Supplemental Information For

Silicon Nanoparticles: Are they Crystalline from the Core to the Surface?

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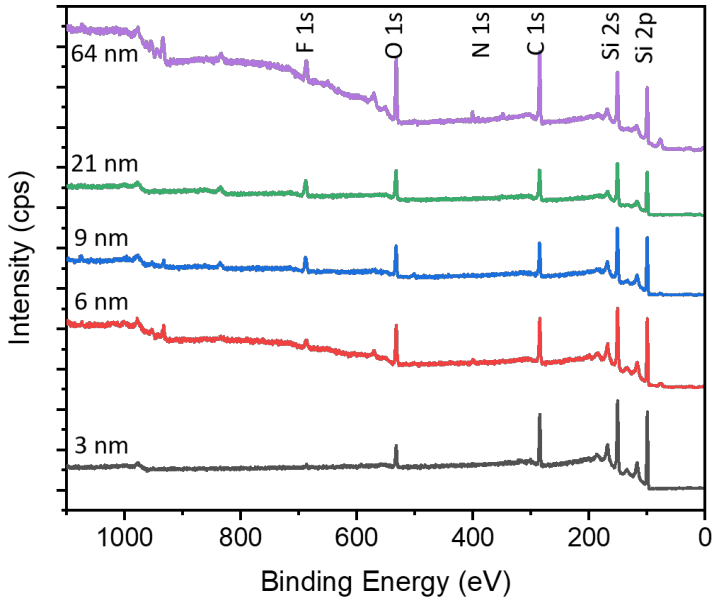
Table of Contents



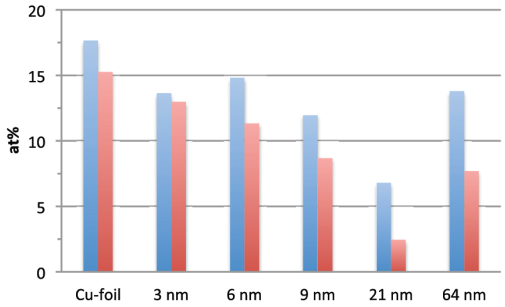
Elemental composition from survey

Sample	C at%	O at%	Si at%	F at%	Cu at%
Cu foil	72.08	17.65	0	0	5.79
3 nm	40.48	13.64	38.08	7.8	0
6 nm	36.66	14.81	44.27	4.25	0
9 nm	36.23	11.97	44.88	6.53	0.39
21 nm	42.07	6.79	50.25	0.88	0
64 nm	40.25	13.79	42.56	2.76	0.63

Peak composition from C 1s

C 1s	C-C/C-H	C-O	C=O	O-C=O
Cu foil	87.37	8.74	3.35	4.54
3 nm	74.01	17.88	2.01	6.1
6 nm	74.07	17.1	3.88	4.95
9 nm	78.46	13.53	2.04	4.2
21 nm	94.17	5.83	0	0
64 nm	83.72	11.59	1.87	2.82

Si 2p	eV	
3 nm	99.43	
6 nm	99.48	
9 nm	99.37	99.57 (10%)
21 nm	99.42	
64 nm	99.43	



	O at% from survey	O at% from C 1s
Cu-foil	17.65	15.26
3 nm	13.64	12.99
6 nm	14.81	11.32
9 nm	11.97	8.68
21 nm	6.79	2.45
64 nm	13.79	7.69

Figure S1: Survey XPS data for 3 nm (black), 6 nm (red), 9 nm (blue), 21 nm (green) and 64 nm (purple), tabulated elemental composition and peak composition for C and O atomic % (at%) from survey.

