

Bioconjugate functionalization of thermally carbonized porous silicon using a radical coupling reaction†

Beniamino Sciacca,^a Sara D. Alvarez,^b Francesco Geobaldo^a and Michael J. Sailor^b

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The high stability of Salonen's thermally carbonized porous silicon (TCPSi) has attracted attention for environmental and biochemical sensing applications, where corrosion-induced zero point drift of porous silicon-based sensor elements has historically been a significant problem. Prepared by the high temperature reaction of porous silicon with acetylene gas, the stability of this silicon carbide-like material also poses a challenge—many sensor applications require a functionalized surface, and the low reactivity of TCPSi has limited the ability to chemically modify its surface. This work presents a simple reaction to modify the surface of TCPSi with an alkyl carboxylate. The method involves radical coupling of a dicarboxylic acid (sebacic acid) to the TCPSi surface using a benzoyl peroxide initiator. The grafted carboxylic acid species provides a route for bioconjugate chemical modification, demonstrated in this work by coupling propylamine to the surface carboxylic acid group through the intermediacy of pentafluorophenol and 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC). The stability of the carbonized porous Si surface, both before and after chemical modification, is tested in phosphate buffered saline solution and found to be superior to either hydrosilylated (with undecylenic acid) or thermally oxidized porous Si surfaces.

Introduction

Porous silicon has been shown to be a useful sensing matrix for many chemical and biological sensor applications.¹ Relevant properties of porous Si include its photoluminescence² and passive optical reflectance properties,³ high surface area, convenient surface chemistry,⁴ tunable refractive index,⁵ and controllable pore sizes⁶ in dimensions appropriate for biomolecule admittance or separation.^{7,8} The porous nature of the material is responsible for the high sensitivity achieved when porous Si structures are configured as optical transducers for sensing vapors⁹ and biomolecules.^{3,10}

Surface stability is an important prerequisite for maintaining stable optical transduction when applying porous Si sensors in atmospheric or biological media.^{11–13} Functionalizing the surface of porous Si is crucial for improving its low chemical stability and several methods have been explored for chemically modifying the freshly etched, hydrogen-terminated porous Si surface.^{4,14,15} Chemical modification also provides a route for conjugation of specific molecules on the surface for selective sensing.^{16,17} Hydrosilylation is one chemical modification method used to improve stability. This method reacts an alkene or an alkyne with the freshly etched Si–H surface in order to generate a stable Si–C bond.¹⁸ It has been used to introduce a carboxylic acid end-group for subsequent attachment of molecules relevant for biosensor or *in vivo* applications, such as oligo(ethylene) glycol¹⁹ and glycerides.²⁰

The discovery by Salonen and coworkers of a carbonization method involving thermal decomposition of the hydrocarbon

acetylene on freshly etched porous Si surfaces²¹ provided a means to dramatically improve the stability of the material while preserving its basic nanoscale structure.²² Carbonization increases the aqueous stability of porous Si by forming a thin silicon carbide-like layer that effectively passivates the internal porous surface. The optical properties necessary for sensing are retained after carbonization, and thermally carbonized porous Si (TCPSi) films have been used to generate stable optical gas sensors.²³

To apply TCPSi as a biosensor, chemical stability must be retained in a physiologically relevant aqueous medium, and the surface chemistry must allow permeation of the aqueous solutions while also allowing the attachment of specific biological capture probes. Typically, harsh chemical treatments are required to functionalize the variety of C–C and C–H bonds that are present on the surface of fibers, nanotubes, or diamond-like forms of carbon,^{24–28} or on silicon carbide.²⁹ Recently, Iijima and coworkers have shown that relatively mild (azo based) radical initiators can be used to modify the surface of silicon carbide nanoparticles.³⁰ In the present work, we explore a mild route to chemically modify carbonized porous Si surfaces based on coupling of a dicarboxylic acid *via* the intermediacy of the radical initiator benzoyl peroxide. The chemistry follows a published procedure to functionalize hydrogenated diamond surfaces,³¹ and it introduces a stable carboxylic acid functionality to the surface. This reaction provides a route for covalent attachment of specific sensing molecules to thermally carbonized porous Si, improving its potential application as a biosensor.

