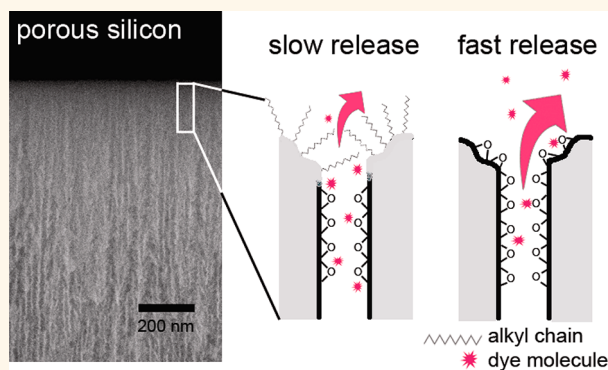


Selective Functionalization of the Internal and the External Surfaces of Mesoporous Silicon by Liquid Masking

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ABSTRACT A general approach for selective, differential functionalization of the interior and exterior surfaces of mesoporous Si is reported. The method employs two immiscible liquids, one inert and the other chemically reactive with the porous Si nanostructure. First, a porous Si sample is prepared by electrochemical etch and then it is mildly oxidized, which places a thin layer of silicon oxide at the surface. The inner pore walls of the partially oxidized porous Si film are then infiltrated with an inert liquid (octane). The sample is then immersed in aqueous solution containing hydrogen fluoride (HF), which serves as the reactive liquid. The hydrophobic phase is retained in the interior of the porous nanostructure, and HF_(aq) attacks only the exposed surfaces of the oxidized porous Si sample, generating a hydrophobic, hydrogen-terminated (Si–H) outer layer. The reaction is self-limiting due to the immiscibility of octane and water, and the extent of penetration of the Si–H surface into the porous layer is dependent on the time of exposure to HF_(aq). The Si–H surface can then be modified by thermal hydrosilylation (1-dodecene or 10-bromo-1-decene) in a subsequent step, resulting in a bifunctional porous Si film containing hydrophobic pore entrances to hydrophilic inner pores. The hydrophobic dodecyl species at the mouths of the pores is found to form a barrier for molecular transport; it decreases the rate of leaching (into water) of a rhodamine test molecule that is preloaded into the sample by >8 fold.



KEYWORDS: porous silicon · surface chemistry · mesopores · controlled release drug delivery · diffusion · hydrosilylation · core–shell nanostructures

Mesoporous materials with engineered surface properties are of interest for molecular separations,¹ catalysis,² drug delivery,³ and chemical sensing.^{4,5} One of the longstanding chemical challenges in the engineering of nanomaterials is to control the placement of different chemistries in spatially distinct regions on a nanoscale object. Examples include Janus particles, where different chemical species are placed on the opposite sides of a nanoparticle,^{6–8} and core–shell nanoparticles, where the interior and the surface of a nanoparticle contain distinct materials.^{9–12} Selective surface modification has been achieved with mesoporous silica nanoparticles either by co-condensation during the sol–gel synthesis or by postsynthetic grafting of commercially available substituted trialkoxy- or trichloro-silanes.⁵ In addition, differential chemistries can be placed in or on porous nanostructures by

using the inherent ability of the pores to exclude molecules larger than a certain size.^{13,14}

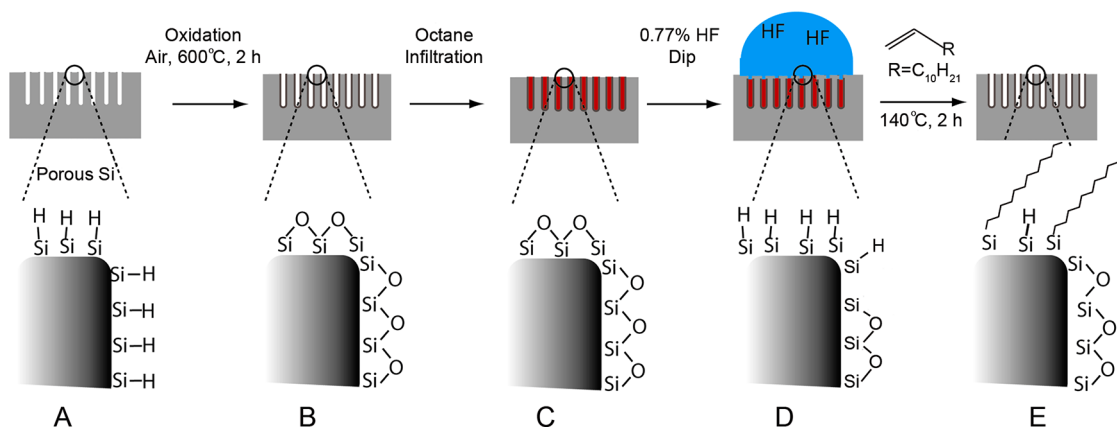
In the case of porous Si, chemical modification is usually performed either after,¹⁵ or in tandem¹⁶ with the electrochemical etching procedure employed in its synthesis. The differential chemistries of surface Si–H, Si–C, and Si–O species on porous Si have been harnessed to prepare Janus-like structures, and various functional groups such as negatively charged oxide or hydrophobic alkanes have been used to impart unique surface properties, such as self-alignment or differential analyte diffusion.^{16–18} These materials are of interest for drug delivery,¹⁹ chemical sensing,^{20,21} energy harvesting,^{22,23} and lab-on-a-drop types of applications.^{24,25} For the porous Si system, the ability to prepare pores of average diameter anywhere from 1 to 300 nm allows the harnessing of surface tension and capillary