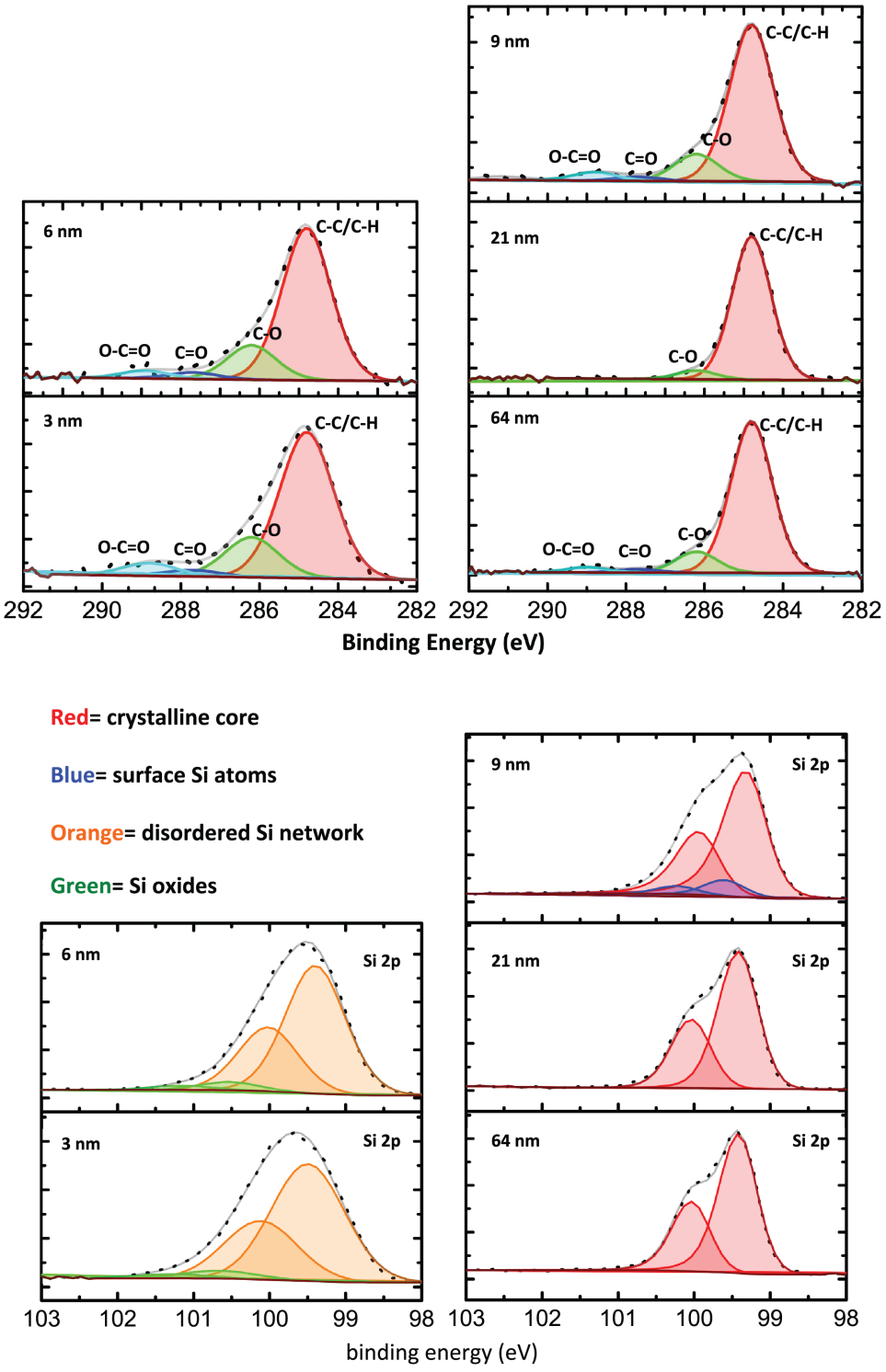


Figure S2: Peak fitting for C and Si XPS data for 3, 6, 9, 21, and 64 nm nanoparticles.

