

Directed Assembly of Single-Walled Carbon Nanotubes via Drop-Casting onto a UV-Patterned Photosensitive Monolayer

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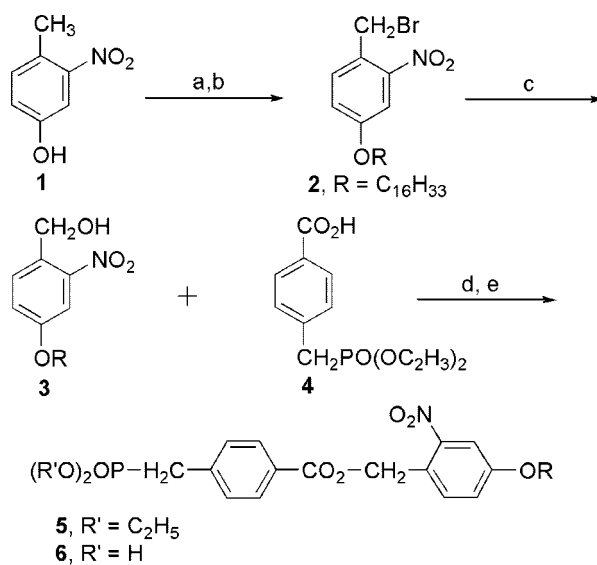
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Over the past decade, single-walled carbon nanotubes (SWCNTs) have emerged as a promising material for use in a variety of electronic applications due to their unique electrical and physical properties.¹ The versatility of SWCNTs yields an impressive range of potential applications, including sensors, flexible electronics, and photovoltaics. Semiconducting nanotubes, in particular, have attracted considerable attention because of their demonstrated performance in field-effect transistors.² However, the fabrication of such devices depends upon the ability to selectively place oriented SWCNTs. The concept of using heterogeneous surface wettability for selective deposition was explored using a multitude of systems,³ including the use of self-assembled monolayers (SAMs) to selectively deposit inorganics from a solution.^{3a,d,4} The wettability of SAMs was also utilized to selectively deposit organics, including polymers,^{3b} polymer microspheres,^{3c} nanoparticles,^{3d} and carbon nanotubes.^{3d,e} Previous work from this laboratory⁵ utilized end groups (i.e., phosphonic acid and hydroxamic acid) that selectively bind to basic oxide surfaces in order to prevent or enhance the adhesion of carbon nanotubes to certain regions of a patterned surface. In these studies, oxide surfaces were patterned lithographically to produce the regions to which the carbon nanotubes would bind. Here, we bypass the need for complex lithography by utilizing a simple and scalable approach to solution-based placement of SWCNTs based on photopatterning a photosensitive self-assembled monolayer.

The key results of this study are the design and synthesis of a photoreactive self-assembling molecule (Scheme 1), the successful patterning of the monolayer by exposure to UV radiation through a mask, and the selective placement of SWCNTs on the patterned monolayer surface. The photosensitive compound (phosphonic acid derivative **6**) was designed to possess the following three properties that are essential to the formation of a UV-patterned SAM: (i) a photoreactive moiety that breaks down or rearranges upon exposure to UV light, (ii) an end group functionality capable of bonding to the oxide surface, and (iii) the ability to undergo a drastic change in surface chemistry (i.e., change from hydrophobic to hydrophilic) upon exposure to UV radiation. The phosphonic acid group in **6** bonds to metal oxides, leading to the formation of uniform SAMs. The molecule is photoreactive and cleaves upon exposure to UV radiation. Additionally, the monolayer is highly hydrophobic before UV exposure due to the presence of a long chain alkyl group, and after exposure, the exposed carboxylic acid end group creates a hydrophilic surface. Selective placement of the SWCNTs was achieved by drop-casting an aqueous dispersion of SWCNTs in 2% sodium cholate surfactant. The aqueous SWCNT solution is repelled by the hydrophobic regions and wets the hydrophilic

Scheme 1



a; C₁₆H₃₃Br, K₂CO₃, DMF, 120 °C. b; NBS, CCl₄, hv,
c; AgNO₃, acetone-H₂O, d; DCC, CH₂Cl₂, r.t.,
e; (CH₃)₃SiBr, CH₂Cl₂, r.t. then H₂O + H⁺

regions of the monolayer. The wettability of the carboxyl-terminated surface, in combination with the affinity of SWCNTs for the carboxyl group (which is not expected to affect transport in the SWCNT),⁶ enabled a high density of SWCNTs to be deposited on the UV-exposed surfaces. The use of the photosensitive monolayer eliminates the need for complex lithography and therefore reduces the number of processing steps. This method is compatible with current silicon microprocessing techniques and could be implemented into a large-scale processing line.