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Scheme 1. Schematic illustration of liquid masking method for selective chemical modification of porous Si films. (A) Freshly etched porous Si consists of a skeleton of crystalline silicon features with hydride species capping the skeleton surfaces. (B) Mild thermal oxidation removes the Si–H species and generates a thin layer of silicon oxide covering the silicon skeleton. (C) The porous Si–SiO₂ layer is then infiltrated with an inert organic liquid (octane). (D) Immersion of the octane-infiltrated sample in aqueous HF forms an immiscible interface that penetrates somewhat into the pores. Action of HF on the silicon oxide removes this oxide and places Si–H species on the outermost portion of the silicon skeleton. (E) Thermal hydrosilylation (140 °C) of the newly generated Si–H surface with 1-dodecene selectively replaces the Si–H species with alkenes, resulting in a spatially resolved surface modification

forces to promote or obstruct the infiltration of reagents for selective modification.²⁶ Recently, a photochemical hydrosilylation reaction has been shown to yield depth-resolved chemical functionalization in porous silicon layers, where the depth of chemical modification depends on the wavelength of light used in the synthesis.²⁷

In this paper, we report a simple strategy for differentially modifying the inner pore walls in porous Si layers. The method uses a hydrophobic organic liquid as a chemical resist; it is infiltrated into the pores to mask the interior of the porous Si film, while the exterior surface and the pore mouths of the film are subjected to an aqueous chemical reaction with HF. This “liquid masking” method yields a hydrophilic silicon oxide surface deeper in the porous layer and a silicon hydride surface nearer to the opening of the pores. The Si–H and Si–O surfaces can then be modified using subsequent, orthogonal chemical reactions. Here we demonstrate a hydrosilylation reaction on the Si–H surface using dodecene, which yields a hydrophobic layer on the pore mouths. The hydrophobic outer layer over a hydrophilic inner pore structure is reminiscent of the structure of a liposome, and selective transport of molecular species (rhodamine B) across the hydrophobic barrier is demonstrated.^{4,26}

RESULTS AND DISCUSSION

Selective Chemical Modification using Liquid Masking. The method for differential modification of the inner/outer surfaces of a porous Si layer is summarized in Scheme 1. The as-formed (freshly etched) porous Si thin film (Scheme 1A) contained hydride species throughout the inner and outer pore surfaces, as confirmed by Fourier transform infrared (FTIR) spectroscopy (Figure 1A): the spectrum displayed a small signal assigned to Si–H

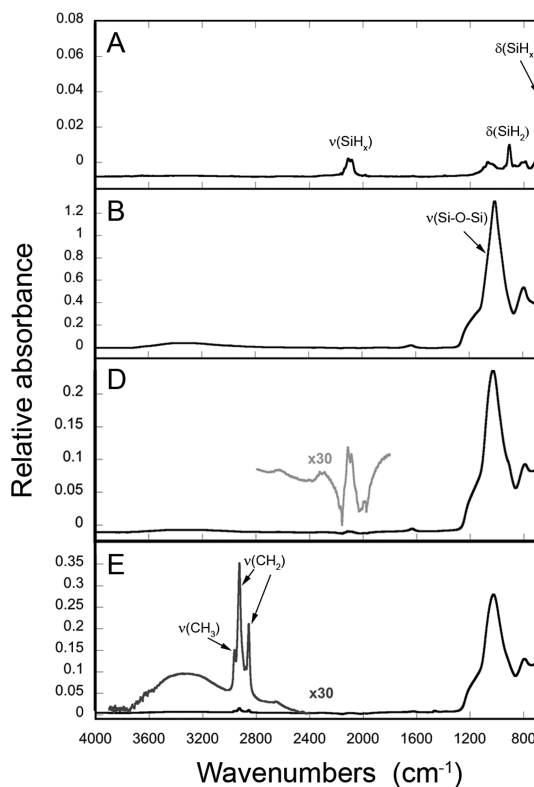


Figure 1. FTIR spectra of a porous Si sample at selected steps of the liquid masking procedure outlined in Scheme 1. (A) Freshly etched porous Si; (B) sample partially oxidized in air for 2 h at 600 °C; (D) after infiltration with octane and exposure to aqueous HF (0.77%) for 600 s. Sample was rinsed and dried prior to acquisition of the spectrum; (E) after thermal hydrosilylation with 1-dodecene. The letter labels of the above spectra correspond to the stages described in Scheme 1. Insets shown in panels D and E are expanded along the y-axis by 30 times.

vibrations, at 2108 and 2084 cm^{-1} (ν_{SiH_2} and ν_{SiH} stretching modes, respectively). Typical porous films consisted of pores of diameter 7 ± 2 nm and film thickness

