Supplementary Information for

Hydrosilylation Kinetics of Silicon Nanocrystals

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Preparation of Silicon Nanocrystals (ncSi)

Reagents and Materials. Trichlorosilane ($HSiCl_3$, 99%) was obtained from Sigma Aldrich, stored in a refrigerator, and used as received. Reagent grade hydrofluoric acid (48% aqueous solution, Caledon Laboratory Chemicals), ethanol (95%, Sigma Aldrich) and 1-decene (Sigma Aldrich, 94%) were used as received.

Hydrogen Terminated Freestanding ncSi Preparation. 10 mL of $HSiCl_3$ (13.4 g, 99 mmol) was added to a glass beaker equipped with a magnetic stir bar and stirred while being cooled in a dry ice/acetone bath (-78 °C) to minimize vapour-phase hydrolysis and condensation reactions before the intended reaction. Distilled water (40 mL, 2.22 mol) was added to the cooled $HSiCl_3$. The clear and colorless $HSiCl_3$ immediately reacted, forming a white precipitate and the evolution of HCl gas. The precipitate remained immersed in the acidic aqueous mixture for 30 min to ensure complete hydrolysis and condensation. The precipitate was then isolated via the removal of the water phase by vacuum filtration and subsequently dried at 100 °C under vacuum overnight. The resulting white solid $(HSiO_{1.5})_n$ glass was maintained under a nitrogen atmosphere to prevent oxidation, and then was placed in a quartz boat and transferred to a high-temperature tube furnace. Samples were thermally processed in a slightly reducing (5% H2/95% Ar) atmosphere from room temperature to a peak processing temperature of 1100 °C at 18 °C/min and maintained there for 1h. After natural cooling to room temperature, the resultant light brown solid ncSi/SiO_2 composite product was mechanically ground with a mortar and a pestle to yield a very fine powder. Two equivalent batches of the ground composite (each contains 0.6 g) were added to polypropylene beakers with magnetic stir bars. Subsequently, for each batch, 10 ml of ethanol and 20 ml of 48% HF (aq) were added to the solid. The mixture was stirred for 1.5 h to etch away the SiO_2 matrix. The ncSi were then extracted from the mixture using 20 ml of 1-decene. The cloudy orange organic layer containing the hydride-terminated ncSi was quickly collected and transferred into a 100ml round bottom flask with a magnetic stir bar and preserved under a flow of N_2 gas.

Functionalization of ncSi. The flask containing the cloudy dispersion of ncSi was attached to a reflux condenser on a Schlenk vacuum line and put under a nitrogen atmosphere. The flask was put under vacuum to remove any dissolved gases from the dispersion, then refilled with nitrogen. For the conventional oil bath method, the dispersion was placed into an oil bath pre-heated to 170 °C with a hot-plate equipped with digital temperature control and left to stir under a nitrogen atmosphere. For the microwave method, the dispersion was placed into the reaction zone of the Discover SP microwave reactor (CEM Corporation) and heated rapidly to 170 °C with 300W full power and in open-vessel mode that allows reflux, and was left to stir at that temperature under a nitrogen atmosphere. The reaction was stopped every 30 min for qualitative observation and removing an aliquot for FTIR characterization by removing the flask from the heating source and rapidly cooling it to room temperature via air flow (for microwave) or by submerging the flask in a cool water bath (for oil batch). At least 1h of purging with nitrogen gas was performed prior to continuing the reaction.

FTIR Characterization of ncSi

0.5ml aliquots of the dispersion were removed from the flask every 30 min when the hydrosilylation reaction was paused for up to 150 min in total for both heating methods. Prior to characterization, the aliquots were treated under identical conditions: dried at 75 °C under vacuum overnight and then placed into an oven at 120 °C for 66.5 hours to remove any excess solvent and oxidize the surface, in case of discrepancies originating from handling. Following this, each aliquot was redispersed in chloroform, then drop-cast onto three IR transparent KBr substrates for spectroscopy (labelled a, b, and c in tables S1 and S2). Fourier transform infrared (FTIR) spectroscopy was performed on a Perkin Elmer Spectrum One FTIR spectrometer. Peak area integrations were performed using the Perkin Elmer Spectrum software for C-H_x (3080 cm^{-1} - 2696 cm^{-1}), Si-H_x (2357 cm^{-1} - 1973 cm^{-1}) and Si-O-Si (1238 cm^{-1} - 904 cm^{-1}), using the wave numbers indicated in the brackets as the starting and ending points for both the integration and baseline correction ranges. Data analysis and fitting was completed using Origin 8.5.