Experimental

Porous Si formation

The porous Si layer was obtained by electrochemical etch of highly boron-doped, monocrystalline, (100) silicon substrates

^aDipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino, 10129, Italy

^bDepartment of Chemistry and Biochemistry, The University of California, San Diego, 9500 Gillman Drive, La Jolla, California, 92093-0358

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(p-type, 0.0005–0.0012 Ω -cm) purchased from Siltronix, inc. The electrolyte was composed of a 3 : 1 mixture of aqueous HF (48%, EMD Chemicals Inc., Gibbstown, NJ) and absolute ethanol (Pharmco-AAPER, Brookfield, CT). The anodization process was performed in the dark at room temperature. A current density of 150 mA cm⁻² was applied for 60 s. The sample was rinsed three times with absolute ethanol and then dried in a stream of dry nitrogen. The freshly etched sample was placed under vacuum for 15 min to remove any ethanol traces.

Porous Si characterization

The optical parameters (thickness and refractive index) were obtained performing a best-fit calculation of the reflectance spectrum, by the means of a simulation program (SCOUT, obtained from M. Theiss Hard- and Software, Dr -Bernhard-Klein-Str. 110, D-52078 Aachen, Germany, Copyright Wolfgang Theiss, www.wtheiss.com) that is based on the transfer matrix method.³² The software generates the theoretical reflectance spectrum of the porous Si film, calculating its effective refractive index using the dielectric function of bulk silicon and assuming a Bruggeman effective medium approximation.³³ Porosity and thickness are the two free parameters of the model; their value is adjusted in a least-squares algorithm in order to obtain the best fit between the experimental and the calculated spectra.

The surface functionalization was characterized after each chemical step using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). A Thermo Scientific Nicolet 6700 FTIR instrument was used for the collection of the spectra. Surface functionalization was also probed by contact angle measurement. Sessile contact angles were measured with a 5 μ L drop of deionized water using images obtained from a digital camera fitted with a macro lens. Values of three separate drops on the same sample were averaged in order to obtain the final reported value for the contact angle.

Thermal carbonization of freshly etched porous Si *via* acetylene thermal decomposition

Thermal carbonization was performed in a tube furnace following the procedure of Salonen and coworkers.³⁴ In order to purge the furnace of oxygen, a purge of 1 L min⁻¹ of N_{2(g)} was maintained for 15 min prior to introduction of acetylene. The temperature was increased to 500 °C in a linear ramp of 50 °C min⁻¹ and acetylene was introduced with a constant flux of 1 L min⁻¹ (the nitrogen flow was maintained constant at 1 L min⁻¹ during this period). The acetylene flow was discontinued after 45 min and the furnace was allowed to cool under a continuous nitrogen flow (1 L min⁻¹) for approximately 30 min before removal of the sample from the tube furnace.

Chemical modification of thermally carbonized porous Si

Carboxylic acid functionalization of the TCPSi layer was carried out in a round bottom flask. For each chip the reagents used were: Toluene (EMD Chemicals Inc, Gibbstown, NJ), Sebacic acid 0.42 M (1 g, Sigma–Aldrich Chemicals, St. Louis, MO), Benzoyl peroxide 0.068 M (0.2 g, Sigma–Aldrich Chemicals, St. Louis, MO) and 16% of DMF (Sigma–Aldrich Chemicals, St. Louis, MO). The reagents were mixed together to dissolve and the

solution was immediately added to the TCPSi chip. The mixture was then bubbled with argon in order to remove oxygen and the flask heated at 75 °C. After 2 h the reaction mixture was cooled to room temperature, the chip was removed, washed with ethanol, acetone, and another rinse of ethanol and then dried in a dry nitrogen stream.