6.1 \pm 0.2 μm (by scanning electron microscopy, Supporting Information, Figure S1), with a total open porosity of 47% (determined by the spectroscopic liquid infiltration method²⁸ assuming a Si skeleton refractive index of 2.48). Mild thermal oxidation (600 $^{\circ}\text{C}$ in air for 2 h, Scheme 1B) removed the Si–H species and yielded a thin layer of silicon oxide coating the entire nanostructured Si skeleton, both inside and outside the pores (FTIR spectrum, Figure 1B). The porosity of the film at this point decreased to 38% (determined by the spectroscopic liquid infiltration method²⁸ assuming porous Si–SiO₂ skeleton refractive index of 1.97). The film was then mounted in a Teflon cell, and a small quantity of octane was introduced to fill the porous nanostructure (Scheme 1C). Although the oxidized surface imparts a hydrophilic nature to the material (sessile contact angle 10 \pm 3 $^{\circ}$), it was found that octane, hexane, 1-octanol, and toluene could penetrate into the oxidized porous Si film. All these liquids were not easily displaced upon immersion in liquid water, with octane showing the best retention behavior. Optical interferometry indicated that less than 3% of the octane in the pores was exchanged by water after 60 min of immersion (Supporting Information, Figure S2). Therefore, octane was used as the masking liquid for the subsequent experiments. Deionized water (2 mL) was added to the cell containing the octane-wetted porous Si film, and the excess octane was observed to float to the surface of the water due to its lower density (0.6986 g/cm³, 25 $^{\circ}\text{C}$) compared to water (0.9970 g/cm³, 25 $^{\circ}\text{C}$).²⁹ An aliquot of 1.55% by volume of aqueous (48%) HF in deionized water (2 mL) was then added to the cell (final HF concentration, 0.77%) and the sample was allowed to sit quiescently for 10 min (Scheme 1D). The FTIR spectrum of a sample removed from the reaction at this point (Figure 1D) displayed bands associated with SiH_x species, at 2112 and 2087 cm⁻¹. It is noteworthy that, although the FTIR spectrum displayed a strong silicon oxide band (\sim 1100 cm⁻¹), the Si–H stretching region of the spectrum showed no evidence of O_xSi–H_y species (silicon hydride stretching modes for silicon containing backbonded oxygen atoms), which are expected to appear in the spectrum at 2160–2260 cm⁻¹. This is indicative of a demarcation between the Si–H and the SiO₂ surface regions of the porous Si–SiO₂ layer. The large increase in sessile contact angle to 102 \pm 3 $^{\circ}$ at this stage of the reaction is consistent with the presence of Si–H species on the outermost surface of the porous Si layer. Thus the mechanism of the reaction is assumed to involve reaction of HF with silicon oxide at or near the water/octane interface. HF is soluble in octane (20 mM at 25 $^{\circ}\text{C}$),³⁰ so the length of time of exposure is expected to have an effect on the extent of diffusion of HF into the organic phase and thus the extent of reaction of HF with the Si–O surface. The expected products of the reaction are silicon fluoride and an Si–H terminated porous Si surface near the water/octane interface.³¹

The silicon hydride surface generated by the liquid masking procedure was then modified by thermal hydrosilylation (Scheme 1E). Thermal hydrosilylation was performed using either 1-dodecene or 10-bromo-1-decene. In the case of 1-dodecene (Figure 1E), C–H stretching vibrations characteristic of the aliphatic organic chain were apparent in the FTIR spectrum at 2959, 2921, and 2852 cm⁻¹, assigned to asymmetric –CH₃, asymmetric –CH₂–, and symmetric –CH₂– stretching modes, respectively. A control experiment in which the oxidized sample was subjected to thermal hydrosilylation conditions (without prior liquid masking/HF exposure) resulted in a sample whose FTIR spectrum displayed peaks at 2964, 2929, and 2857 cm⁻¹ (Supporting Information, Figure S3B). The relative intensity of the asymmetric –CH₃ band, and its observed shift to higher frequency, is consistent with bonding of the organic species to the oxidized porous Si surface *via* an Si–OR motif rather than Si–R, as has been described previously.³² To confirm this, the modified surface was exposed to dilute aqueous ethanolic HF. The FTIR data indicated that the organic species was completely removed from the Si–O surface (Supporting Information, Figure S3D). By contrast, an oxidized sample that had been subjected to the liquid masking procedure and then hydrosilylated with 1-dodecene displayed a spectral pattern consistent with an Si–R bonding motif; this species was not removed upon exposure to dilute aqueous ethanolic HF (Supporting Information, Figure S3E). Thus the liquid masking method generates reactive Si–H species which can be grafted to 1-alkenes *via* stable Si–C bonds. Without liquid masking, bonding of the 1-alkene occurs *via* either physisorption or formation of Si–O–C covalent bonds to the oxide surface, resulting in a surface modification that is less stable.³²

For the reaction of the surface oxide with HF represented in Scheme 1D to proceed, the organic liquid used as the mask (octane) must allow the porous Si–SiO₂ layer to be exposed to the HF reactant, which is impeded due to the immiscibility of the aqueous HF solution with octane. Cross-sectional elemental mapping was used to determine the depth of penetration of the chemical reaction front, using energy dispersive X-ray spectroscopy (EDX) in the scanning electron microscope. To better resolve the depth of the reaction front, 10-bromo-1-decene was used in the hydrosilylation step instead of 1-dodecene. EDX elemental scans for Si, O, and Br were obtained from the top and bottom portions of the porous Si–SiO₂ film, with a resolution of \sim 1 μm (Supporting Information, Figure S4). Confirmatory EDX spectra of 10-bromo-1-decyl-modified and thermally oxidized porous Si surfaces were obtained in plan view (Supporting Information, Figure S5). The EDX spectrum of the top 1 μm of porous Si from the air/porous Si interface, obtained from the cross-sectional image, revealed the presence

