Synthesis of Nanoscale Silicon Oxide Oxidation State Distributions: The Transformation from Hydrophilicity to Hydrophobicity

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Abstract Silicon oxide nanostructures which span the range from hydrophilic to hydrophobic have been synthesized. The surface chemistry of these silicon-based nanostructures was analyzed using a combination of x-ray photoelectron spectroscopy, reflectance infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis. The dominant oxidation state for the nanostructured oxides shifts from an average oxidation state of +III to a combination of +II and +III oxidation states. A correlation of the ability to adsorb water with variations in the surface Si:O ratios was observed showing a transition from hydrophilic to hydrophobic character.

Keywords silicon oxide, nanostructures, hydrophobic, hydrophilic, oxidation state changes, x-ray photoelectron spectroscopy, reflectance infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy

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Introduction

Silica is widely used as a support surface so its surface chemistry is of great importance as it relates to the ability of the material to interact with both polar and semi-polar liquid systems.[1] As hydroxyl groups attach to the silicon atoms of the silica structure at the surface, the silica surface becomes hydrophilic and capable of hydrogen bonding to a number of molecules including water. In concert with the hydroxylation process, there can be a complementary change in the oxidation state of the silicon atom. Concomitantly, the ability of the silica surface to absorb water is intimately related to the nature of the surface silicon oxidation state.[2]

Stable compounds of silicon might be expected to show oxidation states of 0, +II, and +IV associated with the equilibrium solids of silicon and silicon oxide. Literature data for the Si 2p electron binding energy (eBE) from x-ray photoelectron spectroscopy (XPS) measurements of tetravalent silicon in an annealed quartz sample (eBE = 103.4 eV) and zero-valent silicon in an annealed metalloid (eBE = 99.3 - 99.9 eV) [3,⁴] sample have been reported as have XPS peaks at 100.5 and 103 eV [5] for a silicon oxide film prepared by evaporation under vacuum of a silicon monoxide powder. The observed XPS peaks were interpreted as intermediate oxidation states (+I and +III) of Si in a “non-equilibrium” surface oxide film. At the interface of Si and SiO₂, a thin layer of SiO_x has been reported [6] that has been modelled [7] as either (1) a heterogeneous distribution of separate domains with each domain having a phase with the following stoichiometry [Si₂O_n, n = 0, 1, 2, 3, 4], or (2) a single domain of stoichiometry SiO_x where five basic units are present in this film in a random fashion (Si-(Si_{4-n}O_n), n = 0-4). Solids sputtered from Si show oxidation states of silicon 0 to +IV depending upon preparation conditions.

XPS [8] has been used to distinguish between these oxidation states, which appear to be separated by ~ 1.0 eV per formal oxidation state. Data obtained from the NIST XPS Database [9] indicate a range of eBE = 98.7 to 99.6 eV for Si(0), eBE = 101.7 to 102 eV for Si(II), eBE = 101.7 to 103.8 for Si(III), and eBE = 103.0 to 104.1 eV for Si(IV). In a recent analysis of the XPS spectrum of amorphous silicon monoxide, [10] two bands were observed. The binding energies obtained by a deconvolution of these bands were 99.8(1) eV for Si(0), 100.6 eV for Si(I), 101.6 eV for Si(II), 102.7 eV for Si(III), and 103.8 eV for Si(IV). The suboxides (Si(n), n = I, II, III) are not considered discrete compounds but are a result of Si atoms in a matrix of 1, 2, and 3 O atoms and it is thought that these materials are only found in the transition region between Si and SiO₂. [11] This hypothesis may require revision.[1,12]

The current results demonstrate that, at the nanoscale, the mechanism associated with a change in silicon oxidation state, and the transformation from hydrophilicity to hydrophobicity can be correlated with an apparent change in the silicon to oxygen ratio. This change correlates directly with the conversion of silica nanospheres that subsequently agglomerate to form silicon-based nanowires. By increasing the silicon content of the nanostructured oxides that were synthesized, the system can transform from hydrophilic to hydrophobic. We combine the results of XPS, FTIR, SEM and TGA analysis, in concert with molecular electronic structure cluster calculations, to demonstrate the nature of water binding to the resultant silicon surface oxidation states, associated with the oxides and hydroxides, and the notably more hydrophilic character of silicon in its average +III and +IV oxidation states.

