

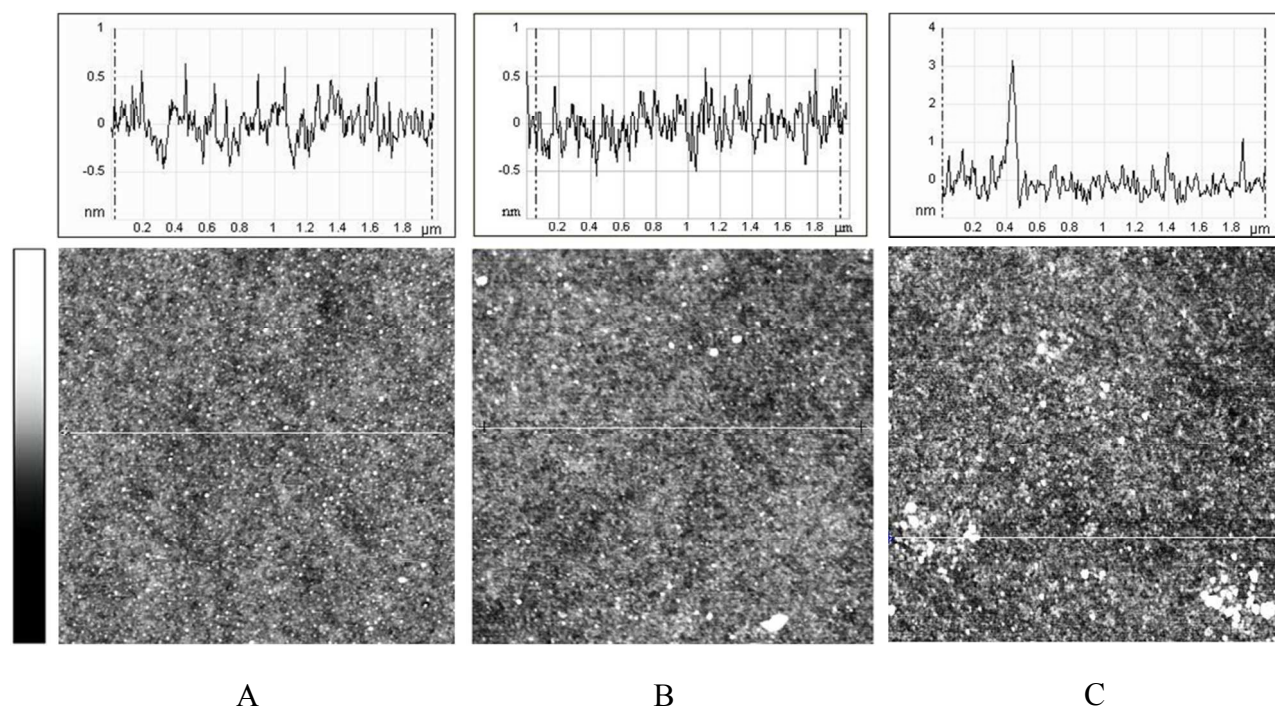
# Angle-Resolved XPS Analysis and Characterization of Monolayer and Multilayer Silane Films for DNA Coupling to Silica

