

Supporting Information

Gas Phase Hydrosilylation of Plasma-Synthesized Silicon Nanocrystals with Short- and Long-Chain Alkynes

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Starting surface for hydrosilylation

Gas – phase hydrosilylation of 1-alkynes and 1-alkenes has been accomplished on H terminated Si nanoparticles. The evolution of the surface coverage and vibrational modes have been monitored with in-situ ATR-FTIR spectroscopy. The starting surfaces of each experiment are similar as evidenced by the SiH_x ($x = 1,2,3$) stretching absorbance observed in figure S1. From the similarity in starting surface, it is concluded that differences observed in the hydrosilylation reaction were due to the different alkynes used in the hydrosilylation.

Kinetics Tracked By Integrated Absorbance in the C-H_x ($x = 1,2$) stretching Region

The surface coverage was also tracked by normalizing the integrated absorbance in the C-H_x ($x = 1,2$) stretching region. Comparison to the kinetics tracked with equation 1 is achieved by normalizing both to their saturation values. The consistency of the kinetics tracked by both of these methods indicates validity of equation 1 and provides evidence of the monolayer nature of the alkenyl coverage. If the process resulted a multilayer, than reaction on an outer carbon shell wouldn't effect inner surface hydrides and the absorbance increase of the C-H_x ($x = 1,2$) region wouldn't track the coverage increases calculated from equation 1 so closely. The kinetics tracked by the integrated absorbance in the C-H_x ($x=1,2$) stretching region is shown in figure S2.

Sequential exposure of phenylacetylene followed by acetylene

Enhanced surface coverage was observed upon sequential exposure of the Si NP surface to acetylene followed by phenylacetylene. The enhanced surface coverage was no longer observed when the order of the exposures was reversed as shown in figure S3.

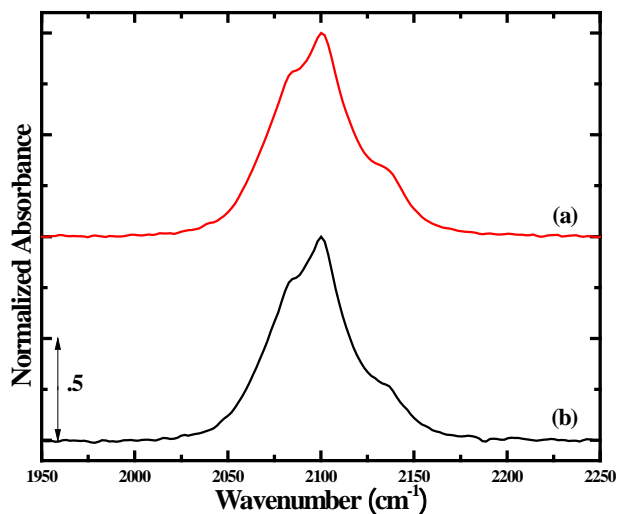


Figure S1. Normalized absorbance due to the SiH_x ($x = 1,2,3$) stretching region of the Si NPs collected after 6 s of growth prior to each hydrosilylation experiment in this study. Spectrum (a), and (b), correspond to the initial hydride composition prior to exposure to phenylacetylene, and acetylene followed by phenylacetylene, respectively. The starting surface in each experiment is very similar.

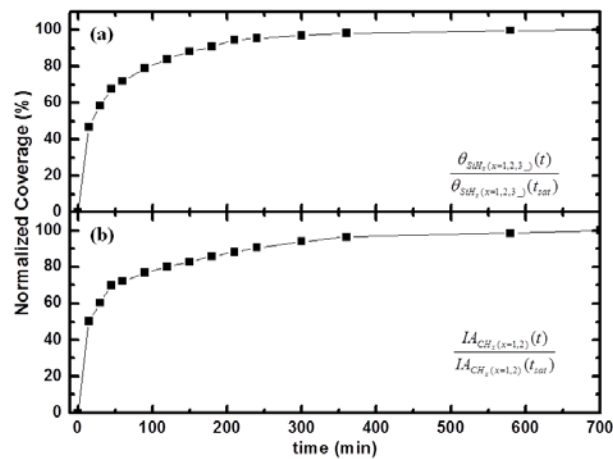


Figure S2: Temporal evolution of the kinetics tracked with the (a) SiH_x ($x = 1,2,3$) and (b) CH_x ($x = 1,2$) stretching regions during exposure of the H-terminated Si NCs to PA. In each case, the surface coverage (a) and the integrated absorbance in the CH_x ($x = 1,2$) (b) were normalized to their saturation values at the end of PA exposure.

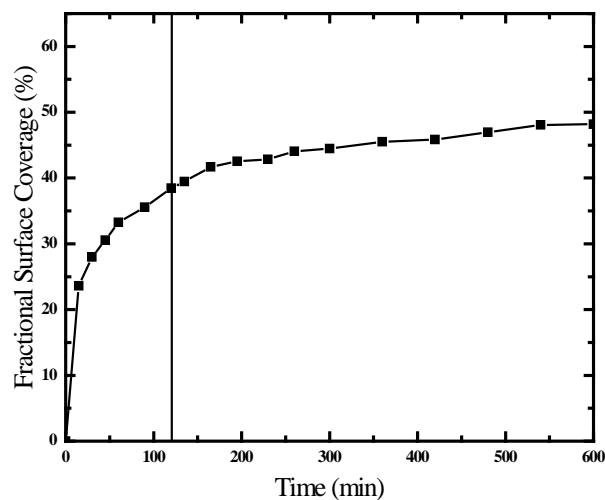


Figure S3. Temporal evolution of the fractional surface coverage of alkenyl species for sequential exposure of phenylacetylene followed by acetylene. The alkyne species were switched after 120 minutes, indicated by the line.