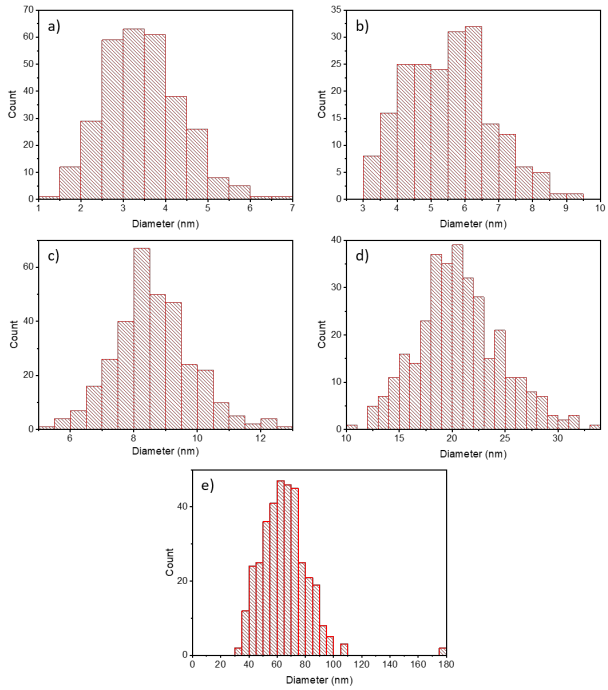


Figure S3: Histograms showing size distributions for (a) 3 nm, (b) 6 nm, (c) 9 nm, (d) 21 nm, and (e) 64 nm H-SiNPs.

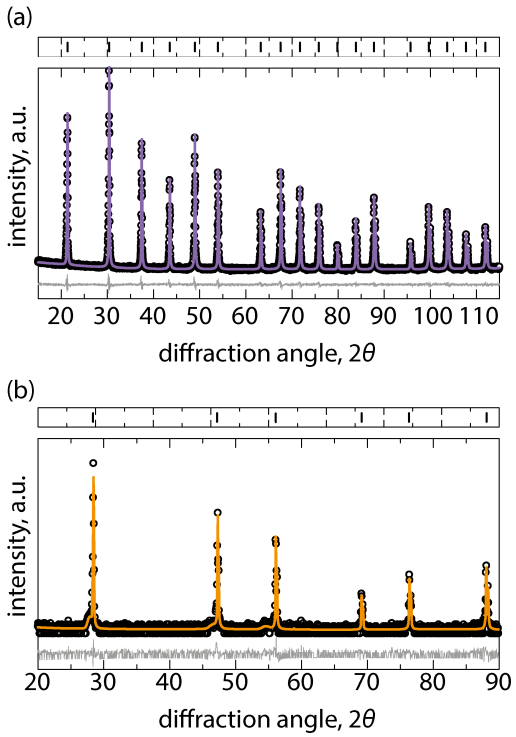


Figure S4. XRD alignment with (a) LaB_6 (NIST) and (b) Si standards.