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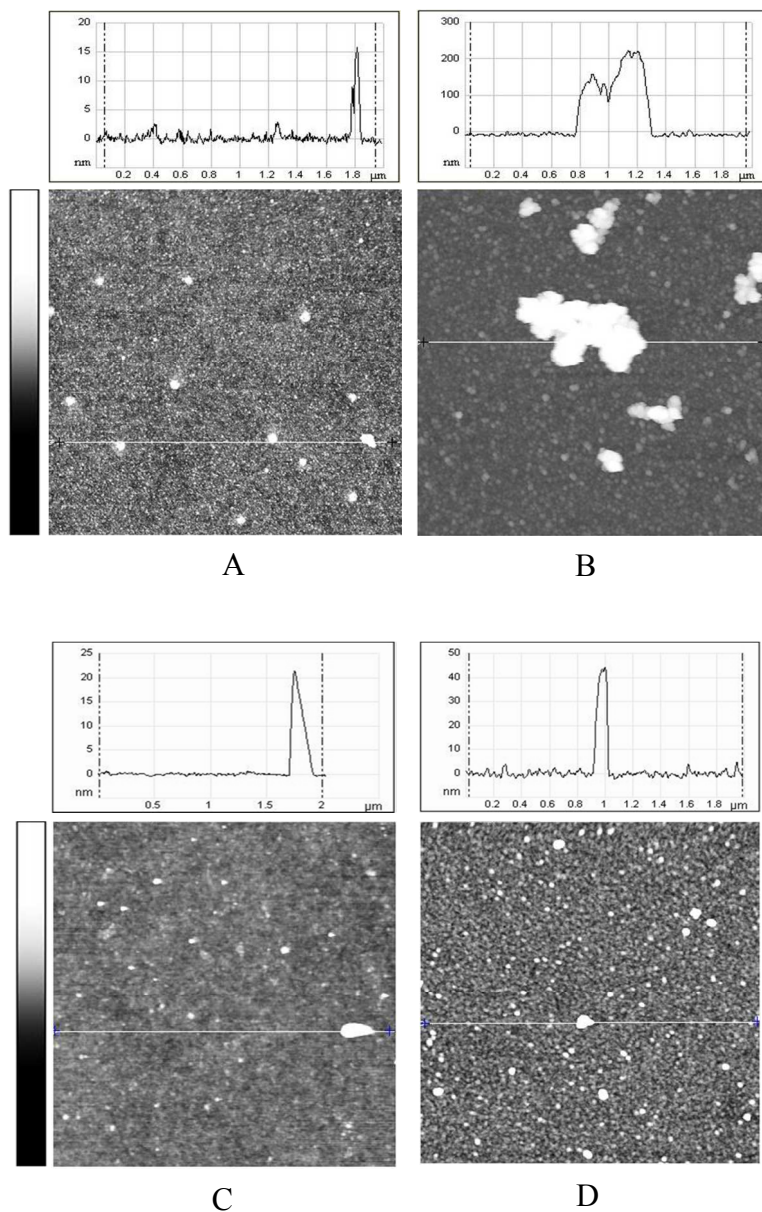
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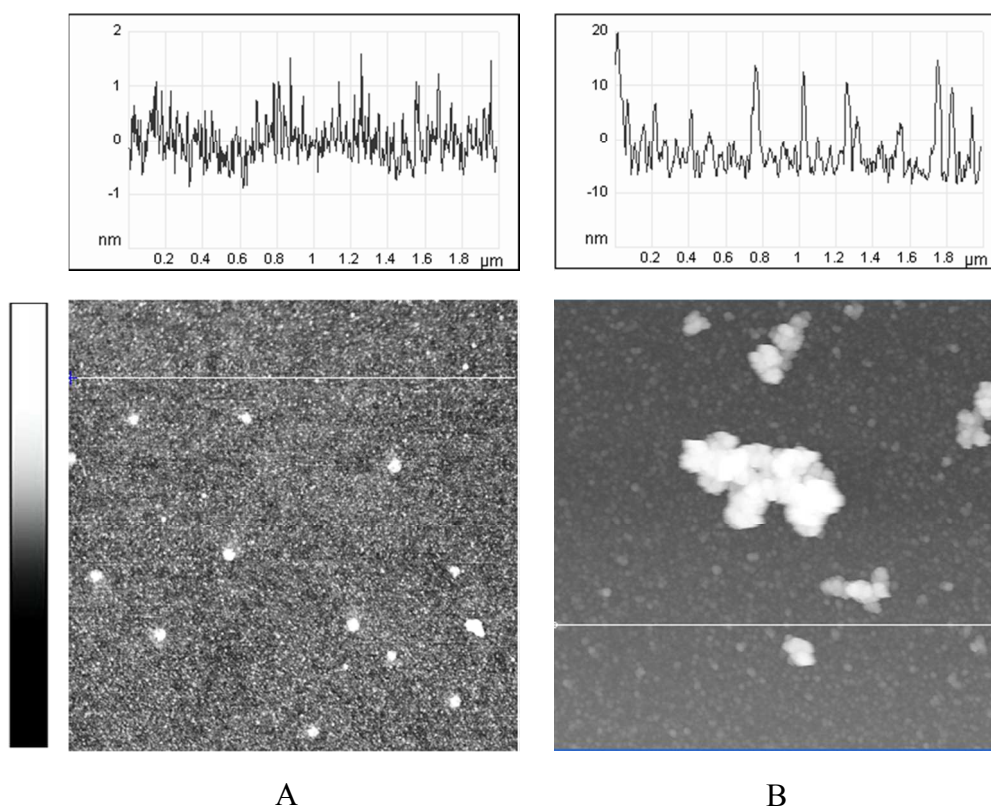