Table for FTIR results

Table S1 FTIR results for oil-bath heating.

	a	b	c
	$A(CH_x)/A(SiH_x)$	$A(CH_x)/A(SiH_x)$	$A(CH_x)/A(SiH_x)$
30 min	4.61609	4.20874	4.03136
60 min	11.87692	10.01544	12.98837
90 min	20.22733	30.86417	22.36973
120 min	36.96698	32.44828	31.6991
150 min	76.28249	67.70619	67.54592

Table S2 FTIR results for microwave heating.

	a	b	c
	$A(CH_x)/A(SiH_x)$	$A(CH_x)/A(SiH_x)$	$A(CH_x)/A(SiH_x)$
30 min	4.54431	4.20036	3.95209
60 min	6.03211	8.08103	11.90741
90 min	14.50605	27.16807	12.3169
120 min	34.95178	31.94907	30.74537
150 min	41.33981	55.85306	45.37638

Figures

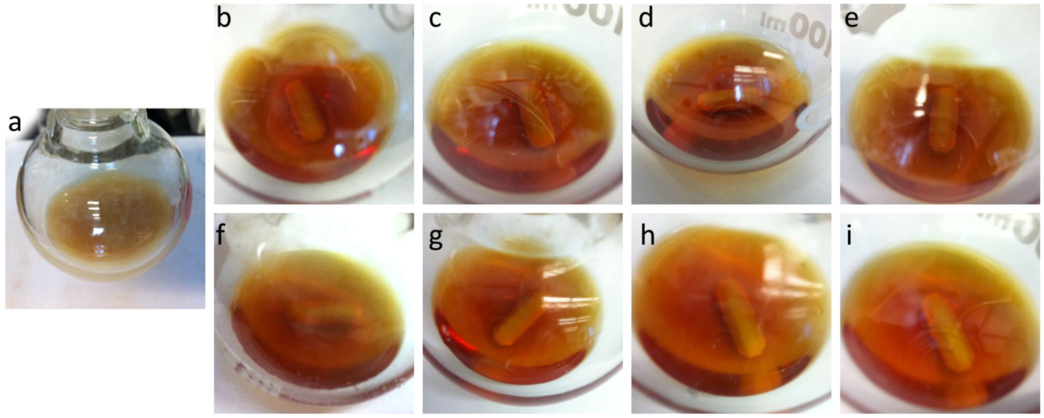

Fig. S1 Photos of the silicon nanocrystal dispersions taken (a) before the hydrosilylation reaction and (b-e) after microwave heating for 30, 60, 90, 120 min and (f-i) after oil bath heating for 30, 60, 90, 120 min, respectively.

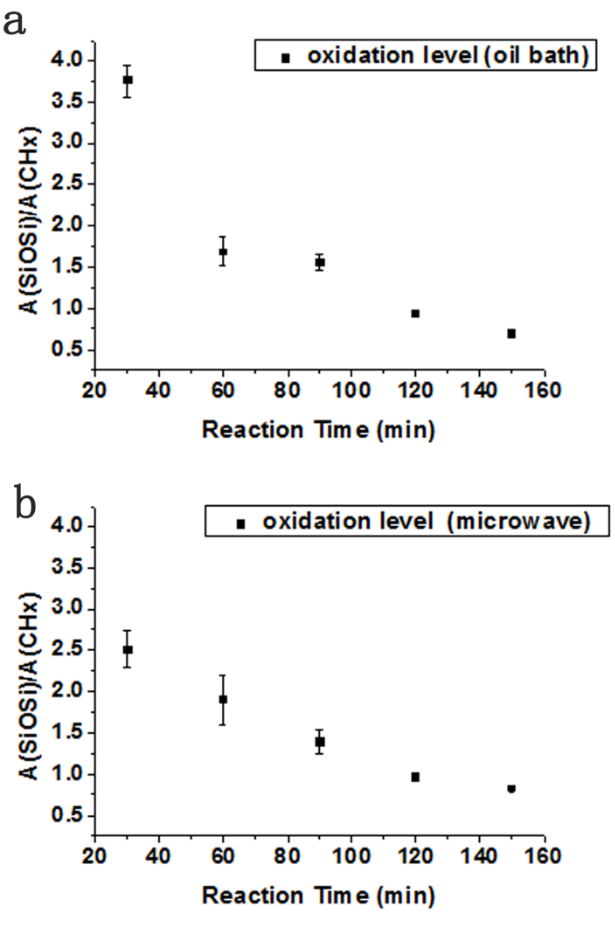

Fig. S2 Area ratios A(SiOSi)/A(CH_x) for different hydrosilylation time, reflecting the oxidation level.

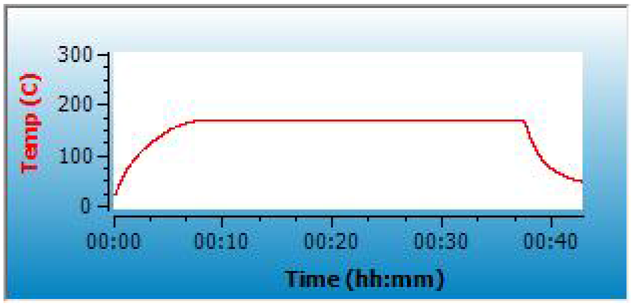

Fig. S3 Temperature curve for 30 min of microwave heating.

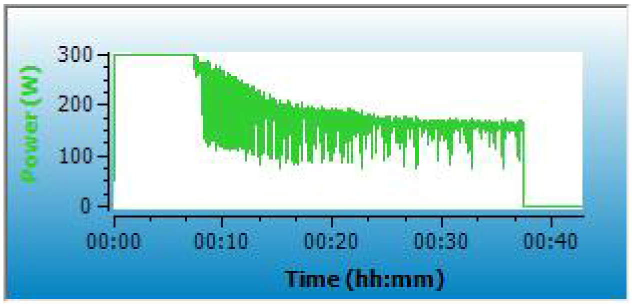

Fig. S4 Power curve for 30 min of microwave heating.