Ester activation of the carboxylic acid-terminated surface was performed in a DMF solution (300 μ L, Sigma–Aldrich Chemicals, St. Louis, MO) 1 M in EDC (Sigma–Aldrich Chemicals, St. Louis, MO) and 1 M in pentafluorophenol (Sigma–Aldrich Chemicals, St. Louis, MO) for 15 min. The porous Si chip was then washed several times with ethanol and placed in an absolute ethanol solution 2 M in propylamine (Sigma–Aldrich Chemicals, St. Louis, MO). After the reaction the chip was washed thoroughly with ethanol.

Hydrosilylation of freshly etched porous Si with undecylenic acid

Hydrosilylation¹⁸ was performed in a Schlenk line in vacuum (<10 mTorr) with neat undecylenic acid at 130 °C for two hours. Prior to the reaction, three freeze-pump-thaw cycles were performed in order to remove oxygen from the reaction. After the reaction the chip was washed with ethanol, acetone, and another rinse of ethanol and dried in a dry nitrogen stream.

Thermal oxidation of porous Si

Thermal oxidation of freshly etched porous Si was performed in a tube furnace (Lindberg/Blue M) at 800 °C for 1 h in ambient air.

Measurement of optical thickness

White light from a tungsten lamp (Ocean Optics LS-1) was fed through one end of a bifurcated fiber-optic cable and focused through a lens onto the surface of the TCPSi film at normal incidence. The light source was focused onto the center of the sample surface with a spot size ~1 mm in diameter. Light reflected from the film was collected through the same optics, and the distal end of the bifurcated fiber optic cable was input to a CCD spectrometer (Ocean Optics S-2000). Reflectivity spectra were recorded in the wavelength range 400–1000 nm, with a spectral acquisition time of 100 ms. Typically 50 spectral scans (5 s total integration time) were averaged. The data spacing of the spectrometer was 0.4 nm.

The value of optical thickness ($2nL$) of the porous film was determined from the fringe pattern in the reflectance spectrum using the equation:

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

where m is the spectral order of the fringe, n is the single-wavelength average refractive index, and L is the physical thickness of the porous layer.³⁵ The quantity optical thickness, $2nL$, was determined by Fast Fourier transformation of the frequency spectrum. In order to perform the Fourier transform of the spectrum, the x -axis was inverted and a linear interpolation was applied such that the data were spaced evenly in units of nm⁻¹. A Hanning window was applied to the spectrum, it was redimensioned to 4096 data points and zero padded to the power of two. A discrete Fourier transform using a multidimensional fast prime factor decomposition algorithm from the Wavemetrics