Experimental and Computational Details

Synthesis To prepare the silica nanostructures used in the present experiments, our tube furnace configuration [13,14,15,16,17] was used to heat a Si/SiO₂ mixture to a typical central region operating temperature well in excess of 1400 °C. With a 1:1 Si/SiO₂ ratio carefully mixed and placed in an alumina crucible in the central region, the starting material is vaporized as it is entrained in Ar. The present experiments were performed with a quartz tube of length 30 inches placed inside the inner alumina tube of the tube furnace to enhance reaction. The 50/50 Si/SiO₂ mixture is heated to temperatures ranging from 1400 to 1440 °C. The tube furnace pressure is set to 240 Torr and the flow rate of the Ar gas is 130 standard cubic centimetres per minute (sccm). The furnace is heated at a rate of 5 °C per minute and maintained at the desired temperature for 12 hours. At 1400 °C, a white powder (Figure 1(a)) of SiO₂ is synthesized as reported earlier.[18] The white powder consists of silica nanospheres. After processing at 1440 °C to obtain a higher silicon content, the samples collected from the tube furnace cold plate and inner wall of the quartz tube contain significantly more silicon and are olive-brown in color. As the temperature is raised from 1400 °C, we generate “off white” samples and, at intermediate temperatures, it is possible to transform to samples which appear yellow in color. Alternatively, the Si/SiO₂ ratio can be increased as we attempt to enhance the formation of Si_xO ($x > 1$) based nanostructures extending to Si₂O.

X-ray Photoelectron Spectroscopy A PHI 1600 XPS Surface Analysis System (Physical Electronics, Eden Prairie, MN) was used to obtain XPS data from an area approximately 800 μm in diameter. The instrument also uses a PHI 10-360 spherical capacitor energy analyzer and an Omni Focus II small-area lens to focus the incident electron beam. XPS data were obtained using an achromatic Mg K_α X-ray source operating at 300 W and 15 kV. Survey spectra were gathered

using an average of 10 scans with a pass energy of 26.95 eV running from 1100 eV to 0 eV. High-resolution spectra were gathered using an average of 15 scans with a pass energy of 23.5 eV and a step size of 0.2 eV. The incident sample angle was held constant at 45°. To determine charge effects, reference was made to the carbon 1s peak and to known Si(IV) reference compounds, with adventitious carbon assigned to eBE = 284.5 eV. Charge effects were assessed for the four samples, whose spectra were taken sequentially. For statistical analysis, measurements were taken on two samples per treatment and two spots per sample. The XPS data was collected and averaged using PHI Surface Analysis Software (Version 3.0, Physical Electronics, Eden Prairie, MN). The XPS data was then analyzed using the Spectral Data Processor, SDP, (Version 4.0, XPS International LLC, Mountain View, CA)

SEM Analysis The SEM analyses performed on the white powder samples shown in Figure 1(a) as well as on the off-white to yellow powders generated in these experiments are virtually identical to SEM (LEO 1530) and TEM (Hitachi HT-2000) results reported previously.[14,17] The samples are found to consist of silicon oxide nanoparticles (nanospheres) which grow in size with increased temperature. Data for the olive brown samples (Figure 1(b)) taken with an Hitachi 3500H is, however, distinct in that the nanostructure distributions appear to be converted to a dominance of Si_xO ($x \geq 1$) nanowires.

TGA The samples (2-5 mg) were characterized for water absorption capacity in a thermal gravimetric apparatus (Cahn microbalance). The pretreatment included an initial heating cycle between room temperature and 1000 °C in flowing inert gas (He: 100 sccm). The purpose of this procedure was to remove volatiles from the surface of the silica powders prior to the initial hydration of the samples. These pretreated powders were exposed to a He gas stream that had been passed through a saturator bubbler held at room temperature

for 2 hours. Afterwards, the weights of the samples were recorded, the dry inert gas stream was replaced, and the temperature increased to 100 °C, whereupon the weight of the partially dried sample was recorded. Next, the temperature programming rate was set to 10 °C/min and the weight recorded continuously until the final temperature was 1000 °C; this temperature cycle was designated as the first heating protocol. Finally the sample was cooled to room temperature with the inert gas stream flowing, and the heating cycle was repeated to document buoyancy effects. We designate this cooling cycle as the second heating protocol. The weights recorded for the first heating protocol were corrected for buoyancy effects using the weight *versus* temperature spectrum for the second heating protocol.