TABLE 1. Summary of Sample Types Used in Rhodamine B Release Studies

sample type	contact angle, deg	dye loading, $\mu\text{g}/\text{mg}^a$
1. no barrier, oxide layer	10 ± 3	81.6 ± 8.9
2. no barrier, dodecyl hydrosilylated oxide layer	43 ± 4	75.1 ± 7.0
3. no barrier, dodecyl hydrosilylated Si—H layer	119 ± 2	13.3 ± 2.3
4. low dodecyl coverage layer on hydrosilylated oxide layer	86 ± 5	40.5 ± 6.4
5. high dodecyl coverage layer on hydrosilylated oxide layer	118 ± 3	16.8 ± 1.9

^aDye loading quantified as micrograms of rhodamine B per milligram of porous Si layer. Dye was loaded from acetonitrile solution. Sample Types 4 and 5 were prepared by liquid masking as described in the text.

of bromine and carbon peaks that can be attributed to grafted 10-bromo-1-decene. Bromine and carbon peaks were absent in the X-ray emission spectrum obtained from the bottom portion of the porous Si layer (near the porous Si/bulk silicon interface), suggesting that the attachment of 10-bromo-1-decene preferentially occurs near the top surface. The results are consistent with the proposed liquid masking mechanism, where reactive hydride species form in the topmost region of the porous layer. The resolution of the EDX method is not sufficient to obtain an accurate assessment of the thickness of 10-bromododecyl layer. The data from grafting of the bromo-dodecyl species supports the conclusion that hydrosilylation occurs only at the surface of the liquid masked film. It should be pointed out that this substituted alkyl chain may also be useful to install more complex or larger molecules.

The chemical reaction between HF and the portion of the porous Si—SiO₂ film exposed by the liquid mask apparently propagates into the porous film at a rate sufficiently slow to allow temporal control of the degree of chemical modification, as discussed above. For this work, two different liquid masked sample types were prepared, along with three control sample types. Characteristics of the five sample types are summarized in Table 1. The first sample, Type 1, was a control sample consisting of the oxidized porous Si film with no further modification. Sample Type 2 was another control sample consisting of the oxidized porous Si film that was then subjected to the thermal hydrosilylation conditions with 1-dodecene. As discussed above, this sample type contains dodecyl species incorporated in the oxide layer. Sample Type 3 was a third control sample consisting of the freshly etched porous Si film (Si—H terminated) that was then subjected to thermal hydrosilylation with 1-dodecene. This sample type is thus fully infiltrated with dodecyl species grafted *via* Si—C bonds, and contains no liquid masked layer. Sample Types 4 and 5 were prepared following the procedure described in Scheme 1D and Figure 2, where the time of exposure to HF_(aq) was varied in order to control the extent of dodecyl modification in the barrier layer. The surface layer of Si—H species formed by liquid mask on either of these sample types was then modified by hydrosilylation with 1-dodecene

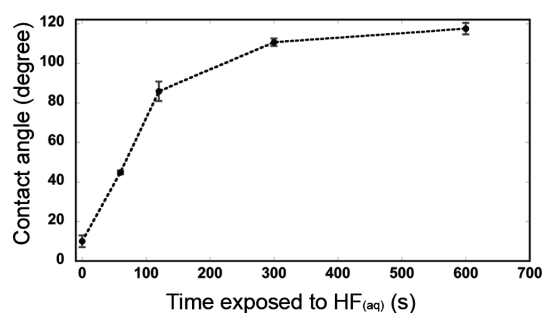


Figure 2. Measured sessile contact angle of 1-dodecyl-modified liquid masked porous Si samples as a function of time of exposure of the octane-masked film to aqueous HF. The liquid (octane) masked film was exposed to 0.77% aqueous HF (as indicated in Scheme 1D) for the indicated time, and the resulting Si—H surface layer was subsequently modified by thermal hydrosilylation of 1-dodecene as indicated in Scheme 1E. Time points at 120 and 600 s correspond to the exposure times used to prepare liquid masked sample Types 4 and 5, respectively. Triplicate measurements; error bars indicate one standard deviation.

(step E in Scheme 1).¹⁵ Sample Type 4 was less extensively modified, and displayed a contact angle significantly lower than sample Type 5. Both sample Types 4 and 5 are expected to contain a lower oxide layer with properties similar to control sample Type 2. Table 1 compares contact angles measured on the different sample types. Sample Type 1 was not exposed to aqueous HF (time point 0 in Figure 2), and this oxidized porous Si surface was quite hydrophilic. The contact angle increased significantly with HF exposure times between 0 and 300s and then leveled off for times greater than 300 s (Figure 2), indicating that the extent of the reaction that forms hydride species can be readily controlled. Extending the aqueous HF exposure time of the octane-infiltrated porous Si film to 10 min yielded, upon subsequent thermal hydrosilylation with alkene, a very hydrophobic top surface with contact angle $118 \pm 3^\circ$ (sample Type 5).

