behaviour.

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