**Figure S1.** AFM images representative of (A) oxygen plasma cleaned silica substrate, (B) 19 h APDMES deposition and (C) 19 h APDMES sample treated with Sulfo-EMCS. Height scale is 5 nm for all images. Horizontal lines indicate where the line scans are taken. The rms roughnesses are (A) 0.230, (B) 0.333 nm 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.

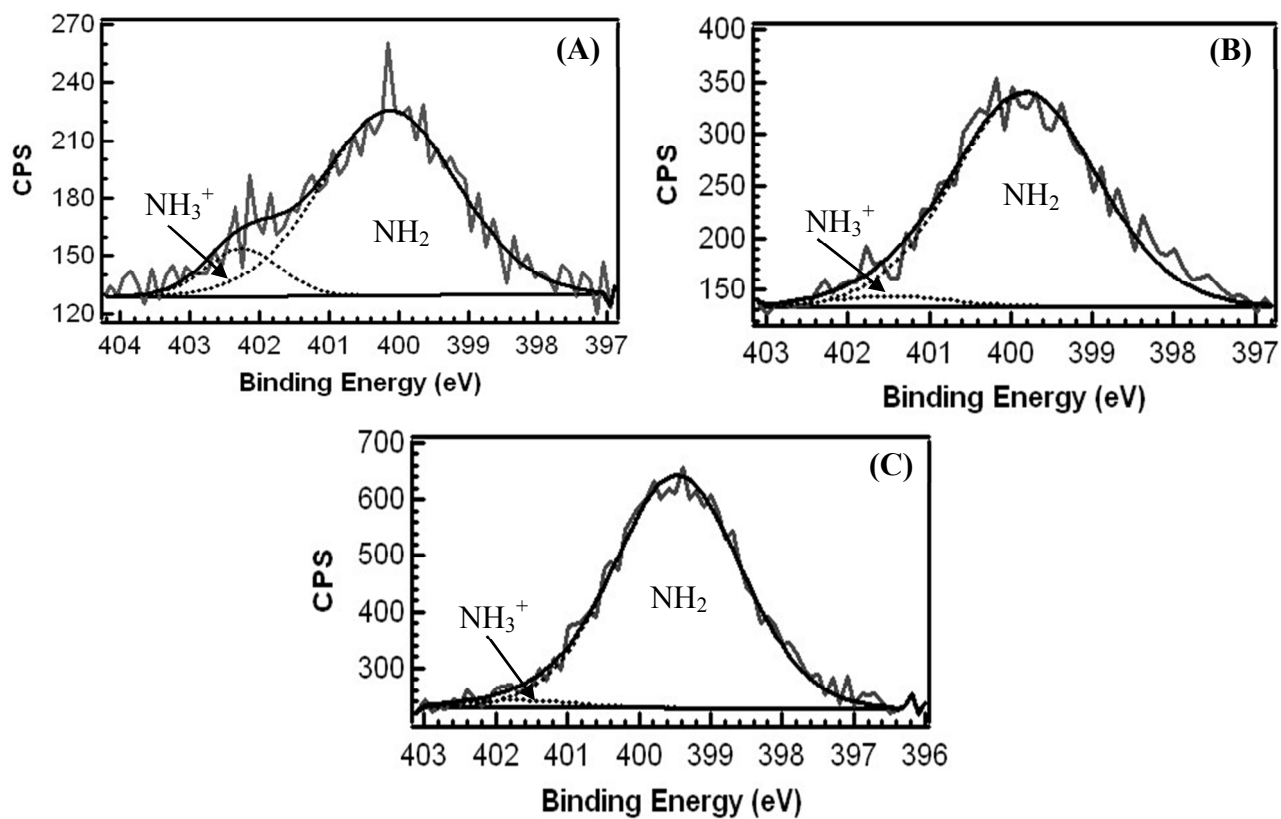


**Figure S2.** AFM images representative of (A) 1 h APTES deposition, (B) 19 h APTES deposition, (C) 1 h APTES sample treated with Sulfo-EMCS, (D) 19 h APTES sample treated with Sulfo-EMCS. (A) and (C) both have a height scale of 10 nm; (B) and (D) have a height scale of 350 nm and 30 nm, respectively. 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