Reflectance FTIR Spectroscopy Each silica specimen was removed from a homemade vacuum storage chamber (storage pressure 5 μ -Torr). The samples denoted as being open to the atmosphere were placed in a room temperature environment to expose them to atmospheric conditions for a period of time (~72 hours as indicated) before being scanned. The samples labeled “vacuum” were immediately scanned after being removed from the vacuum chamber. The samples were analyzed using a Tensor 37 Fourier Transform Infrared Spectrometer FTIR (Bruker Optics). The sample powders were characterized using a Seagull diffuse reflectance accessory from Harrick Scientific Products Incorporated. All reflectance spectra were taken at a 45° incidence angle, using an aluminum mirror for the background scan, and at a wavenumber resolution of 2 cm⁻¹.

Results

XPS Analysis Four silica samples underwent XPS analysis: (1) a white powdered sample (Figure 1(a)), (2) a mottled off-white powder (light), (3) a yellow to yellow-brown

powder, and (4) an olive brown agglomerate (Figure 1(b)). The olive-brown agglomerate continues to float when placed in DI water displaying what appears to be a distinctly hydrophobic character. The white powdered sample, consisting of silica nanospheres similar to those previously prepared, clearly becomes hydrated when placed in DI water, and appears to be hydrophilic.^{19,20} The XPS data obtained for the Si 2p_{3/2} and O 1s regions are shown in Figure 2. There is a clear downward shift of the Si 2p eBE for samples prepared at higher temperatures and increasing Si:O ratios. The eBE decreases in the order white > off-white > yellow > olive-brown. Concomitantly, there is a shift to lower eBE for the O 1s spectra as a function of increased temperature and Si:O ratio. There is a clear change from those features associated with ~Si(IV) to those associated with the lower oxidation states of the silicon oxides (Si_xO, x > 1). Note that the eBE decreases in the same order as for the Si peaks.

Attempts were made to deconvolute the data obtained for silicon and oxygen by using 0.8 and 1.0 eV as the minimum separation between the eBE's of the deconvoluted peaks. This minimum separation for the eBE's of different species appears to be validated in the case of the Si 2p_{3/2} data as a previous study has demonstrated that the eBE's of Si species developed upon oxidizing the surface of Si(100) were separated by approximately 1 eV.[7] The data based on this analysis and on a comparison with the known binding energy of Si(IV) is given in Figure 3 and in Figure 4 for the O peaks. The peak area data analysis was used to determine the relative abundance of Si(0), Si(I), Si(II), Si(III), and Si(IV) (Table 1) of the four powders considered in this study. These mole percentages were used to estimate the average oxidation state of the Si species in the samples. It is apparent from the data in Figures 3 and 4 and Table 1 that, as the synthesis preparation

temperature and effective Si:O product ratio increases, the overall oxidation state of the Si in the samples is reduced. The data analysis suggests that whereas the lower temperature “white” silica sample is strongly dominated by the +III oxidation state of silicon, as previously noted,²⁴ the olive-brown silica sample with a greater Si:O ratio has an equally strong component of Si(+II) and demonstrates a clear shift to lower silicon oxidation states. The DFT B3LYP/DZVP2 average 2p eBE’s on Si decrease with increasing Si:O(-II) ratio as well (see Supporting Information). In most cases, adsorption of H₂O to the Si further reduces the average 2p eBE on Si. In contrast, the DFT O 1s eBE for the oxygens in the model Si cluster do not show any regular pattern whether H₂O is adsorbed or not.