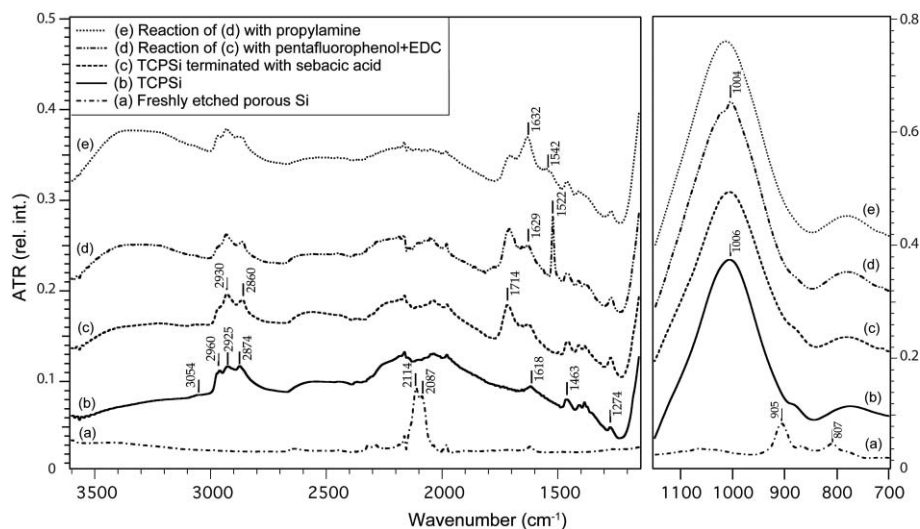


Fig. 1 Attenuated total reflectance (ATR) spectra of porous Si samples obtained at key points in the transformation of freshly etched porous Si to a chemically stable surface suitable for bioconjugation. (a) freshly etched porous Si, displaying bands characteristic of the hydride (Si–H) terminated surface; (b) thermally carbonized porous Si, prepared by exposure of porous Si to acetylene gas at high temperature; (c) product of benzoyl peroxide-mediated grafting of sebacic acid to the carbonized surface; (d) product of EDC-mediated coupling of pentafluorophenol to the free carboxy group of the surface-bound sebacic acid species; (e) result of replacement of the pentafluorophenol group by propylamine. The spectra shown at the right are obtained in the spectral range of 1150–700 cm^{-1} ; the strong band associated with the carbonized porous Si surface is the most dominant feature.

Inc. (www.wavemetrics.com) IGOR program library (FFT) was applied. The Fourier transform of the spectrum yields a peak whose position on the x -axis corresponds to the value $2nL$, corresponding to the effective optical thickness of the film for a reflection mode experiment. This peak was monitored in real-time for optical thickness changes during the aqueous stability experiments.

Aqueous stability experiments

Samples were exposed to aqueous PBS buffer (phosphate buffered saline, 1X, pH = 7.4, obtained from Gibco, Inc.) in a flow cell apparatus using a flow rate of 1 mL min^{-1} in an open loop (single-pass) configuration. The flow cell was constructed of plexiglass, consisting of an inlet and an outlet, and was connected to a CBS Scientific MPP100 peristaltic mini-pump. The flow cell, as previously described,³⁶ was fitted with an optical window to allow acquisition of reflectivity spectra from the porous Si surfaces during the stability experiments.

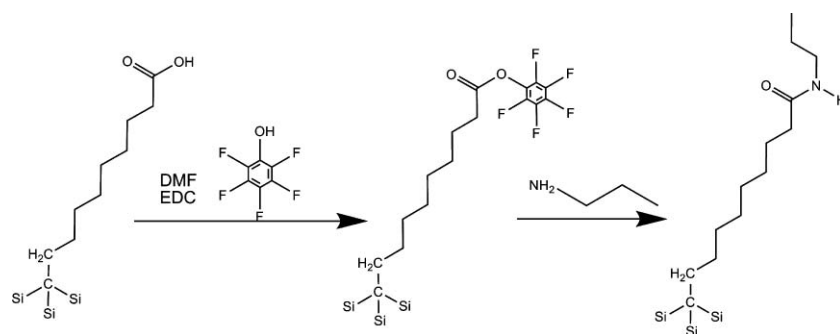
Results and discussion

Electrochemical anodization of highly doped p-type silicon produces an optically flat thin film of nanoporous Si with a high surface area. The interference spectrum reflected from the thin film was collected and fit to a spectrum generated using the transfer matrix method, allowing the determination of thickness and porosity. Analysis revealed that the etch parameters (150 mA cm^{-2} for 60 s) produce a film $5 \mu\text{m}$ in thickness with 64% porosity.

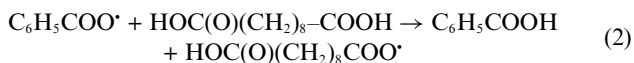
Fig. 1 presents ATR-FTIR spectra of a porous Si samples at various stages during the chemical functionalization procedure developed in this paper. Immediately after electrochemical anodization, the spectrum displays bands characteristic of Si–H and

SiH₂ stretching vibrations, at 2087 and 2114 cm^{-1} , respectively;³⁷ a band associated with the Si–H deformation mode is also present at 905 cm^{-1} (Fig. 1a).³⁸ After thermal carbonization of the porous Si sample by acetylene decomposition, bands assignable to stretching vibrations of saturated C–H bonds are observed in the 2870–2970 cm^{-1} range, and an intense band at 1006 cm^{-1} is also apparent, assigned to wagging and rocking modes of C–H_x (Fig. 1b).^{21,39} Weak absorption bands that can be assigned to unsaturated carbon species are also observed in the FTIR spectrum: 3050 cm^{-1} ($\nu_{\text{C-H}}$, aromatic stretching) 1618 cm^{-1} ($\nu_{\text{C=C}}$, double bond stretching) 1463 cm^{-1} ($\nu_{\text{C=C}}$, aromatic stretching).