Monitoring of Liquid Transport through Dodecyl-Modified Porous Si Samples. Despite the strong hydrophobic nature of the topmost, dodecyl-modified layer of the porous Si film generated by the liquid masking method, the EDX analysis (Supporting Information, Figure S3) showed that the lower portion of the porous Si film remained oxidized. Thus the structures are somewhat reminiscent of an inverse micelle, consisting of a hydrophobic film coating an inner hydrophilic core.³³

Unlike a micelle, the structures formed by liquid masking are rigid, and they can be probed by optical interferometry. Lipid-coated porous Si films have been prepared previously, where a lipid bilayer was physisorbed to a rigid, oxidized porous Si film.^{34–37} In those structures, the lipid layer was mobile, and it often displayed pinholes and discontinuities.³⁸ In the present system, the hydrophobic dodecene layer was covalently grafted to the porous Si layer, and it apparently formed a uniform, continuous coating. We probed the transport of water across this dodecyl-modified porous Si surface layer and into the underlying hydrophilic porous Si–SiO₂ layer using optical interferometry. A CCD-based spectrometer and white light source were coupled to the optics *via* a bifurcated optical fiber that allowed acquisition of optical reflectance spectra at a time resolution of 1 s. Reflective interferometric Fourier transform spectroscopy (RIFTS)³⁹ was employed, which quantified the appearance of water in the underlying porous Si layer as a shift in its optical thickness due to an increase in the average refractive index of the porous layer as air filling the pores was displaced by water.

The optical reflectance spectrum of a dodecyl-modified sample in air (Figure 3A) displays Fabry-Pérot interference fringes, corresponding to constructive and destructive interference from light reflected at the air/porous Si and porous Si/crystalline Si interfaces.⁴⁰ The peak maximum for each of the spectral fringes follows the Fabry-Pérot interference relationship represented by eq 1 in normal incidence:

$$m\lambda = 2nL \quad (1)$$

where m is the spectral order of the fringe at wavelength λ , n is the average refractive index of the porous layer and its contents, and L is the physical thickness of the film. The liquid masked layer in the top portion of the film did not display sufficient refractive index contrast to be distinguished from the underlying oxidized layer in the interference spectrum, and so the contents of the entire layer are probed as an average in this experiment. In the RIFTS method,³¹ the fast Fourier transform (FFT) of the frequency spectrum (inset, Figure 3A) yields a peak whose position along the x -axis represents the value of the effective optical thickness (EOT), or $2nL$, from eq 1.

The optical measurement conveniently monitors the infiltration of water into the porous Si–SiO₂ layer in real time. The samples were mounted in a sealed cell fitted with the optical microscope/spectrometer focused on a ~ 1 mm spot on the porous Si sample. The spectral data from a control experiment, performed on a porous Si–SiO₂ film that had not been subjected to the liquid masking procedure (represented by step B in Scheme 1) is shown in Figure 3B. Introduction of water to the sample chamber resulted in an instantaneous increase in the value of $2nL$ measured from the sample, as the liquid water replaced the air in the 38% porous film. Using the thickness of the porous Si film

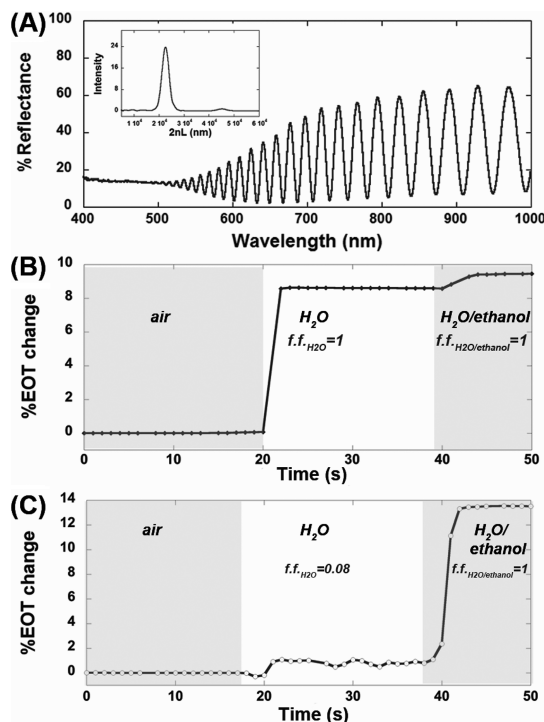


Figure 3. Experimental optical response vs time data showing the penetration of liquid water ($n_D = 1.333$) or a 1:1 water/ethanol (equal volume) solution ($n_D = 1.3598$), as indicated, through a hydrophobic dodecyl barrier layer grafted to the top portion of a partially oxidized porous Si–SiO₂ film. The barrier layer was prepared by the liquid masking method described in Scheme 1, and water infiltration to the partially oxidized porous Si–SiO₂ film was quantified by reflective interferometric Fourier transform spectroscopy (RIFTS). (A) Optical reflectance spectrum of a typical sample prepared by liquid masking. Sample consists of ~ 6 μm -thick surface-oxidized, hydrophilic porous Si–SiO₂ layer underneath a dodecyl-terminated, hydrophobic layer. The inset shows the FFT of the frequency spectrum; the peak position yields the value of $2nL$ (the effective optical thickness) of the film. (B) The quantity $2nL$ measured as a function of time during water infiltration into a control sample consisting of partially oxidized porous Si, without the hydrophobic barrier layer. The terms “ $f.f.$ liquid” refer to the fractional filling of the indicated liquid in the porous layer in the indicated temporal region of the curve. (C) The quantity $2nL$ measured as a function of time during water infiltration into a sample containing a dodecyl barrier layer. The contact angle of barrier layer in this experiment was $118 \pm 3^\circ$.

measured by SEM and the refractive index of air ($n_D = 1.00$) and water ($n_D = 1.333$) at 20°C ,²⁹ a fit to the Bruggeman effective medium model^{41,42} was used to determine the fractional filling of the porous volume occupied by the infiltrated liquid. A fractional filling value of 1.0 was observed, indicating full infiltration of water in this sample.

