

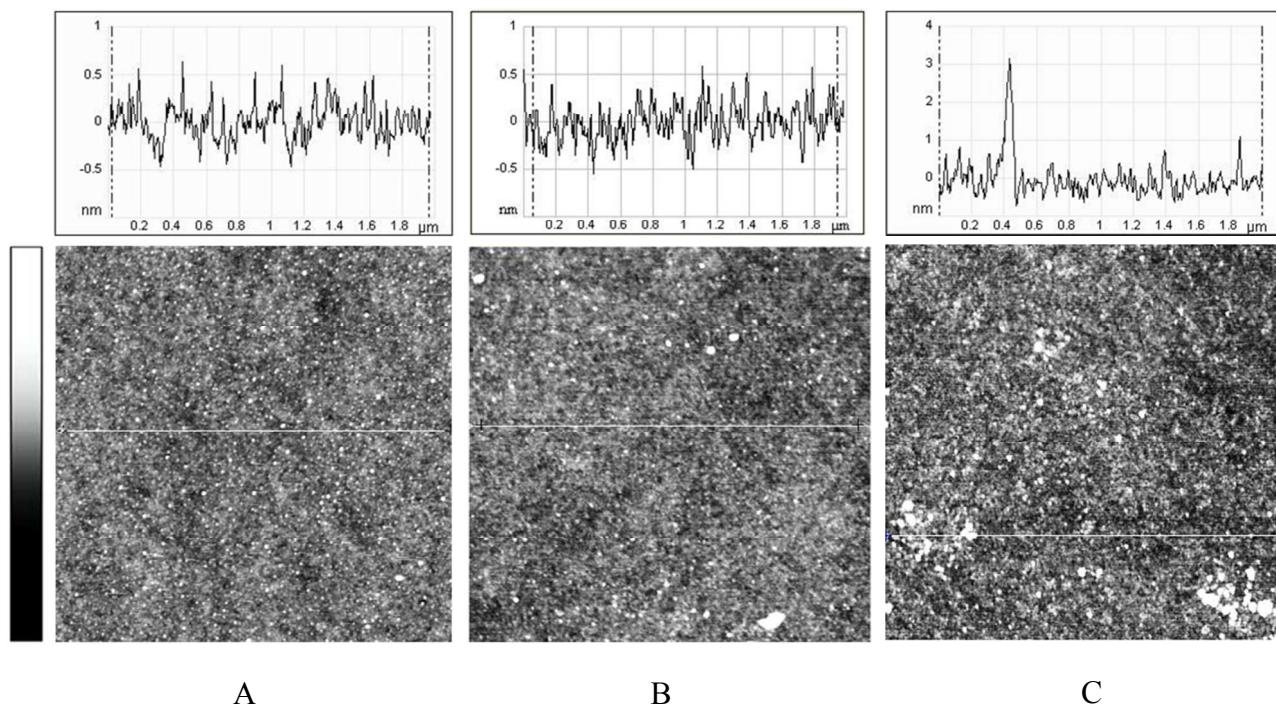
# Angle-Resolved XPS Analysis and Characterization of Monolayer and Multilayer Silane Films for DNA Coupling to Silica