We have previously examined samples of Cab-O-Sil by XPS.[1,23,24] The XPS spectrum of a Cab-O-Sil sample displays a single peak at 100.47 eV with an Au 4F_{7/2} reference peak at 84.12 eV. When charge corrected for the actual Au 4f_{7/2} eBE of 84.00 eV, the Cab-O-Sil sample displayed a Si 2p eBE of 100.35 eV. [9,23]

TGA The silicon samples were characterized for water absorption capacities to determine how the preparation conditions would influence the surface chemistry. Those samples analyzed were: 1) a white sample, analogous to that shown in Figure 1(a), 2) an intermediate yellow sample, and 3) an olive-brown sample, analogous to that shown in in Figure 1(b). We hypothesize that the hydrophilic/hydrophobic nature of the surface can be interrogated using the water adsorption capacity. These data obtained are shown in Table 2. The weight changes associated with the difference in the first two columns of evaluated weights represent the amounts of weakly adsorbed water on the sample. The differences in weight between the second and third columns represent the amount of water that was strongly adsorbed to the samples and is most closely

associated with the surface chemistry of hydrophilicity and hydrophobicity. From these data, we conclude that the white sample is more hydrophilic than the yellow and olive-brown samples.

SEM and EDS Analysis The SEM analysis of white (Fig 1(a)), off-white, and olive-brown (Fig. 1(b)) powders, Figure 5, yields results similar to that previously recorded. **[Error! Bookmark not defined.,15,17,18]** The observed features correspond to small silicon nanospheres for the synthesized light white powder samples. The yellow powders correspond to much larger, partially agglomerated, nanospheres. The olive-brown samples (Figure 1(b)) correspond predominantly to silicon-based nanowires (Figure 5) whose EDS spectrum in Figure S1 (a) indicates an excess of silicon over oxygen. In contrast, the EDS of the white powdered sample (Figure 1(a)) (Figure S1(b)) corresponds to a silicon oxide sample with a notably higher oxygen to silicon ratio.

Reflectance FTIR Spectroscopy Reflectance IR spectra for the white (Fig. 1(a)) and olive-brown (Fig. 1(b)) samples are shown in 6 and Figure S2. The spectrum in Figure S2(a) compares the reflectance (%transmittance) for a sample taken from a container exposed to the atmosphere for 72 hours after preparation and the same sample after vacuum drying at 10 mTorr for 24 hours. The peak at $\sim 1640\text{ cm}^{-1}$, the larger broad peak near 3410 cm^{-1} , and the sharp peak near 3746 cm^{-1} (which is much more pronounced in Figures S2(b) and 6 (for the white silica samples)) correspond to the bending and stretching modes of molecular water. These assignments are based on the frequencies for free H_2O which are 3756 cm^{-1} (asymmetric stretch), 3657 cm^{-1} (symmetric stretch), and 1595 cm^{-1} (bend). [21] The broad peak centered near 3400 cm^{-1} is due to the presence of water clusters or small water droplets and is red-shifted and broadened due to the presence of hydrogen bonding in the water present on the surface. The multiple, slightly pronounced, peaks near 2345 and 2370 cm^{-1} correspond to the CO_2 doublet

(antisymmetric stretch) due to room air²⁶. The strong absorptions below 1286 cm^{-1} are associated with SiO_x lattice (siloxane) Si-O and Si=O stretches and Si-O-H bends. The peaks at ~ 1875 and near 2000 cm^{-1} could be due to hydrides of Si and Al as discussed below.

Similar features, albeit at distinctly different intensities, are associated with the spectrum in Figure S2(b) which corresponds to the lower-temperature generated “white” silica. The spectrum obtained for this sample is distinct from that obtained for the olive-brown sample in that it demonstrates a significant water uptake indicated by the increased intensity for the 3410 cm^{-1} and 3746 cm^{-1} features. Figure 6 also demonstrates that the spectrum obtained for the “white silica” vacuum sample still has a considerable contribution from adventitious water, the broad feature at 3410 cm^{-1} .

The spectra in Figure S2 are quite distinct in other ways. The spectra in Figure S2(a) demonstrate that the olive-brown sample (Fig. 1(b)) with its higher silicon to oxygen ratio is able to slowly absorb and readily desorb water. This is also apparent in the observed weak 3746 cm^{-1} feature. The “white silica” sample (Fig. S2(b) and 6) appears to absorb and retain water much more readily and to only slowly desorb water, especially as evidenced by the stronger broad 3410 cm^{-1} and notable sharp 3746 cm^{-1} water absorption features. The key difference between the two limiting forms of silica for which we have evaluated infrared spectra in this study relates to their ability to absorb and desorb water. The efficiency of water absorption and desorption clearly increases with increasing Si:O ratio as the olive-brown sample, while it can take up water, releases water much more readily than does the “white” silica sample, which itself is an efficient water sorbent.