The experimental protocol followed in the water infiltration experiments involved the addition of a small quantity of ethanol to the sample cell several seconds after water was introduced. The purpose of the ethanol addition was 2-fold: (1) ethanol reduces the surface tension of water and thus allows it to more thoroughly wet the nanometer scale pores in the film;

and (2) the larger refractive index of ethanol ($n = 1.3611$) introduces a secondary increase in the value of $2nL$. Both of these factors provide verification of the fraction of the porous film that has been infiltrated by water. In the case of the control sample consisting of porous Si–SiO₂ with no hydrophobic barrier layer (Figure 3B), ethanol addition resulted in an increase in $2nL$ that fit the calculated prediction for a fully infiltrated layer.

The presence of the thin hydrophobic layer on the top portion of the film dramatically changes its behavior with water. As the contact angle measurements demonstrate, the dodecyl-terminated layer is quite hydrophobic, and it was found to effectively exclude water from the underlying porous Si–SiO₂ layer. The addition of water to the optical cell resulted in a fractional filling of only 0.08 with this sample (Figure 3C). When ethanol was added to the water, rapid penetration of the hydrophobic layer was observed, and complete infiltration of the porous Si–SiO₂ layer occurred within 4 s. In the data shown in Figure 3C, the sample was stable, with no additional water infiltration observed, for 20 s prior to ethanol addition. In separate experiments (not shown), it was found that pure water penetrated the hydrophobic barrier layer very slowly. We conclude that the presence of the hydrophobic barrier layer effectively impedes the penetration of water molecules into the pores.

Controlled Release of Small Molecules through the Dodecyl Barrier Layer. The ability of the hydrophobic barrier layer to exclude and impede the transport of water has interesting implications for controlled release drug delivery. Since the first reports of the bioactivity of porous Si in 1995,⁴³ porous Si has been widely studied as a potential drug delivery material.^{19,44,45} To test the ability of water-soluble molecules to escape through the dodecyl barrier layer, rhodamine B was loaded into the oxidized layer by physical adsorption from an acetonitrile solution. The mass of rhodamine B loaded into the porous Si samples was confirmed by absorbance spectroscopy. Acetonitrile was chosen as the loading and extraction solvent due to the hydrophobic nature of the modified samples. The loading efficiencies for rhodamine B in the five sample types are given in Table 1. The general trend that can be seen in the data of Table 1 is that the greater the hydrophobicity of the sample, the lower the quantity of hydrophilic dye that can be loaded. The more extensively dodecyl-modified sample Type 5 was found to load less dye per milligram of porous Si than the less extensively modified sample Type 4. The control sample Type 3, consisting of a fully dodecyl-terminated layer, held an amount of dye similar to the extensively dodecyl modified sample Type 5. The oxidized but unmodified sample Type 1 held the most dye of all the samples. The Type 1 sample was the most hydrophilic

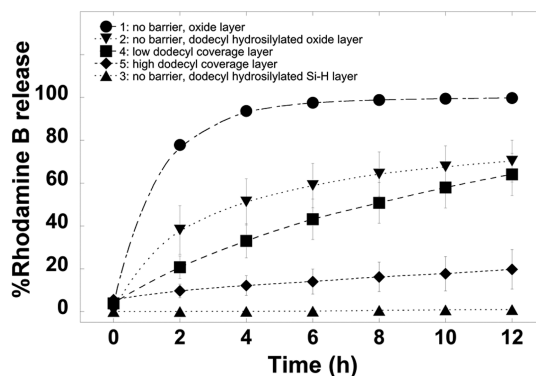


Figure 4. Release profiles of rhodamine B into aqueous PBS buffer from partially oxidized porous Si layers containing different top barrier layers and interior surface chemistries: (●) sample Type 1, porous Si/SiO₂ layer with no barrier layer (sample not subjected to liquid masking procedure); (▼) sample Type 2, porous Si/SiO₂ layer subjected to hydrosilylation conditions but containing no liquid masked barrier layer; (■) sample Type 4, porous Si/SiO₂ layer subjected to liquid masking procedure, with low dodecyl coverage in top barrier layer; (◆) sample Type 5, porous Si/SiO₂ layer subjected to liquid masking procedure, with high dodecyl coverage in top barrier layer; (▲) sample Type 3, freshly etched porous Si hydrosilylated with 1-dodecene throughout the layer. Each data point in the curves was averaged from three samples and the error bars indicate standard deviation.

of the samples, and so its high loading capacity is consistent with the hydrophilic nature of rhodamine B molecules.⁴⁶ The control sample Type 2, consisting of an oxide layer that had been made partially hydrophobic by incorporation of dodecyl species but with no barrier layer, showed loading capacity similar to, but slightly less than the Type 1 oxide layer. This Type 2 sample contained more dye than either of the “barrier layer” samples (Types 4 and 5).