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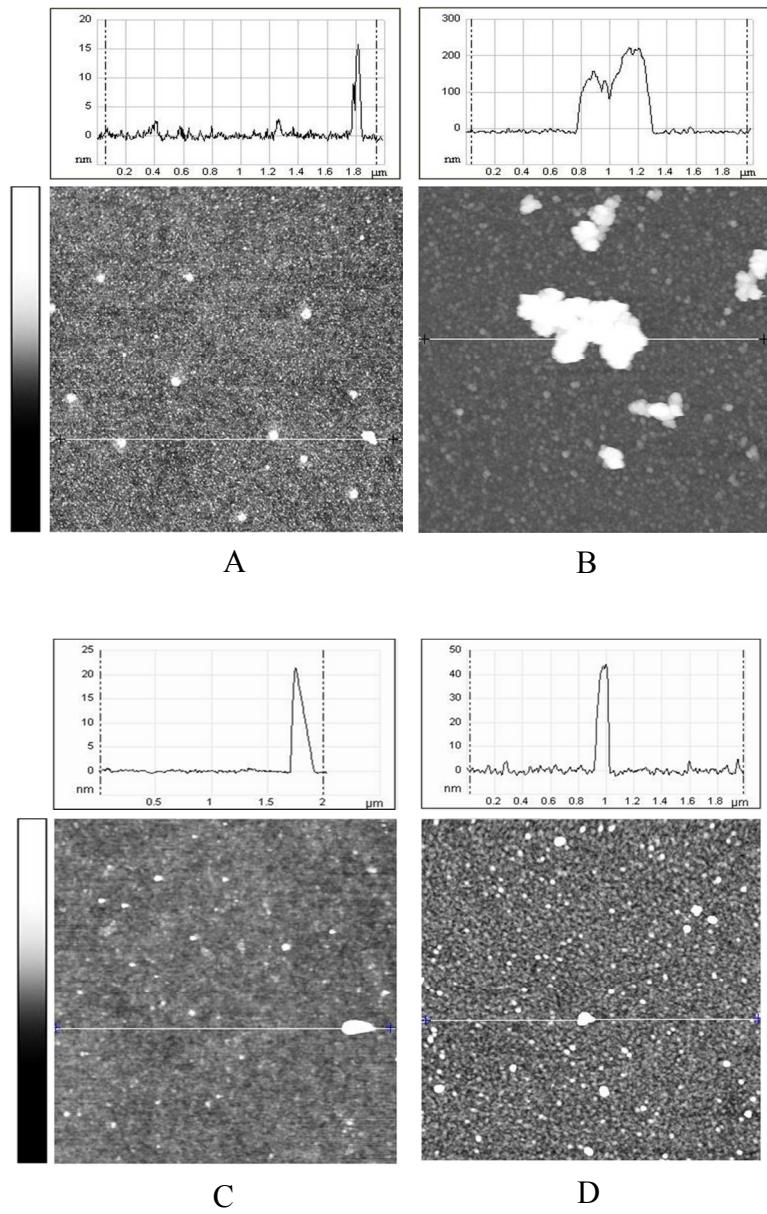
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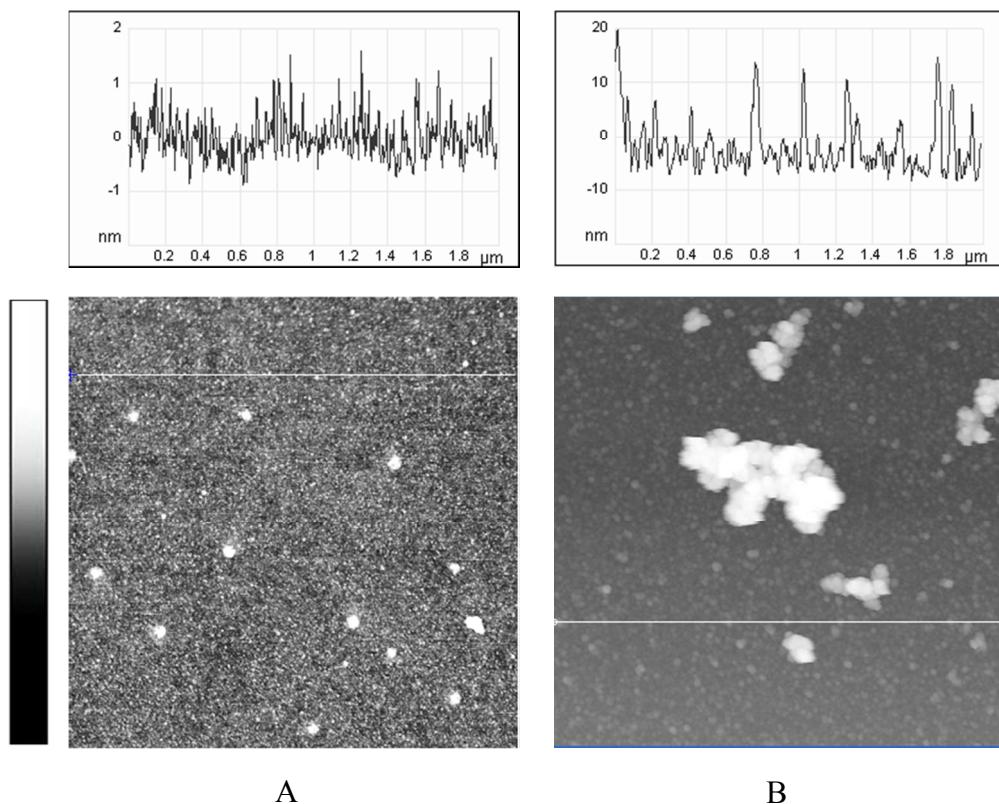


**Figure S1.** AFM images representative of (A) oxygen plasma cleaned silica substrate, (B) 19 h APDMES deposition and (C) 19 h APDMES sample treated with Sulfo-EMCS. Height scale is 5 nm for all images. Horizontal lines indicate where the line cans are taken. The rms roughnesses are (A) 0.230, (B) 0.333nm and (C) 0.532. The AFM images have an area of  $4 \mu\text{m}^2$ . Note (A) and (B) are also reported in the Supporting info for Shircliff et al. *ACS Applied Materials & Interfaces*. **2011**, **3**, 3285-3292 and are provided here for convenience of comparison to the Sulfo-EMCS-treated sample.