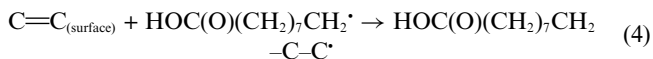
After functionalization with sebacic acid, a new band is apparent in the FTIR spectrum centered at 1714 cm^{-1} (Fig. 1c). Changes in intensity of the bands in the 2860–2960 cm^{-1} region are also apparent. The band centered at 1714 cm^{-1} is assigned to the free carboxylic acid group of the grafted sebacic acid species. The absence of an absorption band that can be assigned to an ester functionality indicates, in our opinion, that a mechanism different from that proposed in reference (31) is operating in the present system. Whereas the reaction of Ida *et al.*³¹ assumes the organic species becomes attached to the surface *via* a C–O bond, the reaction mechanism proposed here results in attachment of the organic species to the carbonized surface *via* C–C bonds. The one-electron oxidation of aliphatic carboxylic acids generally results in rapid decarbonylation *via* the well-known Kolbe electrolysis reaction, and radical-induced decarbonylation of aliphatic diacids has been reported to follow a similar pathway.⁴⁰ In the present system, it is proposed that benzoyl peroxide abstracts a hydrogen atom from one of the carboxylic acid groups on sebacic acid (eqn (2)). Decarbonylation of the resulting radical species generates the aliphatic radical by eqn (3). A similar mechanism has been proposed by Jin *et al.* for one-electron oxidations of dicarboxylic acids in sub- and supercritical water.⁴¹



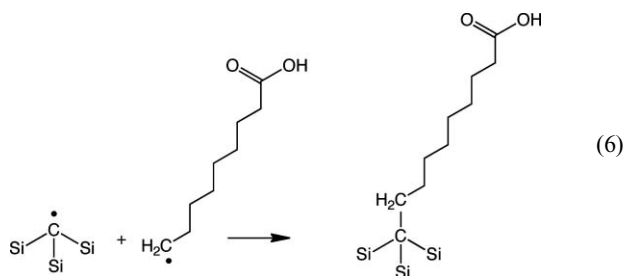
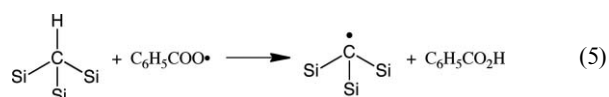
Scheme 1 Strategy for chemically modifying carbonized porous Si. The surface-bound aliphatic carboxylic acid species was bound to the surface by benzoyl peroxide mediated grafting of sebacic acid. Steps involved to bind propylamine to the functionalized porous Si surface are shown. DMF = dimethyl formamide, EDC = 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide.



The grafting reaction is proposed to take place by reaction of the sebacic acid radical with species on the carbonized porous Si surface. Taking into account the chemical groups present on the carbonized surface, two possible reaction pathways can be suggested: one involving a direct reaction with unsaturated groups already present in the carbonized surface (eqn (4)),



and the other involving reaction with radicals produced on the carbonized porous Si surface. These surface radicals could be generated by hydrogen atom abstraction by the benzoyl peroxide radical (eqn (5)–(6)):



This latter mechanism involving generation of surface radicals by benzoyl peroxide has been suggested by Ida, *et al.*³¹ as the dominant reaction in the benzoyl peroxide/diamond system. At this time we cannot provide an unambiguous assignment of the dominant mechanism for the porous Si carbide modification reaction.

After the grafting reaction, the sample was rinsed several times with an ethanolic HF solution (3 : 1 ethanol:48% aqueous HF) in order to clean the surface and remove any silicon oxide-related species. No change in the FTIR spectrum was observed (data not shown). The result demonstrates that the chemical modification of the carbonized porous Si surface generates a stable,

covalently bound carboxylic acid group that can be used for further bioconjugate chemical modifications.