Electronic structure calculations. We have previously shown that the most efficient binding of water is to the +3 and +4 oxidation states of silicon with the strongest binding corresponding to

the rearranged structure of an Si_2O_3 singlet (See Table S1 for a summary) at the DFT B3LYP/DZVP2 level.[1] The complexation energies of water to the silicon in the formal +III and +IV oxidation states are comparable. The complexation energies of water to the lower oxidation states of Si are predicted to be notably weaker. This suggests that the +I and +II silicon suboxides might uptake water and form surface hydroxyl groups at a considerably slower rate than a surface consisting primarily of +III and +IV oxidation states. This is consistent with the recently observed induction period for the phenol hydroxylation reaction [23,24] on fumed silica and the nature of silica moisture uptake isotherms.[1,2,3]

The calculated vibrational frequencies (Table S1 and Figure S3) for a variety of clusters are consistent with the observed FTIR reflectance spectra obtained in the present study. Most of the Si-O bond stretches are in the range of 800 to 1000 cm^{-1} , the Si-O-H bends are in the region of 800 to 900 cm^{-1} and the Si=O stretches are in the region of 1200 to 1300 cm^{-1} . The calculated values are harmonic frequencies and the experimental values include an anharmonic correction so the calculated frequencies will be too high as compared to experiment. We note that the O-H stretches for an oxygen bonded to Si are predicted to be slightly higher than those from H_2O . The calculated vibrational frequencies provide a consistent model of the vibrational modes characteristic of the surface of the nanosilicon structures we generated in this study. Further, the FTIR data are consistent with the deconvoluted XPS distributions and the water complexation energies.

We suggest that the peaks around 1900 to 2000 cm^{-1} could be due to metal hydride Al-H or Si-H stretches (see Supporting information Table S2). The Al could come from the alumina crucible used to hold the Si/ SiO_2 mixture or the alumina tube which exceeds the length of the inner quartz tube used in the vaporization of the silica.

Conclusions

Silicon oxide nanostructures which span the range from hydrophilic to dominantly hydrophobic have been synthesized demonstrating the transition from mixed $\text{Si(III)} > \text{Si(IV)} \approx \text{Si(II)}$ to $\text{Si(II)} \approx \text{Si(III)} > \text{Si(I)}$ oxides. The surface chemistry of these nanostructured systems which vary in their Si:O ratio are correlated with the formation of silica (SiO_2) nanostructures (~nanospheres) that agglomerate and transition to nanowires. The dominant oxidation state for the nanostructured oxides is found to shift from an average oxidation state of +III to a combination of +II and +III. In contrast, fumed silica has been found [1] to be in the +I oxidation state and not the +IV oxidation state. The decrease in the Si oxidation state and the formation of silicon nanowires is commensurate with an increased Si:O ratio and a change from hydrophilic to hydrophobic character. Even though the average oxidation state of the olive-brown silica is considerably lower than that of the “white” powdered nanosilicon samples, it considerably exceeds that of fumed silica (+I). Thus, the differences between the olive-brown nanostructured silica generated in the present study and fumed silica are inherent to the ability of the nanostructured material to take up water more readily. This is consistent with the predicted ability [1] of the higher oxidation states to bind water more readily based on electronic structure calculations (see Supporting Information). As the value of x in Si_xO increases from $x = 2$, the average oxidation state of the Si decreases and the material becomes hydrophobic, whereas for x decreasing from 2, it becomes more hydrophilic as the Si oxidation state increases leading to more polarity and an improved ability to adsorb H_2O molecules. It is important to note that the value of x varies due to how the nanosilicon samples are synthesized and treated. All of the experimental and

computational data are consistent with these conclusions about the transformation from hydrophilic to hydrophobic.

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Figure Captions

Figure 1: Silicon/Oxygen nanostructured powders synthesized at two distinct temperatures and experimental conditions (a) 1400 °C process. b) 1440 °C process.

Figure 2: XPS spectra (a) Silicon 2p_{3/2} spectra of the four samples of silicon nanostructured powders and wires. (b) O 1s spectra of the four samples of the silica nanostructured powders and wires.

Figure 3 (a) Higher resolution Si 2p XPS spectrum for white silica nanostructured powders. (b) Higher resolution Si 2p_{3/2} XPS spectrum for predominantly olive-brown nanostructured wires.

