Electronic Supporting Information

A method to derivatize surface silanol groups to Si-alkyl groups in

carbon-doped silicon oxides

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Figure S1. ¹H-NMR (C₆D₆, 400 MHz) spectra of the reaction mixture during the synthesis of TBDMS triflate after 2, 24, 48 and 72 hours respectively. The increase in peak intensities at δ 0.60 (s, 9H) and δ -0.00 (s, 6H) corresponding to TBDMS triflate can be observed and corresponded to 30, 60, 98 and 100% completion of the reaction.



Figure S2. GCMS results of isolated TBDMS triflate.



Figure S3. ¹H-NMR (CDCl₃, 400 MHz) spectra during the synthesis of tertbutyldimethylsilane after 2, 24, 48 and 72 hours respectively. Magnified regions of δ 0.00 and δ 3.64 ppm are shown on right and left of the original spectra. The appearance of multiplet at 3.64 (m, 1H) after 24 hours of reaction suggests the formation of hydrogen terminated product. The decrease in the peak intensities of the reactant and increase in peak intensities of the product are observed. The spectra for the product and reactants are also shown for comparison.



Figure S4. ¹⁹F-NMR (CDCl₃, 400 MHz) spectra during the synthesis of tert-butyl dimethylsilane after 2, 24 and 48 hours respectively. Fluorine peak intensity at δ - 76.84ppm corresponding to the reactant TBDMS triflate decreases during the reaction and it becomes undetectable after 48 hours.



Figure S5. GC-MS results of tert-butyldimethylsilane synthesis displaying appropriate product parent peak.



Figure S6. ¹H-NMR (DMSO-d₆) spectra during the synthesis of tert-butyltrimethylsilane after 2, 24 hours of reaction. Gradual increase in peak intensities at δ 0.93 (s, 9H), δ 0.01 (s, 9H) with 1:1 ratio corresponding to methyl groups of the product, i.e., tert-butyl and three methyl groups on silicon are observed.



Figure S7. GCMS results of tert-butyltrimethylsilane synthesis.



Figure S8. ¹H-NMR (DMSO– D_6) of triphenylsilane. Peaks at δ 5.39 (s, 1H), δ 7.5 (m, 15H) were assigned to hydrogen terminated silicon (Si-H) and protons of phenyl groups.



Figure S9. Experimental setup of silica gel (top) and CDO (bottom) reactions using chemical reaction scheme illustrated above.



Figure S10. ¹⁹F NMR study of silica gel reaction with triflic anhydride. In a control experiment, a strong peak at -72.6 ppm corresponding to fluorine of triflic anhydride can be observed. In a reaction with silica gel, the peak intensity at -77.3 ppm corresponding to triflic acid increases and saturates after 48 hours of reaction.



Figure S11. FT-IR spectral comparison of pure silica gel before and after treatment with 1-Octadecene in the presence of UV light. Note the lack of CH stretch vibration from alkyl chains in 2800 to 3000 cm⁻¹ region, which rules out physi-adsorption as a potential cause of the observed peaks in Figure 2 presented in the main manuscript. These curves are shifted vertically by an arbitrary offset for better presentation.







Figure S12. Control experiments showing that only the porous structure of CDO traps DIABAL-H from anhydrous toluene solution. A. Silica Gel, B. SiO_x wafer C. CDO wafer. Only C indicates the presence of C-H stretch vibrations in the 2850-2950 cm⁻¹ region



Figure S13. FT-IR spectral comparison of clean CDO, (i.e., before reaction) and CDO after treatment with 1-octadecene in the presence of UV light. Note, missing peaks corresponding to C-H vibrations in 2800 to 3000 cm⁻¹ region imply that Octadecene is not trapped in the pores of CDO.

Clean CDO



Octadecene derivatized CDO



Octadecene derivatized CDO After 9 months



CDO wafer	Contact angle (deg.)
Before reaction	$36 \pm 3^{\circ}$
After reaction	81 ± 2°
9 months later	82 ± 3°
14 months later	$82 \pm 2^{\circ}$

Octadecene derivatized CDO After 14 months



Figure S14. Time dependence of the water contact angle on CDO surface after octadecene derivatization.



Figure S15. A comparison of IR spectra immediately after octadecene derivatization and after one-year storage. It illustrates the lack of degradation of derivatized alkyl chain under ambient conditions.





Figure S16. FTIR spectra of SiO_x and CDO wafers before and after OTS derivatization.



Figure S17. AFM image of clean CDO coupon collected on Park System XE-120, in noncontact mode. Probe tip radius is about 10 nm and line scan spacing is 2 nm. Please note the vertical scale in picometers indicating the nanoporous nature of the CDO.



Figure S18. Island type growth observed on octadecene derivatized a)SiO_x and b) CDO surfaces. Note step heights are about 4-6 nm tall.

Table S1. Average roughness and island heights extracted from AFM analysis of derivatized SiO_x and CDO surfaces. Average roughness was determined in regions where islands were not present.

[1	
Surface	Average Roughness (nm)	Island Height (nm)
SiO _x (Clean)	0.41 ± 0.01	
SiO _x (OTS)	0.31 ± 0.02	ND
SiO _x (Oct.)	0.34 ± 0.01	2-5
CDO (Clean)	0.37 ±0.06	
CDO (OTS)	0.20 ±0.03	2-6
CDO (Oct.)	0.22 ± 0.04	2-5

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C-V of three samples

Figure S19. Capacitance vs. voltage curves measured using Hg probe method. Hg contact area was 3.1×10^{-3} cm². Samples 1, 2 and 3 are underivatized CDO, OTS and Octadecene derivatized CDO wafers respectively. We are indebted to a team headed by Dr. Chen of Four Dimensions Inc. for collecting these data.







Figure S20. FT-IR study of themal stability of A) clean CDO , B) octadecene derivatized CDO and C.) OTS derivatized CDO. The samples were treated to 400 °C in tube furnace under N_2 environment for 25 minutes.

XPS Data analysis

- Peak fitting and data analysis was done by using PHI Multipak[™] (Software for complete AES and XPS data analysis) application provided by the manufacturer of the XPS instrument (ULVAC-PHI,INC.).
- True fitting of the sub peaks were done by considering chi squared value.

True fitting or confidence in fitting $\alpha = \frac{1}{chi squared value}$

Manufacturer suggests, while doing the peak fitting, the chi squared value should be at least 1.0 value. For the high resolution Silicon Si(2p) peak fitting presented in the Figure 5, the chai squared values obtained were 0.05, indicates most trustable fitting.

Peak intensities of Si, C, O elements in survey spectrum of Clean CDO & CDO after Octadecyl derivatization

Element	Clean CDO	CDO after Octa Derivatization
Si (2p)	22.5 %	22.7 %
C(1s)	15.5 %	48.0 %
0 (1s)	62.0 %	29.2 %

Peak intensities of –O-Si-O-, -Si-O-C, -Si-C- bonds in High resolution Si (2p) of Clean CDO & CDO after Octadecyl derivatization

Bonds	Clean CDO	CDO after Octa Derivatization
-0-Si-0-	25.30 %	13.70 %
-Si-O-C-	57.35 %	54.20 %
-Si-C-	17.35 %	32.10 %