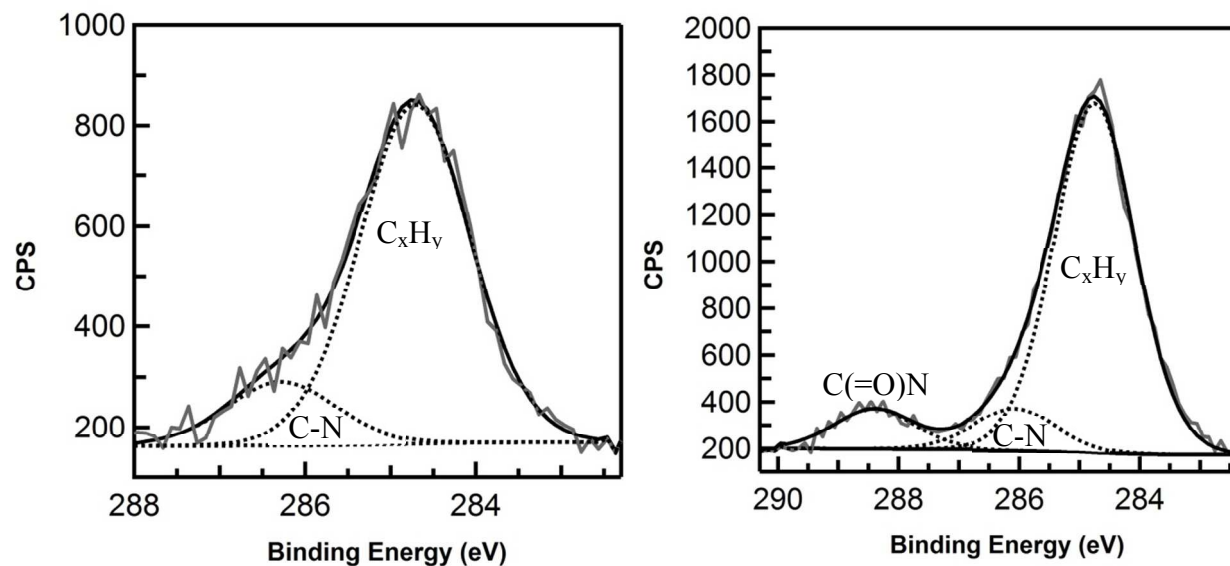
aggregates, which is likely due to the vertical polymerization of APTES and is also observed in the Sulfo-EMCS treated sample (C). For the 19 h APTES deposition, aggregates up to 200 nm in height are observed, similar to reported values. Aggregates up to 50 nm are measured in the Sulfo-EMCS treated 19 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.



