Ordered arrays of carbon nanotube segments by directed assembly

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Single wall carbon nanotubes (SWCNTs) combine nanometer size and outstanding electronic properties, making them prime candidates for future nanoelectronic applications. Progress toward this goal is hampered by their small size and the fact that these nanostructures are synthesized either at high temperatures or in solution. These factors make it difficult to organize SWCNTs into complex architectures, a key requirement for their exploitation. We are developing approaches leading to the controlled and ordered arrangement of SWCNT segments on lithographically patterned and chemically functionalized surfaces. In this work we present two techniques to achieve self-assembled arrays of SWCNT segments with control over their position and orientation.

In one approach a "breadboard" consisting of nanometer-size metallic nanodots is patterned by nanoimprint lithography and self-aligned pattern transfer [1]. These nanodots are selectively functionalized with amine groups and serve as anchors to covalently bind end-functionalized SWCNT segments (Fig. 1a). The SWCNT segments are formed by wrapping them with single-stranded DNA (ssDNA) and sonicating in water to form short, monodisperse ($L = 148 \pm 93$ nm) segments separated by size selective chromatography [2]. Binding occurs via a covalent linkage between the amine groups on the dots and carboxyl groups at the ends of the SWCNT segments. This attachment at the ends assures precise control on the nanotubes position. Capillary force drying gives directionality to the assembly, which results in parallel arrays of SWCNT segments (Fig. 1b). The nanodots are sufficiently small, ~ 5 nm, such that only a small number of SWCNT segments can bind to each one, allowing near-single-molecule control. Furthermore, the nanodots can be patterned as close as 20 nm apart or less, so that dense arrays of SWCNTs can be achieved.

In a second approach, we use electron beam lithography to pattern hydrophilic regions on a hydrophobic substrate. The regions are designed to match the size of SWCNT segments, which selectively bind to the hydrophilic areas, due to the ssDNA wrapping. Lines are patterned with lengths matching the length of the SWCNT segments and widths varying from 10 nm to 40 nm (Fig. 2a). The SWCNT segments selectively bind to the patterned hydrophilic regions as a result of the ionic buffer solution in which they are dispersed. This hydrophilic interaction results in precise, directed assembly of the SWCNTs on the surface with control over position and orientation. By varying the width of the patterned lines, we can optimize the binding yield of individual SWCNT segments (Fig. 2b). With this technique it is possible to organize CNT segments with different orientations on the same substrate.

In this work we demonstrate how the combination of precise lithographic patterning and selective modulation of surface chemistry and surface energy can be used to produce ordered arrays of SWCNT segments. This strategy has great potential for the implementation of complex CNT-based devices and circuits.

1. Schvartzman, M. and S.J. Wind, *Robust Pattern Transfer of Nanoimprinted Features for Sub-5-nm Fabrication.* Nano Letters, 2009. **9**(10): p. 3629-3634.
2. Zheng, M., et al., *DNA-assisted dispersion and separation of carbon nanotubes.* Nature Materials, 2003. **2**(5): p. 338-342.

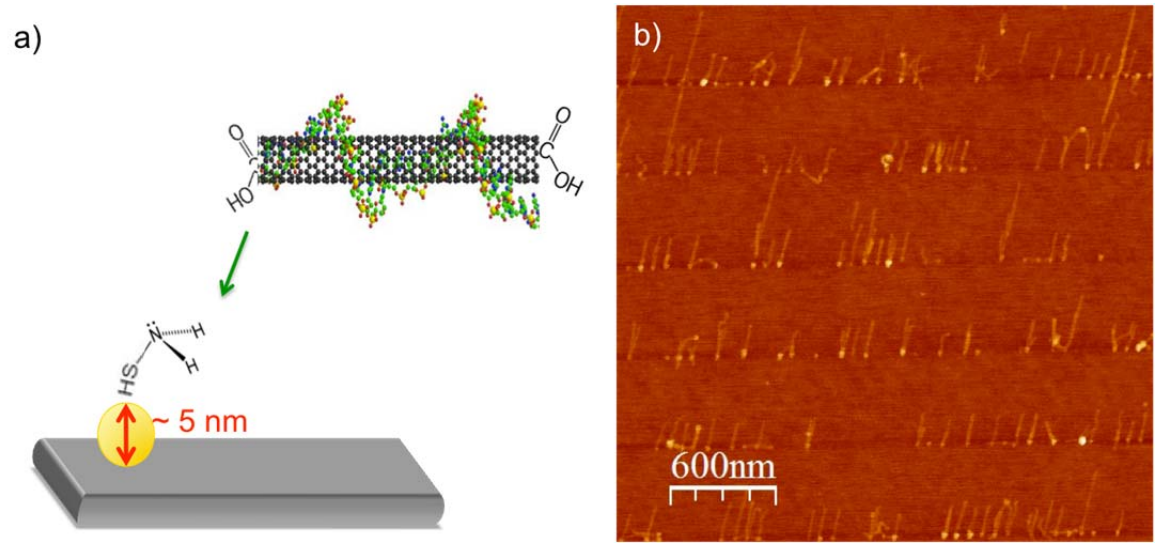

Figure 1. a) Schematic of SWCNT segments covalently attached to AuPd nanodots functionalized with amine groups. b) AFM image of aligned SWCNT segments covalently attached to AuPd nanodots patterned in lines with in-line spacing of 70 nm. Directional assembly is achieved by controlled capillary force drying.

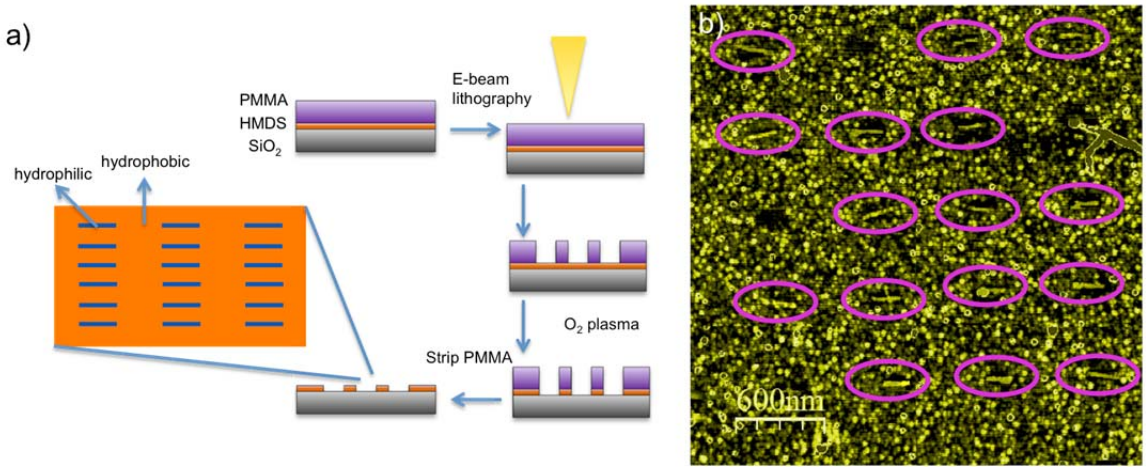

Figure 2. a) Schematics of the fabrication process of hydrophilic lines on a hydrophobic -HMDS coated- substrate. b) Colorized AFM image of single SWCNT segments (circled in purple) on hydrophilic lines patterned on a hydrophobic substrate.