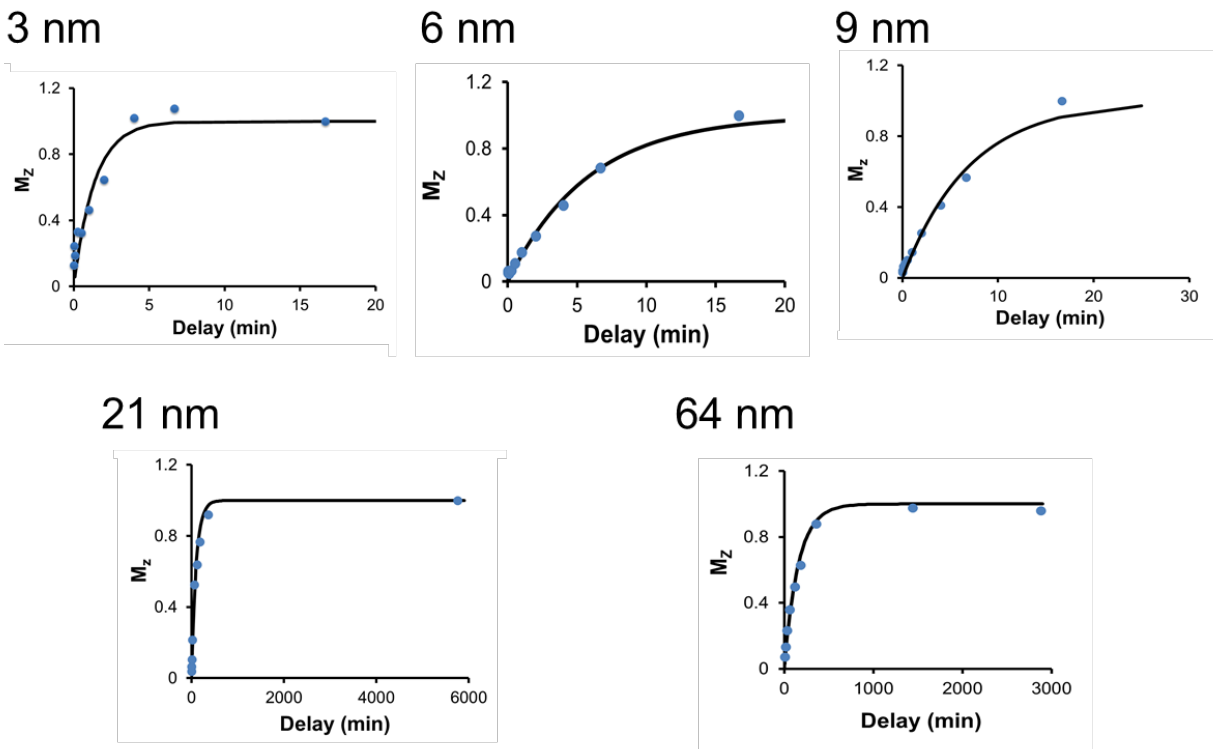


Figure S5: T_1 buildup curves for H-SiNPs, fitted using a mono-exponential longitudinal magnetization recovery for smaller H-SiNPs (3 and 6 nm) and a bi-exponential recovery for larger H-SiNPs (9, 21, and 64 nm).

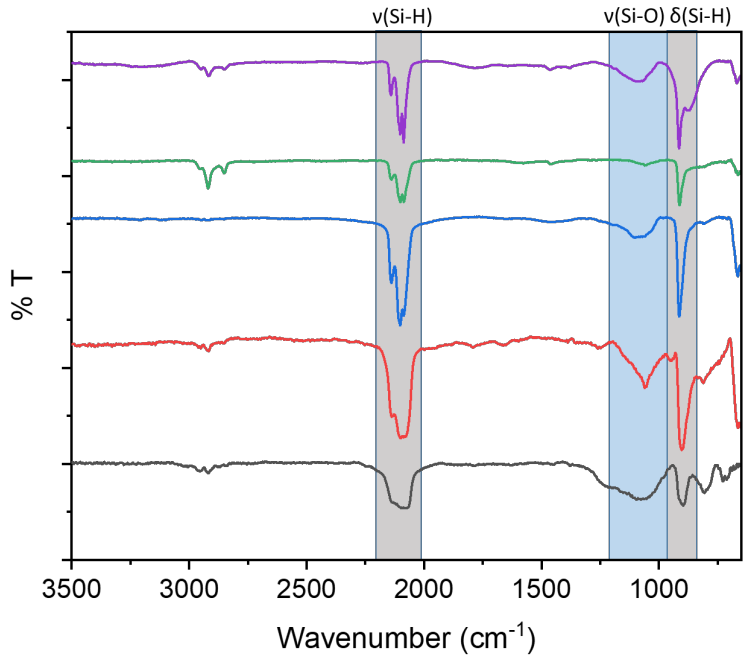


Figure S6: FTIR spectra for H-SiNPs annealed at 1500 °C (purple), 1400 °C (green), 1300 °C (blue), 1200 °C (red), and 1100 °C (black). The spectra show peaks associated with Si-H (highlighted in gray) and Si-O (highlighted in blue).