In order to demonstrate a bioconjugate coupling reaction that would be useful for biosensor or drug delivery applications, attachment of pentafluorophenol to the surface carboxyl species was performed using a standard carbodiimide coupling reagent (Scheme 1). The characteristic peaks of pentafluorophenol appear at 1522 cm⁻¹ (vibration associated with the halogenated aromatic ring) and at 1004 cm⁻¹ ($\nu_{\text{C-F}}$ stretching) in the ATR-FTIR spectra (Fig. 1d). A weak absorption band appears at 1629 cm⁻¹, which is assigned to urea-based byproducts.⁴²

Pentafluorophenol functions as a good leaving group for an incoming amine, which then replaces the ester with an amide bond. The ATR-FTIR spectrum of the propylamine-modified surface is presented in Fig. 1e. A shoulder appears at 1542 cm⁻¹ ($\nu_{\text{N-H}}$ bending, $\nu_{\text{C-N}}$ stretching - Amide II band of secondary amines) and the band at 1632 cm⁻¹ ($\nu_{\text{C=O}}$ stretching - Amide I band of secondary amines) is strongly increased, indicating formation of an amide as outlined in Scheme 1.

Two control experiments were performed to test the reaction mechanism proposed above. Reactions run in the absence of benzoyl peroxide or sebacic acid display significant differences in the ATR-FTIR spectra obtained at the end of the procedure. The ATR-FTIR spectrum of a surface exposed to benzoyl peroxide in the absence of sebacic acid (Supplemental Fig. S1) shows that the surface is terminated with benzoyl peroxide groups as indicated by bands at 1710 cm⁻¹ ($\nu_{\text{C=O}}$ Aryl ester) and 711 cm⁻¹ ($\nu_{\text{C-H}}$ mono-substituted benzene). When benzoyl peroxide is omitted and the surface is exposed to sebacic acid under otherwise identical reaction conditions, only a small absorption band at 1714 cm⁻¹ for the dicarboxylic acid is apparent in the spectrum (Supplemental Fig. S1†). The peak is no longer present in spectra of samples that have been subsequently rinsed with ethanolic HF solution (3 : 1 ethanol:48% aqueous HF), indicating that the sebacic acid is only physisorbed in the absence of the radical initiator. When benzoyl peroxide and sebacic acid are both present (Fig. 1c), the aliphatic C-H bands at 2928 cm⁻¹ and 2858 cm⁻¹ and the carboxyl C-O band at 1714 cm⁻¹ are significantly more intense.

Water contact angle measurements were obtained on the samples in order to quantify the change in surface hydrophilicity caused by the chemistry. Immediately after thermal carbonization of the porous Si surface, the measured contact angle is 116°, indicating a significantly hydrophobic surface. The contact angle

decreases to a value of 21° after the radical modification reaction, consistent with the large degree of hydrophilicity that is expected to be imparted by the carboxylic acid groups attached to the surface.

Most chemical and biochemical sensing methods that use porous Si as an optical element require that the material display significant structural integrity and chemical stability. In particular, biosensors using optical thin films (such as Fabry-Perot films, rugate filters, and Bragg stacks) usually require that the material be stable in aqueous media or biological environments for the duration of the analysis.¹ Fabry-Perot based porous Si sensing elements rely on a thin film interference pattern observed in the optical reflectivity spectrum. The Fourier transform of the spectrum yields a value of the optical thickness (nL), where n is the composite refractive index and L is the thickness of the porous layer.⁴³ This methodology has been used for sensitive detection of analyte entrance into the pores; the net refractive index increases for analytes (such as organic molecules or proteins) whose index of refraction is larger than the index of air or an aqueous buffer matrix.¹ One of the limitations of this approach is oxidation or dissolution of the porous Si matrix, which produces a decrease in refractive index that results in undesirable zero point drift of the baseline signal from the optical sensor.^{44–47}