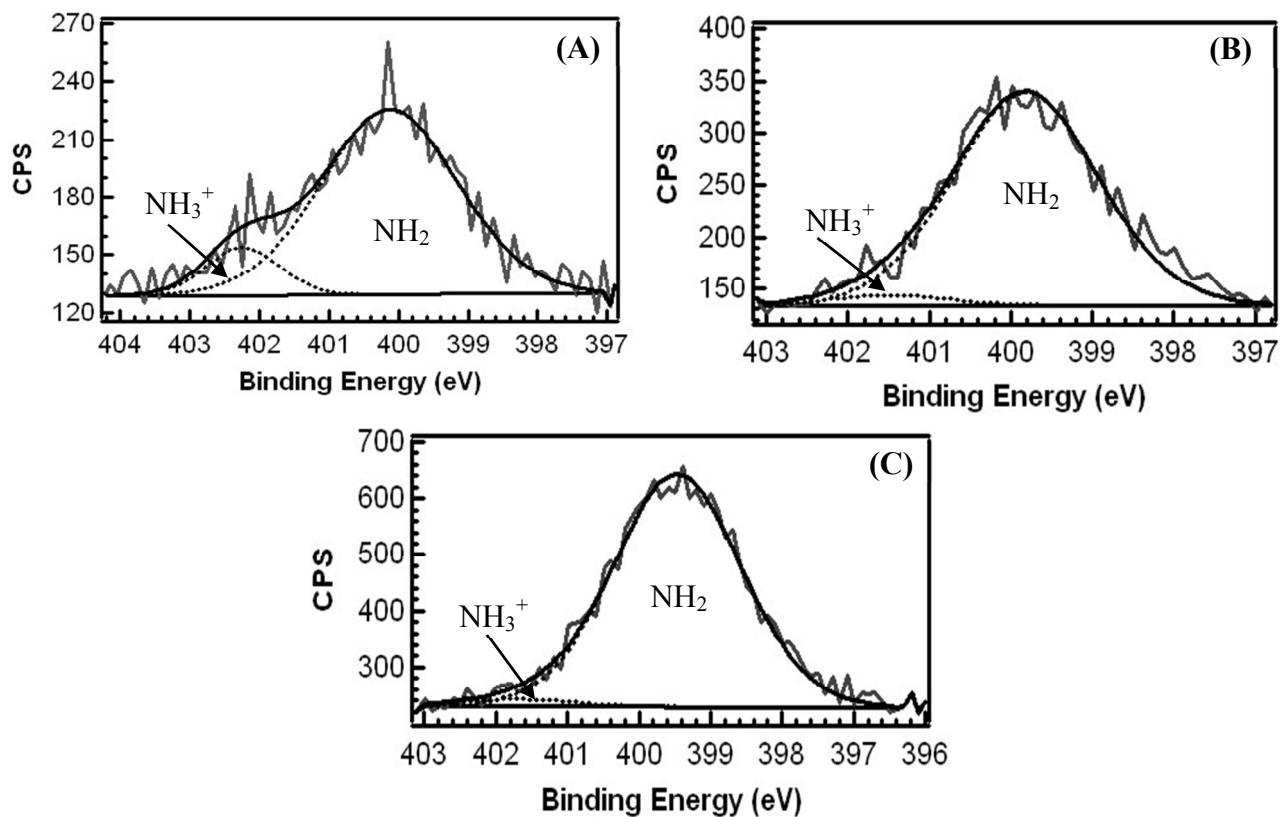


**Figure S2.** AFM images representative of (A) 1 h APTES deposition, (B) 19 h APTES deposition, (C) 1 h APTES sample treated with Sulfo-EMCS, (D) 19 h APTES sample treated with Sulfo-EMCS. (A) and (C) both have a height scale of 10 nm; (B) and (D) have a height scale of 350 nm and 30 nm, respectively. Horizontal lines indicate where the lines cans are taken. The rms roughnesses are 0.624 nm for the 1 h APTES deposition and 0.650 nm for the Sulfo-EMCS treated 1 h APTES sample. The 1 h APTES deposition shows the initial formation of film