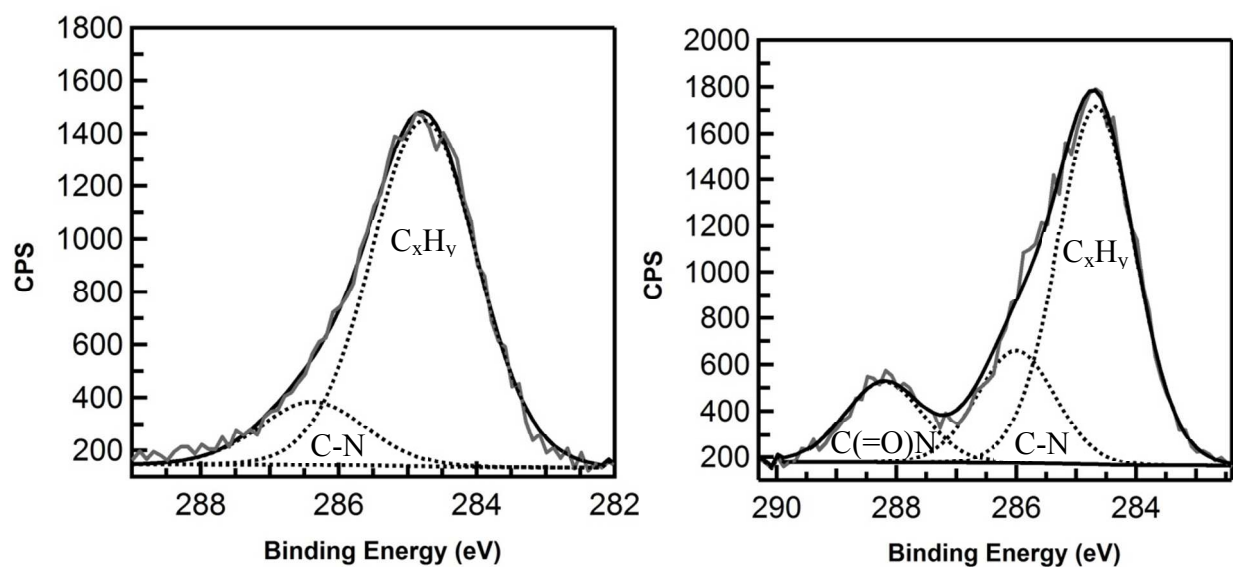
**Figure S3.** Horizontal line scans of AFM images above in Figure S2 A (1 h APTES) and B (19 h APTES). These line scans show the rms roughness of the silane films outside of the aggregates: (A) 0.439 nm and (B) 3.91 nm. (A) and (B) have a height scale of 10 nm and 350 nm, respectively.



**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  $\text{NH}_3^+$ .

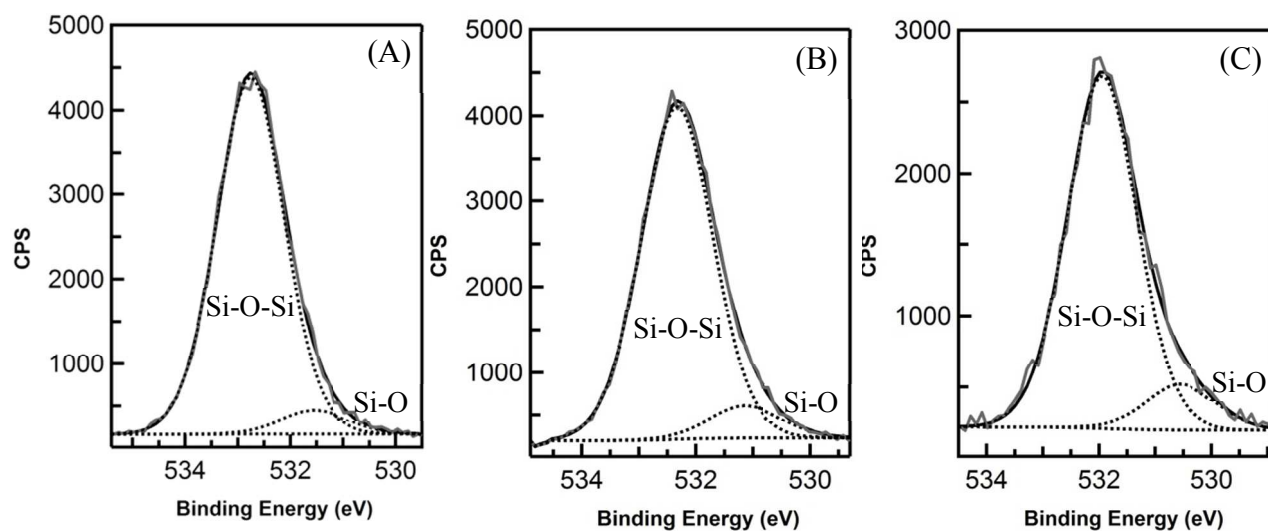


**Figure S5.** C 1s high-resolution XPS spectra (at a  $15^\circ$  TOA) for a 19 h APDMES film (left) and the APDMES-treated surface after reaction with Sulfo-EMCS (right). The amide peak (C(=O)N) is absent in the spectrum for the APDMES-treated samples, but is present on the Sulfo-EMCS-treated surface.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



**Figure S6.** C 1s high-resolution XPS spectra (at a 15° 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).