Two classes of surface chemistries have been employed to increase the chemical stability of porous Si for sensor applications: those using silicon–oxygen bonds and those using silicon–carbon bonds. Silicon–carbon bonds can be generated on porous Si by hydrosilylation of terminal alkenes,^{4,14} electrochemical reduction of alkylhalides,⁴⁷ or reaction with alkyllithium reagents.¹⁵ Silicon–oxygen bonds are generally produced using thermal^{16,48} or electrochemical⁴⁹ oxidation reactions. However, no approaches to prepare stable Si–C or Si–O surfaces from porous Si have been completely successful. Silicon oxide generated by thermal oxidation (porous SiO₂) is susceptible to hydrolysis in aqueous media,^{50,51} and surfaces modified with Si–C bonds tend to yield low coverage, leaving residual reactive Si–H or Si–Si bonds that are attacked by oxidants.^{47,52,53} The excellent chemical stability reported by Salonen and coworkers^{23,54,55} for thermally carbonized porous Si suggests that it might provide the long-term stability required for many biosensor and aqueous sensor applications. With this aim in mind, we tested the stability of the functionalized thermally carbonized porous Si samples in aqueous phosphate buffered saline (PBS, pH 7.4) solutions using the optical interferometric method.⁴³

The reflectance spectrum of a freshly etched porous Si sample is shown in Fig. 2a, revealing the Fabry-Perot fringes characteristic of the optical interference pattern. After thermal carbonization, distinct interference fringes are still observable (Fig. 2b) thereby showing that the carbonized surface retains sufficient optical transparency to allow optical biosensing. Although thermal carbonization can leave black, optically dense carbonaceous deposits that completely obscure the optical interference spectrum, prior studies have shown that when the reaction is carried out at moderate temperatures (500 °C, as in the present study) the deposit is sufficiently thin to yield adequate optical transparency while retaining the desired chemical stability of a silicon carbide-like surface.^{23,56}

To test the stability of thermally carbonized porous Si, we monitored the reflectance spectrum over time under a constant flow of phosphate buffered saline (pH 7.4) for 2 h. We com-

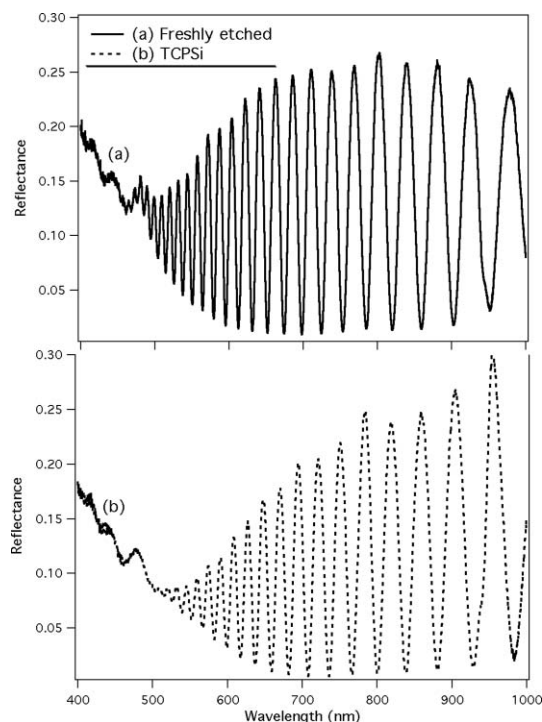


Fig. 2 Reflectance spectra of (a) freshly etched porous Si sample and (b) thermally carbonized porous Si sample.