The rate of release of the rhodamine B test molecule is also reduced in the more hydrophobic sample types. To test the dye release characteristics, the samples were immersed in a phosphate buffered saline (PBS, pH = 7.4) solution and the appearance of the dye in solution was monitored by absorbance spectroscopy for a 12 h-period (Figure 4). Due to the low wettability of the hydrophobic dodecyl barrier layer, transport of dye from the partially oxidized reservoir layer into aqueous solution is expected to be impeded, as the aqueous medium does not easily penetrate the pores. As shown in Figure 4, egress of rhodamine B from the Type 1 samples (hydrophilic oxide with no barrier layer) displayed a typical burst release characteristic, with 100% of the loaded molecule released into solution within 12 h. The samples containing the dodecyl modified oxide layer all showed somewhat slower release characteristics. The control sample Type 2, containing no barrier layer with a dodecyl-modified oxide, released only 70% of the loaded rhodamine B within 12 h. The sample Type 4, containing the minor barrier layer over a dodecyl-modified oxide, displayed a somewhat lower rate of release; only 60% of the dye

was released within 12 h. The sample Type 5, containing the most extensive dodecyl barrier layer, exhibited a significantly lower rate of release, with only 20% of the dye released in the 12 h study period. Control sample Type 3, containing a fully dodecyl-terminated surface, displayed the slowest release, with only 1% of the dye released in 12 h. As expected from its highly hydrophobic nature, this sample type also displayed a very low capacity for the hydrophilic dye. The control experiments (sample Types 2 and 3) described above establish the limiting capacity and transport rates of the hydrophilic and hydrophobic surface types that are generated by the liquid masking procedure. In particular, the control experiment where there is no barrier layer and just the hydrosilylated oxide “reservoir” layer (sample Type 2) establishes the intrinsic release rate and loading numbers for the barrier-free film (rapid release, high loading capacity). Similarly, sample Type 3, which contains only a hydrosilylated Si–H surface, establishes the intrinsic release and loading characteristics of the hydrophobic barrier layer (slow release, low loading capacity). The dye release rates and loading capacities of the liquid masked samples fall between these two limits, demonstrating the ability of the liquid masking procedure to provide control over these parameters.

This study focused on chip-based films, that is, porous layers still attached to a silicon wafer. However, the liquid masking method reported here may also be useful to prepare micro- or nanoparticles as carriers for drugs or other molecules. The preparation of micro¹⁶- and nanoparticles⁴⁷ from porous Si has been described, as has their use as *in vivo* drug delivery materials.^{48–53} A key feature of the approach is it provides a simple means to harness the chemistry of porous Si to place a thin hydrophobic barrier layer over a hydrophilic reservoir layer. Alternate chemistries, where the inner reservoir layer of the material is hydrophobic and the exterior is hydrophilic, should also be possible with this approach.¹⁶ With the present formulation, the slowing of release of a highly water-soluble molecule was demonstrated; as observed in the control experiments, this is difficult to achieve without the hydrophobic barrier layer. The oxidized inner pores can potentially accommodate a wide range of molecules, including larger proteins. It has previously been shown that the relatively large pore

dimensions (>20 nm) accessible in the porous Si system and the biodegradable oxide surface allow loading of antibodies with little loss of activity upon release.⁵⁴ The inert nature of the oxidized surface may also be more compatible with redox-active drugs, compared to the native Si–H surface present in freshly etched or hydrosilylated porous Si.⁵⁵

CONCLUSIONS

The data demonstrate that the liquid masking approach can prepare Janus-type porous Si nanostructures with controllable hydrophobicity/hydrophilicity characteristics. The layers formed by liquid masking modify the loading capacity and diffusional properties of the porous nanostructures; in this work the potential utility of such materials was demonstrated with a notional controlled drug release experiment using a hydrophilic test molecule, rhodamine B. The presence of octane (the liquid mask) within the oxidized porous nanostructure controlled the diffusion of the aqueous HF developer into the porous nanostructure, which provided control over the surface coverage and depth of penetration of the silicon hydride species available for subsequent modification. Thermal hydrosilylation conditions (using dodecene) modifies both the silicon hydride species at the outer layer and (to a lesser extent) the oxidized silicon surface in the inner layer of the porous Si/SiO₂ film; the resulting hydrophobic outer layer displayed contact angles ranging from 86° to 118°, depending on the length of time the liquid masked layer was exposed to the aqueous HF developer. The outer hydrophobic surface acted as a barrier for water infiltration that was monitored using optical interferometry. One application of this hydrophobic barrier layer was demonstrated for controlled release of small molecules, and the data show that the variable degree of modification afforded by the liquid masking method allows the control of the rate of release of a hydrophilic molecular payload (rhodamine B). It was found that the loading capacity and the rate of release of the hydrophilic dye depended on the degree of hydrophobic modification of the porous Si sample: the greater the hydrophobicity, the lower the capacity, and the lower the rate of release. Thus the liquid masking method should provide an ability to fine-tune the delivery of drugs from porous Si films or particles.

EXPERIMENTAL SECTION

Chemicals and Materials. Highly boron-doped 0.9–1 mΩ-cm resistivity, (100) oriented and polished p-type silicon wafers were obtained from Siltronic, Inc. Hydrofluoric acid (48% aqueous, ACS grade) was obtained from Macron Chemicals, Fisher Scientific. Absolute ethanol (200 proof) was obtained from Rossville Gold Shield Chemicals. Octane (puriss. p.a., ≥99.0%), hexane (CHROMASOLV Plus, ≥95%), 1-octanol (~99%), toluene

(anhydrous, 99.8%), 1-dodecene (95%), mesitylene (98%), 10-bromo-1-decene (97%), and rhodamine B (dye content 90%) were obtained from Sigma-Aldrich and used without further purification. Phosphate buffered saline (10×, pH 7.4) was obtained as a stock solution from Mediatech, Inc. and diluted 10-fold by the addition of deionized water prior to use. Acetone (HPLC grade) and acetonitrile (certified ACS, ≥99.5%) were obtained from Fisher Scientific.