Figure 4: (a) Higher resolution O 1s XPS spectrum for nanostructured white silica powder. (b) Higher resolution O 1s XPS spectra of predominantly nanostructured olive brown wires

Figure 5 (a). EDS spectrum of silicon nanowires as shown in Figure 1(b). Note the ratio of silicon to oxygen. (b) EDS spectrum of silicon oxide powder (~ nanospheres) as shown in Figure 1(a). Note the ratio of silicon to oxygen.

Figure 6: Overall comparison of the IR spectra for white and olive-brown nanostructured samples. The gauge for comparison of each spectrum is the rightmost point to the right of the figure. The greatest water absorption is for the “white” silicon sample in air (gray) followed by the “olive-brown” sample in air (green) and the “white” silica sample under vacuum (red)

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Table 1

Table 1. High Resolution XPS Deconvoluted Data for Silica Powders

Sample	Electron Binding Energies eV					Estimates of Si Oxidation State Percentages					Average Si Oxidation State
	Si(0)	Si(I)	Si(II)	Si(III)	Si(IV)	Si(0)	Si(I)	Si(II)	Si(III)	Si(IV)	
White			101.21	102.25	103.28	0	0	18.7	57.45	23.85	3.05
Light	99.38	100.49	101.50	102.48	103.50	4.20	5.15	25.15	44.75	20.80	2.73
Yellow	98.88	100.55	101.57	102.47	103.57	3.55	11.65	41.95	34.40	8.45	2.33
Brown	98.93	100.30	101.31	102.19	103.25	5.35	11.05	37.65	36.65	9.35	2.34

Table 2

Table 2: Water Adsorption Capacities for Silica Powders?

Sample	Weight (mg) in air saturated at 25 °C	Weight (mg) in dry air at 100 °C	Weight (mg) after heating to 1000 °C	$\Delta W_{\text{sat}}/W_{\text{sat}}$ expressed as percentage ^a	$\Delta W_{\text{dried}}/W_{\text{dried}}$ expressed as percentage ^b
White	4.07	4.035	3.96	0.88%	1.89%
Light Yellow	14.40	5.95	6.02	142%	-0.4%
Olive-Brown	1.55	1.498	1.485	3.50%	0.88%

^a $\Delta W_{\text{sat}} = W_{\text{sat}} - W_{\text{dried}}$ where W_{sat} is the weight of the sample shown in column 2 of Table 2 and W_{dried} is the weight of the sample shown in column 3 of Table 2.

^b $\Delta W_{\text{dried}} = W_{\text{dried}} - W_{1000}$ where W_{dried} is the weight of the sample shown in column 3 of Table 2 and W_{1000} is the weight of the sample shown in column 4 of Table 2.

Figure 1

Figure 1: Silicon/Oxygen nanostructured powders synthesized at two distinct temperatures and experimental conditions (a)1400 °C process. b) 1440 °C process.

Figure 2

Figure 2. XPS spectra (a) Silicon 2p_{3/2} spectra of the four samples of silicon nanostructured powders and wires. (b) O 1s spectra of the four samples of the silica nanostructured powders and wires.

Figure 3

Figure 3. (a) Higher resolution Si 2p XPS spectrum for white silica nanostructured powders. (b) Higher resolution Si $2p_{3/2}$ XPS spectrum for predominantly olive-brown nanostructured wires.

Figure 4

Figure 4: (a) Higher resolution O 1s XPS spectrum for nanostructured white silica powder. (b) Higher resolution O 1s XPS spectra of predominantly nanostructured olive brown wires

Figure 5

Figure 5 (a). EDS spectrum of silicon nanowires as shown in Figure 1(b). Note the ratio of silicon to oxygen. (b) EDS spectrum of silicon oxide powder (~ nanospheres) as shown in Figure 1(a).Note the ratio of silicon to oxygen.

Figure 6

Figure 6: Overall comparison of the IR spectra for white and olive-brown nanostructured samples. The gauge for comparison of each spectrum is the rightmost point to the right of the figure. The greatest water absorption is for the “white” silicon sample in air (gray) followed by the “olive-brown” sample in air (green) and the “white” silica sample under vacuum (red).

TOC Figure