Electronic Supplementary Material (ESI) for ChemComm.

Nanoscale Patterning of Self-assembled Monolayers using DNA Nanostructure Templates

*Sumedh P. Surwade, Feng Zhou, Zhiting Li, Anna Powell, Christina O'Donnell, and Haitao Liu**

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

* To whom correspondence should be addressed: hliu@pitt.edu

Supporting Information

1. Materials

Octadecy trichlorosilane (ODTCS) and aminopropyl triethoxysilane (APTES) were purchased from Sigma Aldrich. Silicon wafers [110] was purchased from University Wafers. Synthetic and M13mp18 DNA for preparing the origami[1] were purchased from IDT and New England Biolabs, respectively. The silicon substrate was cleaned with hot piranha solution (7:3 concentrated H_2SO_4: 35% H_2O_2) prior to use. *Warning: Piranha solution presents an explosion danger and should be handled with extreme care; it is a strong oxidant and reacts violently with organic materials. All work should be performed in a fume hood. Wear proper protective equipment.*

Tapping mode atomic force microscopy was carried out on a Veeco Dimension 3100 in air.

X-ray photoelectron (XPS) spectra were collected on a custom built multi-technique surface analysis instrument operating at a base pressure of less than $1x10^{-10}$ torr. Spectra were collected

using the Al-Kα X-ray line and a Leybold-Heraeus EA-10 hemispherical energy analyzer typically operating with a bandpass of 50 eV. Data analysis was carried out using in house written software for both background subtraction and peak fitting.

2. Methods

2.1. Triangular DNA origami preparation

The DNA origami triangles were prepared using a previously published procedure.[S1] In a typical procedure, the desired set of 253 shorts strands (16 nM) were mixed with M13mp18 (1.6 nM) in a 100 µL total volume of 1X Tris-Acetate-EDTA (TAE) buffer (400 mM Tris acetate, 10 mM EDTA, 20 mM Na^+) with 12.5 mM magnesium acetate (pH=8.3), a 10 fold excess of short strands. The sample was then annealed from 95 ºC to 20 ºC at the rate of 1 ºC/min. After the completion of annealing, excess staples were removed from the origami solution by washing at least 3 times with 300 µL of TAE/Mg^{2+} buffer in 100 kDa MW centrifuge filters (Microcon YM-100, Millipore, Billerica, MA) on a single speed bench top microcentrifuge (VWR Galaxy Ministar) for 30 – 90 seconds. It is ensured that the filter is not centrifuged to dryness and there is always 50 – 100 µL of the sample left in the filter. After filtration the origami solutions were stored at 4 ºC.

2.2. Assembly of DNA nanostructure on Si substrate

The DNA nanostructure solution (2 µL) was pipetted onto a clean silicon wafer and left undisturbed for 30 min in a closed container with its lid covered by a moistened kimwipe to minimize evaporation. The substrate was then dried by blowing N_2 gas such that the drop of buffer solution on the substrate is drove in one direction. The substrate was then immersed in 1:9

water:ethanol solution for 3 sec (twice) to remove the salt impurities and then blow dried using N_2 gas.

2.3. Patterning of Octadecyl trichlorosilane (ODTCS) on Si substrate

Si substrate with the self-assembled DNA nanostructures is placed inside a vacuum desiccator containing a 5 ml vial of ODTCS. The pressure inside the desiccator is brought down to ~45 mtorr using a vacuum pump and the desiccator is left undisturbed under static vacuum. After approximately 24 hours, the substrate is removed and sonicated in DI water for 30 seconds to remove DNA nanostructures resulting in nanoscale patterns of ODCTS self-assembled monolayers on Si substrate.

Note: The ODTCS is transferred to the vial inside a glove box under nitrogen atmosphere and the vial is placed quickly under desiccator to avoid exposure to atmospheric moisture.

2.4. Patterning of ODTCS + aminopropyl triethoxysilane (APTES) patterns on Si substrate

Si substrate patterned with ODTCS is placed inside a desiccator containing a 5 ml vial of APTES and left undisturbed with desiccator lid closed doe ~ 24 hours. APTES vapor assembles on the Si substrate not covered by ODTCS pattern resulting in ODTCS + APTES patterns with nanometer scale resolution. The sample is sonicated in DI water for 30 seconds and blow dried using nitrogen.