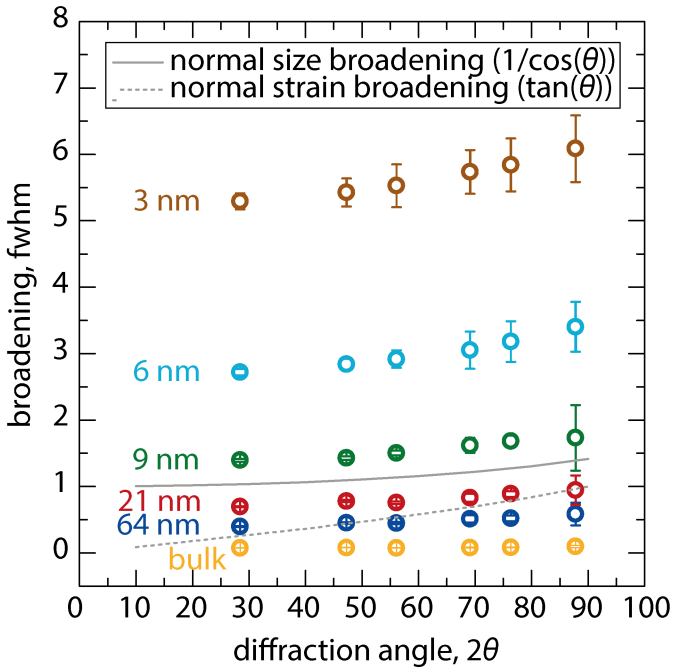


Figure S7. XRD Peak broadening distribution for nanocrystalline materials.

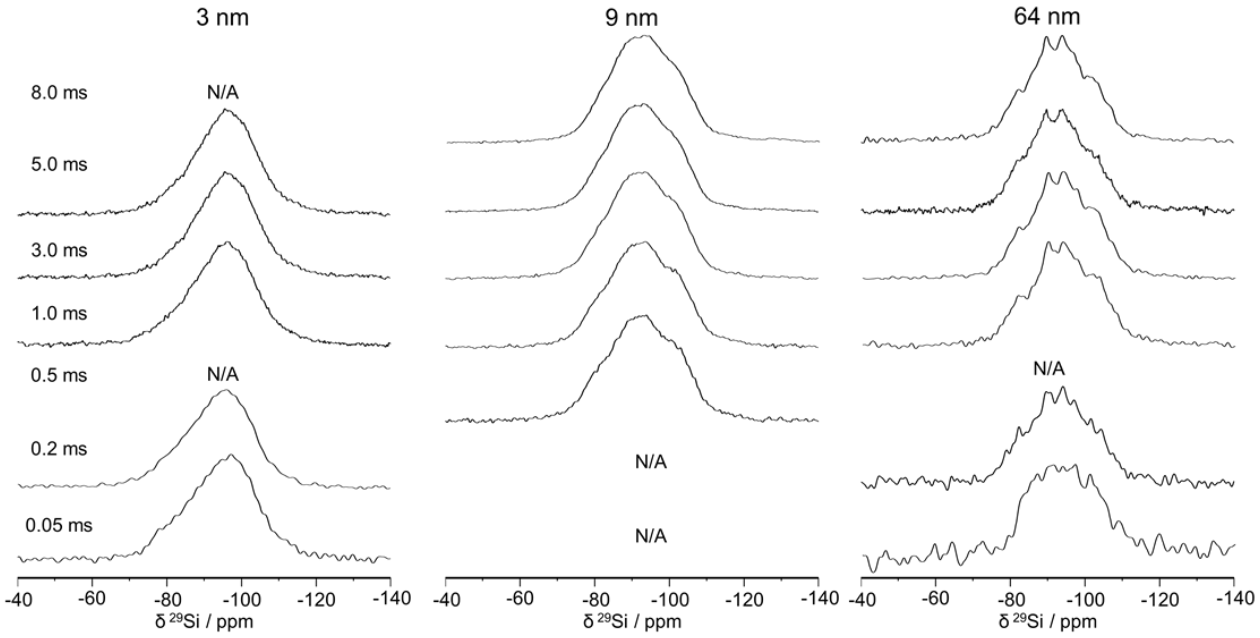


Figure S8: Contact time array for ^{29}Si CP MAS ranging from 0.05 to 8.0 ms for 3, 9, and 64 nm H-SiNPs.