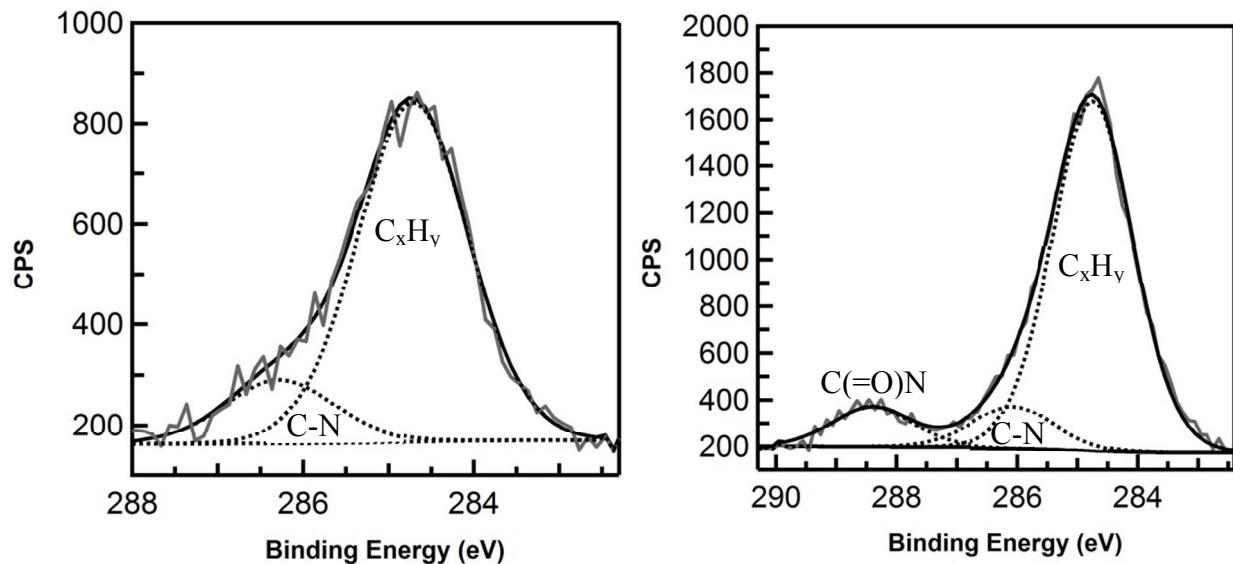
aggregates, which is likely due to the vertical polymerization of APTES and is also observed in the Sulfo-EMCS treated sample (C). For the 19 h APTES deposition, aggregates up to 200 nm in height are observed, similar to reported values. Aggregates up to 50 nm are measured in the Sulfo-EMCS treated 19 h APTES sample (D). Note the heterogeneity of APTES films and how samples can be relatively smooth in one area but have agglomerates in another.



**Figure S3.** Horizontal line scans of AFM images above in Figure S2 A (1 h APTES) and B (19 h APTES). These line scans show the rms roughness of the silane films outside of the aggregates: (A) 0.439 nm and (B) 3.91 nm. (A) and (B) have a height scale of 10 nm and 350 nm, respectively.