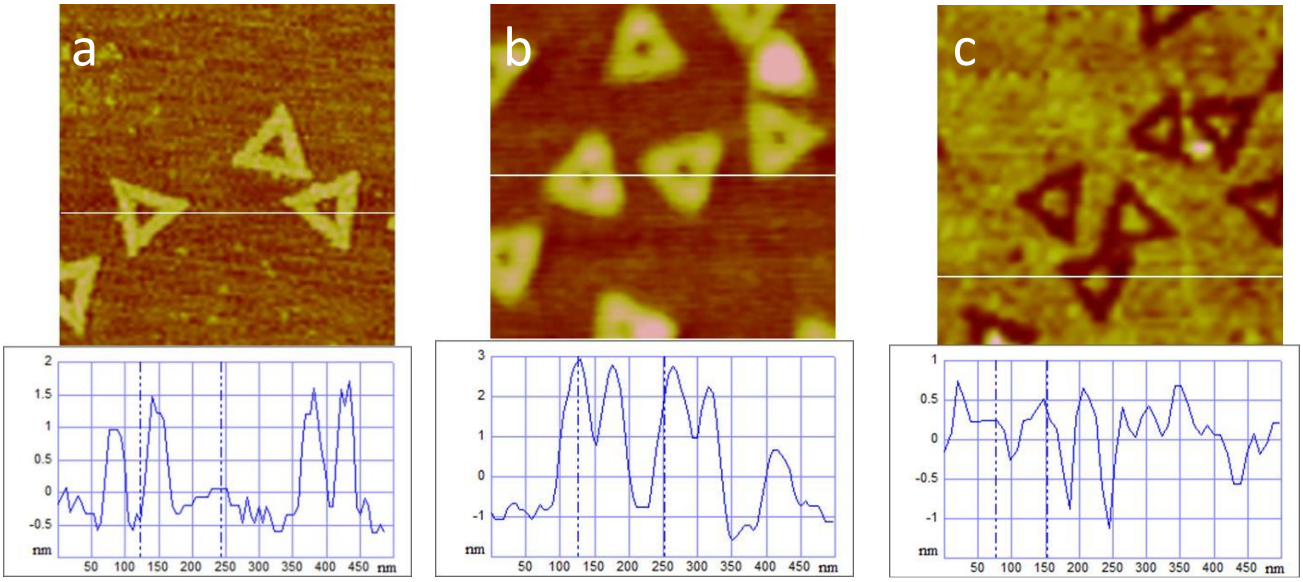

Figure S1. Zoom in AFM image of (a) DNA nanostructures assembled on a Si substrate; (b) sample (a) after exposure to ODTCS; and (c) sample (b) after sonication in DI water to remove DNA. The white line indicates the line of cross section.

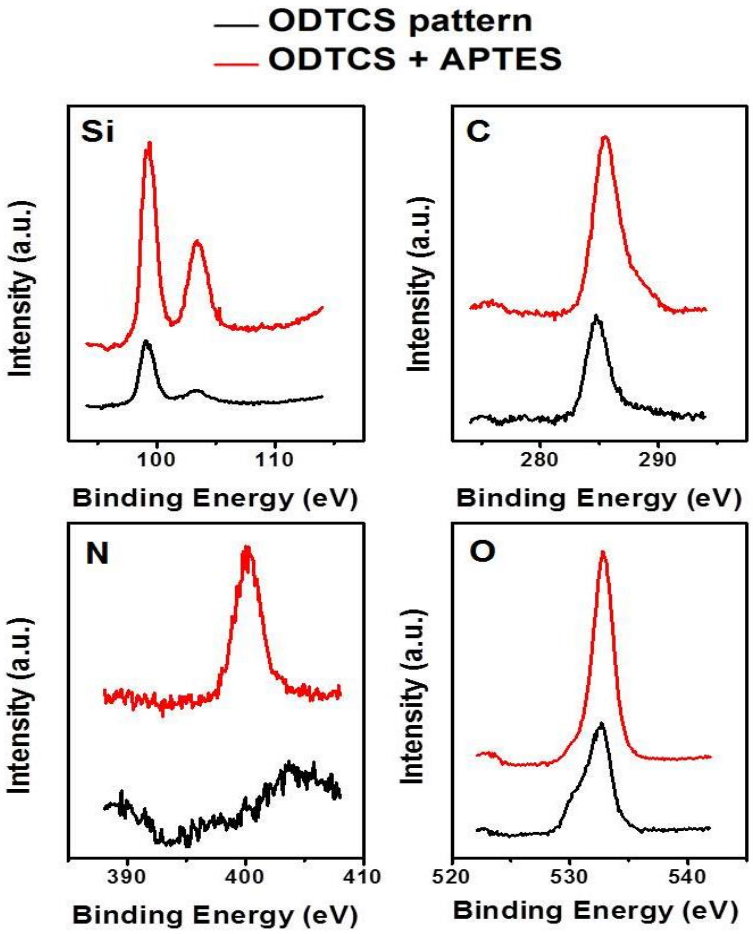

Figure S2. XPS scan of individual elements for ODTCS pattern substrate (black) and ODTCS + APTES pattern substrate (red).

Table S1. Contact angle measurements on substrate patterned with SAM.

	Sample	Contact Angle
1	ODTCS on Si (control)	96˚ 
2	DNA + ODTCS	111˚ 
3	Sample 2 after removing DNA	111˚ 
4	ODTCS + APTES patterns	88˚ 

References

S1 Rothemund, P. W. K. Folding DNA to create nanoscale shapes and patterns. *Nature* **440**, 297-302 (2006).