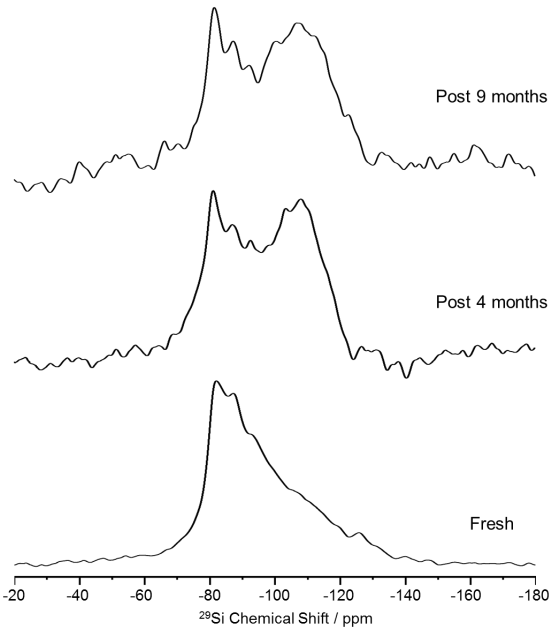


Figure S9: Silicon-29 NMR spectra for 9 nm H-SiNPs purposefully oxidized over a period of 9 months to illustrate the effect on the NMR spectra of contamination by oxygen under ambient storage. Presence of Si-O species at δ_{iso} of ~ −110 ppm 4 and 9 months post-synthesis.

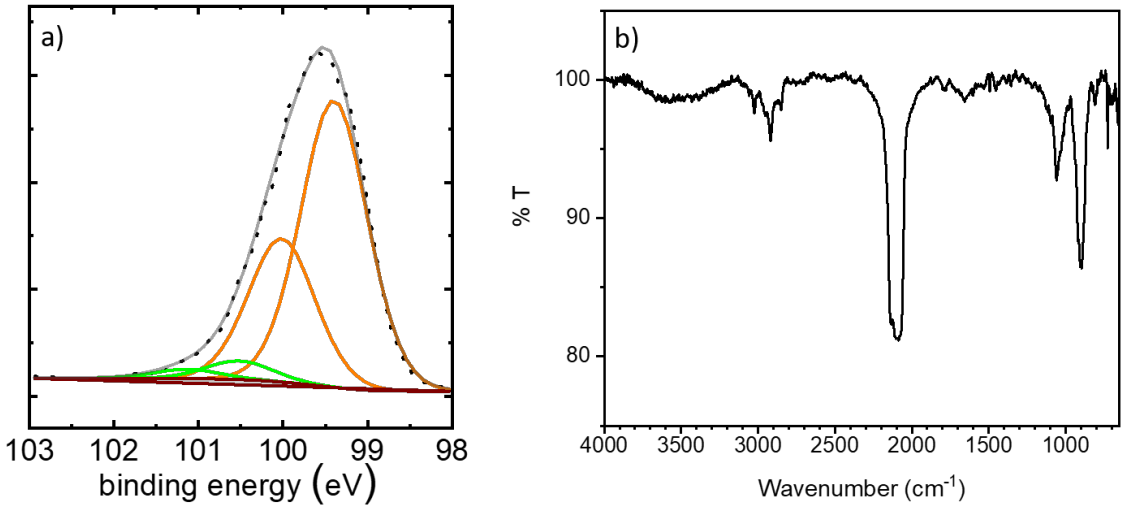


Figure S10: Sample of the post-NMR analysis of the H-SiNPs (6 nm) using (a) Si 2p high resolution XPS data (with only the $2p_{3/2}$ shown for clarity) and (b) FTIR spectra of 6 nm H-SiNPs.