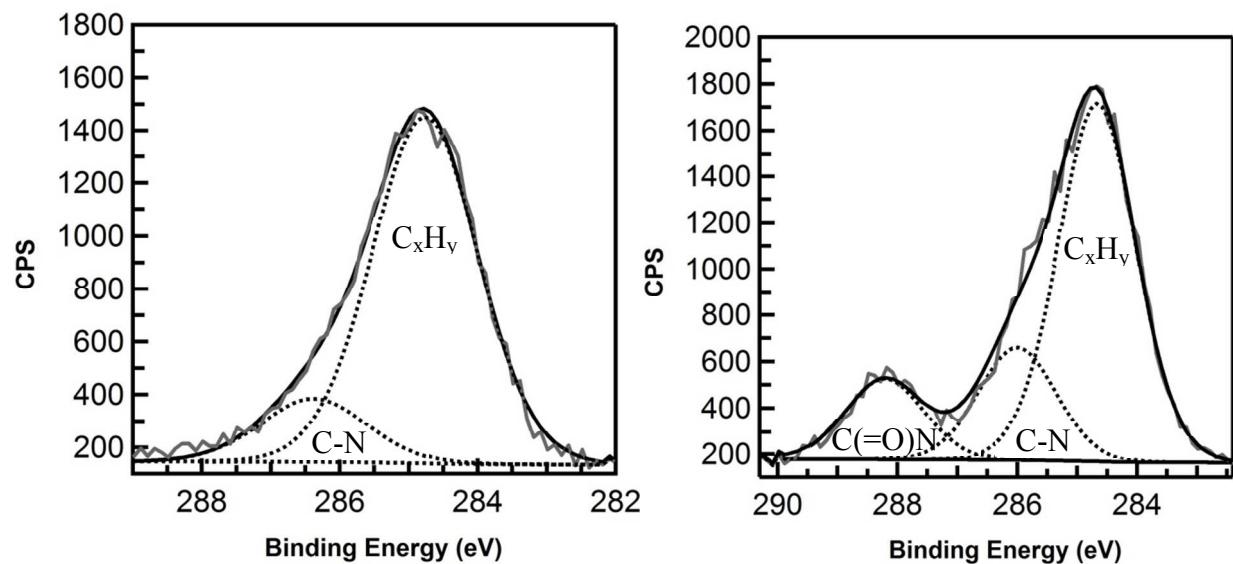


**Figure S4.** N 1s high-resolution XPS spectra collected at 15° TOA for (A) APDMES 19 h, (B) APTES 1 h and (C) APTES 19 h films. These illustrate that the amide peak ( $\text{C}(=\text{O})\text{N}$ ) is not found in the silane-only treated surface and also illustrates the ratio of  $\text{NH}_2$  to  $\text{NH}_3^+$ .

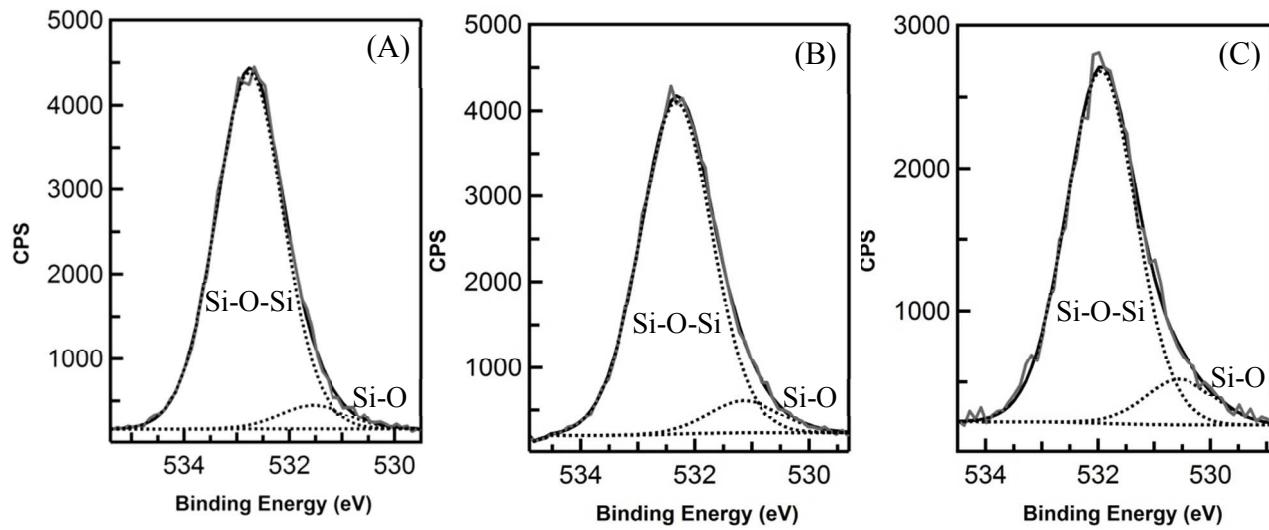


**Figure S5.** C 1s high-resolution XPS spectra (at a 15° TOA) for a 19 h APDMES film (left) and the APDMES-treated surface after reaction with Sulfo-EMCS (right). The amide peak ( $C(=O)N$ ) is absent in the spectrum for the APDMES-treated samples, but is present on the Sulfo-EMCS-treated surface. This is indicative of Sulfo-EMCS attachment to the APDMES-treated surface.

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**Figure S6.** C 1s high-resolution XPS spectra (at a  $15^\circ$  TOA) for a 19 h APTES film (left) and the APTES-treated surface after reaction with Sulfo-EMCS (right). The amide peak ( $C(=O)N$ ) is only present on the Sulfo-EMCS-treated surface; indicative of Sulfo-EMCS attachment to APTES molecules on the silica surface.



**Figure S7.** O 1s high-resolution XPS spectra (at a 15° TOA) for silica treated with (A) 19 h APDMES, (B) 1 h APTES and (C) 19 h APTES. Si-O represents the silane attached to silica, whereas Si-O-Si represents the silica substrate. The Si-O peak modestly increases from left to right; the respective values are 6% (19 h APDMES), 8% (1 h APTES) and 11% (19 h APTES).