Exposure to UV light promotes cleavage of the phosphonic acid molecule at the nitrobenzyl ester junction, yielding a carboxyl-terminated surface. Patterning of the monolayer using UV light through a mask will create a surface of alternating alkyl-terminated (hydrophobic) and carboxyl-terminated (hydrophilic) regions (Figure 1a). Figure 1b illustrates the reaction yielded by exposing the photosensitive SAM **6** (HD-UV-PA) to UV light.⁷

The initial surface of bare HfO₂ is very hydrophilic with a water contact angle of less than 10°. After self-assembly of the HD-UV-PA monolayer, the water contact angle value of the HfO₂/HD-UV-PA surface is 92 ± 5°. Comparatively, the reported water contact angle of an octadecylphosphonic acid (ODPA) monolayer on the native oxide of aluminum is 122°. The slightly lower water contact angle measured for the phosphonic acid monolayer from **6** compared

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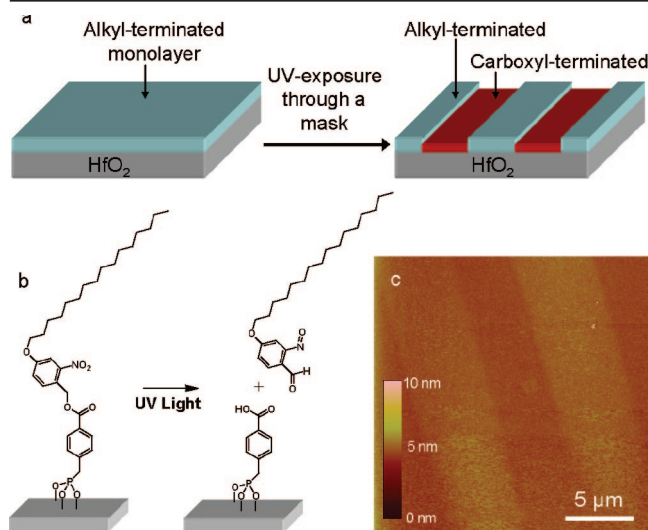


Figure 1. (a) Illustration of creating the photopatterned monolayer, (b) illustration of the UV-induced reaction of SAM **6**, and (c) AFM image of the photopatterned monolayer surface.

to that of the ODPA monolayer is probably due to the larger footprint of the former leading to a lower density of alkyl chains on the surface after assembly. After blanket UV exposure, the water contact angle of the monolayer decreased significantly, yielding a water contact angle of about $15 \pm 5^\circ$ after a 45 min exposure. Bain et al. reported water contact angles of approximately 5° for carboxyl-terminated alkane thiols of various chain lengths on gold.⁹ The higher contact angle measured for the carboxyl-terminated monolayer is also attributed to the larger molecular footprint of the HD-UV-PA molecule.

Due to the large size of the cleaved portion of the assembled molecule (approximately 2 nm fully extended), atomic force microscope (AFM) images were useful in verifying the monolayer reaction. Figure 1b shows an AFM image of the patterned HD-UV-PA surface. The measured height difference between the UV-exposed and unexposed regions of the monolayer was approximately 0.7 nm (Supporting Information). The lower value of the measured height difference compared to the theoretical value is most likely due to the flexibility of the alkyl chain. The monolayer reaction was also verified by X-ray photoelectron spectroscopy through the elimination of the N 1s peak in the spectrum after UV exposure (Supporting Information).

Deposition of the aqueous solution of SWCNTs by drop-casting on the patterned monolayer surface yielded the desired combination of excellent selectivity and densely packed SWCNTs. Since the unexposed areas of the monolayer are very hydrophobic, the aqueous SWCNT solution prefers to wet the areas that have been exposed to UV light, forming microdroplets on the exposed areas. The solvent then evaporates leaving the SWCNTs on the carboxyl-terminated surfaces. Figure 2 shows a $20 \mu\text{m}$ AFM image of drop-cast SWCNTs on a patterned HD-UV-PA surface. Higher resolution images of the hydrophobic and hydrophilic regions of the monolayer after SWCNT deposition are shown adjacent to the $20 \mu\text{m}$ image in Figure 2.

It should be noted that some local ordering of bundled SWCNTs is visible in the AFM image shown in Figure 2. This type of “woven” structure has been noted previously¹⁰ and was attributed in part to the motion of the liquid–solid–air contact line.

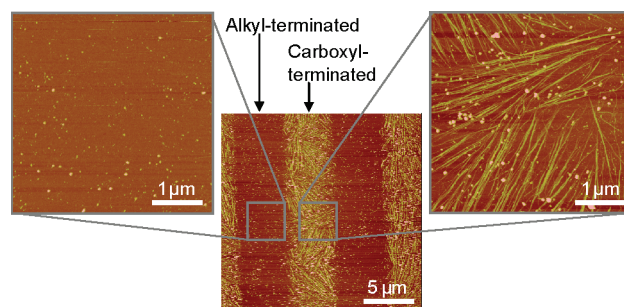


Figure 2. AFM image of the UV-patterned HD-UV-PA-modified surface after drop-casting SWCNTs from a H_2O /methanol solution (3:1 volume). The higher resolution images on the left and right illustrate the high selectivity of the deposition.

In conclusion, we have patterned the surface of an oxide substrate to produce both hydrophobic and hydrophilic regions using self-assembly of a photosensitive compound. The use of UV light to pattern the surface energy of a monolayer is scalable and can be readily implemented in current semiconductor processing. Moreover, the combination of UV patterning with simple solution processing methods yields patterns of SWCNTs with excellent selectivity and high density. Further development of this process, including the use of more advanced exposure techniques, may lead to a simple and effective method for the selective placement and alignment of individual SWCNTs.

Acknowledgment. This material is based on work partially supported by DARPA under Contract N66001-06-C-2047. J.A.B. thanks the University of Washington Center for Nanotechnology for the Nanotechnology Fellowship. The authors thank Dr. Dario Goldfarb for use of the photopatterning equipment, and the IBM MRL fabrication facility for fabrication of wafers and deposition of dielectrics.

Supporting Information Available: Detailed synthesis experimental procedures and SAM characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA802407F