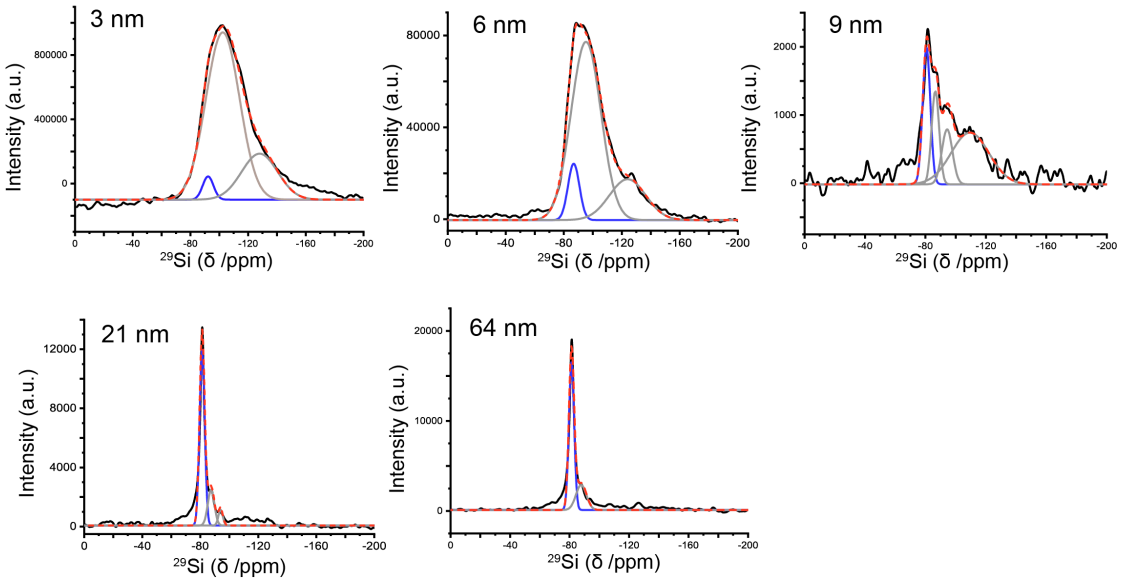


Figure S11: Estimated core (blue) vs surface/subsurface (grey) fractions from ^{29}Si MAS NMR (Bloch) using appropriate delay times (i.e., 5 x T_1). The black line is the experimental data and the red dashed line is the fitting envelope.

Table S1: List of common ^{29}Si chemical shifts for silicon containing materials.

Bonding Environment	Chemical Shift (ppm)	Ref
Amorphous – SiO_2 Quartz – SiO_2 Cristobalite – SiO_2	-110 -107 -109	4, 5
SiO_5 / SiO_6	-150 / -200	4
SiN_4	-49 ($^{[4]}$Si) / -225 ($^{[6]}$Si)	4, 6
SiC_4	-18	4
$OSi\text{-}H_x$ / $HO\text{-}Si(\text{-}OSiH_x)_x$	-89 to -109	7, 8, 9
$\text{-}SiH_3$ / $\text{-}SiH_2$ / $\text{-}SiH$	-90 to -110	10,11
Molecular – $H_3Si\text{-}SiH_3$; $H_2Si(\text{-}SiH_3)_2$; $HSi(\text{-}SiH_3)_3$; $Si(\text{-}SiH_3)_4$	-103 to -165	9, 12

Table S2: Calculated fraction of surface, sub-surface and core Si species based on the model by Zhao *et al.* and Avramov *et al.*[2,3]

Particle Size /nm	Estimated % Fraction of atoms in each structural component		
	Surface	Subsurface	Core
64	1	4	95
21	5	17	78
9	11	37	52
6	17	50	33
3	27	62	11

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