Preparation of Porous Si Samples. Mesoporous Si films were prepared by anodic electrochemical etch of highly boron-doped p-type silicon in a 3:1 v/v solution of 48% aqueous hydrofluoric acid and ethanol in an electrochemical cell that exposed 1.2 cm² of the wafer to the electrolyte, as previously described.³¹ A constant current density of 15 mA/cm² was applied for 9 min, using a 16 mm diameter ring-shaped Pt wire loop as the counter electrode. Subsequent to etching, samples were rinsed with ethanol and dried under a stream of dry nitrogen.

Chemical Modification of Porous Si Samples. The partially oxidized porous Si–SiO₂ films were prepared by thermal oxidation in tube furnace (Lindberg Blue M) at 600 °C for 2 h in ambient air. Alkane-grafted porous Si surfaces were prepared by thermal hydrosilylation of the liquid-masked samples with neat 1-dodecene or a 10% (v/v) solution of 10-bromo-1-decene in mesitylene. Using standard Schlenk and syringe inert atmosphere handling methods,⁵⁶ the samples were submerged in the alkene and degassed with 3 freeze–pump–thaw cycles prior to heating at 140 °C for 2 h in a nitrogen environment. The modified samples were then rinsed with acetone and ethanol to remove excess alkene.

Scanning Electron Microscopy. An FEI XL30 ultrahigh resolution scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV was used to obtain plan-view and cross-sectional images of the samples. Samples were not coated with metal or carbon prior to imaging, and low beam currents were used to avoid sample charging artifacts. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on plan-view and cross-sectional samples using a Philips XL-30 Field Emission ESEM with Oxford EDX attachment.

Infrared Spectroscopy. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were acquired on a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a Smart iTR accessory for ATR sampling; 128 scans were averaged. Spectral resolution was 4 cm⁻¹ over the range 600–4000 cm⁻¹.

Water Contact Angle Measurement. Water contact angle measurements were obtained by imaging water droplets placed on horizontally oriented porous Si samples using a Canon EOS XSi digital camera with 100 mm macro lens. Droplets of 5 μ L deionized water were placed on the sample surfaces. The contact angle was measured from the acquired images using Adobe Photoshop CS4 (Adobe Systems, Inc.) Each reported contact angle represents the average of triplicate measurements at different locations on the porous Si surfaces.

Optical Reflectance Spectra. The thin film interference spectra were obtained in a 180° reflectance configuration, collected using an Ocean Optics 4000 CCD spectrometer fitted with a bifurcated fiber optic cable. An unpolarized tungsten light source was focused onto the porous Si surface with a spot size of approximately 1 mm². Reference spectra were obtained from a broadband metallic mirror (model 10D20ER.2, 25.4 mm diameter front-surface silver mirror on a Pyrex glass support, Newport Corporation). Optical spectra were processed using a computer and algorithms described previously.³¹

Porosity and Fractional Filling Determinations by Spectroscopic Liquid Infiltration Method (SLIM). The SLIM method was used as described in the literature.³¹ Briefly, two reflectance spectra of the porous Si film were obtained: (1) with the sample in air and (2) with the sample wetted with ethanol. The values of $2nL$, obtained from the Fourier transform of the optical spectra, were fit to a two component Bruggeman model using the values of the refractive index of air and ethanol to determine the porosity and the thickness of the porous Si film. The thickness values determined in this fashion were validated on similar samples using cross-sectional SEM imaging. The fractional filling of water into the porous Si–SiO₂ layer was calculated with a similar optical measurement and model, using the thickness and porosity values previously determined from the SLIM measurements. The refractive index of all liquids used were independently measured with a Mettler Toledo Refracto 30GS refractometer.

Loading of Rhodamine B into Modified Porous Si Films. The organic dye rhodamine B was used as a test molecule for loading into the porous Si–SiO₂ matrix. The functionalized porous Si chip

was immersed in 1 mL of 0.2 mg/mL rhodamine B in acetonitrile in a glass vial and agitated for 12 h at room temperature. The sample was then removed and rinsed with acetonitrile to eliminate excess free dye not loaded into the porous reservoir. To determine the loading efficiency, the loaded dye was extracted from the porous matrix by immersion in acetonitrile for 16 h at 37 °C with mild agitation. The quantity of rhodamine B released into solution was determined from the absorbance spectrum, collected in the spectral range 400–650 nm using a SpectraMax absorbance spectrometer (Molecular Devices). The concentration of rhodamine B was determined from calibration curves of the absorbance at 552 nm and assuming Beer's law.

Dye Release Studies. Porous Si–SiO₂ chips containing loaded dye were first dried in vacuum. Samples were then immersed in 1 mL of aqueous phosphate buffered saline (PBS) solution (pH 7.4) at 37 °C with mild agitation. The supernatant containing released dye was collected every 2 h over a 12 h period and replaced with 1 mL of fresh buffer. Concentrations of the released rhodamine B were determined from the absorbance at 552 nm, using calibration curves of the dye in PBS.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Plan-view and cross-sectional scanning electron microscope images of freshly etched porous Si film; optical measurement of the fractional filling of organic liquids in a partially oxidized porous Si–SiO₂ film as a function of time exposed to liquid water; EDX spectra from selected plan-view and cross-sectional regions of a liquid masked porous Si film modified with 10-bromo-1-decene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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