pared the thermally carbonized surface and its derivatives to hydrosilylated porous Si. Hydrosilylation is a common route used to modify porous Si with Si–C bonds and improve its aqueous stability.^{4,14,52,53} Hydrosilylation using undecylenic acid is of particular interest for biosensing applications because it introduces a carboxylic acid functional group on the distal end of the molecule that can be used for further bioconjugation chemistries.⁵¹ The optical thickness (nL) of the various modified porous Si samples was monitored for decreases in refractive index (n) or thickness (L), which are indicative of degradation of the surface (Fig. 3). The data presented in Fig. 3 are representative of the results from several experiments on each sample type: (a) thermally carbonized porous Si, (b) thermally carbonized porous Si modified by radical coupling of sebacic acid, (c) thermally oxidized porous Si, and (d) porous Si hydrosilylated with undecylenic acid. For all chemistries studied, the optical thickness of the sample decreases upon exposure to the flowing buffer solution, indicative of slow degradation and dissolution of the porous film. The thermally carbonized and the sebacic acid-terminated surfaces show the smallest rate of decrease in optical thickness, indicating that they undergo the least degradation in aqueous buffer. By comparison, a fully oxidized (1 h @ 800 °C in air) porous Si surface displays a similar degradation rate as the thermally carbonized and sebacic acid-terminated surfaces, and the hydrosilylated surface displays significantly poorer stability. While we did not perform a direct comparison, the relative slopes of the curves shown in Fig. 3 suggest that this surface chemistry is less stable than the electrochemical grafting/methyl end-capping chemistry of ref. 47. However, the present approach is a more rapid functionalization method that does not require stringent anaerobic conditions. It is noteworthy that the stability of the thermally carbonized surface does not change after chemical modification

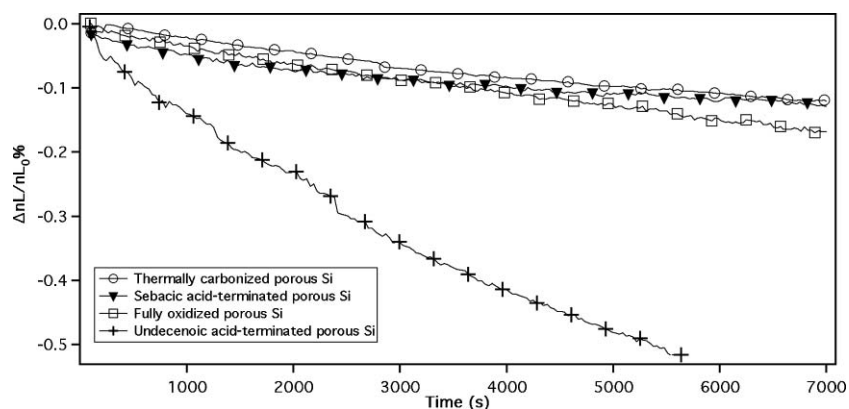


Fig. 3 Degradation curves comparing the aqueous stability of porous Si modifications: thermally carbonized porous Si (open circles), thermally carbonized porous Si modified by radical coupling of sebacic acid (solid triangles), thermally oxidized porous Si (open squares), and porous Si hydrosilylated with undecylenic acid (crosses). Data are presented as the fractional change in optical thickness (nL) as a function of time in flowing aqueous PBS buffer (pH 7.4) solution. The quantity $\Delta nL/nL_0$ % is defined as the percent change in optical thickness (product of refractive index n and physical thickness L) divided by the initial value of nL (nL_0) obtained within 10 s of introduction of the PBS solution to the sample.

with sebacic acid. By contrast, molecules grafted to porous Si by electrochemical coupling tend to make the surface less stable if they contain a functional group (such as an ester).⁴⁷ Thus the present chemistry yields a stable yet easily modifiable surface that is readily implemented.

Conclusions

A method to functionalize thermally carbonized porous Si by radical coupling of sebacic acid has been developed, and the capability to further modify the surface using standard bioconjugate chemistry methods was demonstrated. The initial functionalization reaction is proposed to proceed by benzoyl peroxide-mediated generation of radicals both on the surface of thermally carbonized porous Si and at one end of the dicarboxylic acid. The radical is generated on the dicarboxylic acid by oxidative decarboxylation, and the organic species is proposed to be attached to the surface through a C–C bond. Conjugation chemistry that exploits the terminal free carboxylic acid group on the resulting surface was demonstrated using EDC-mediated coupling of propylamine. The stability of the sebacic acid-modified surface was established by exposure to aqueous buffer solutions, and this surface chemistry is found to be comparable to a non-functional thermal oxide, and superior to the widely used carboxy-terminated surface prepared by the thermal hydrosilylation route. These results demonstrate the potential of thermally carbonized porous Si (formed by thermal decomposition of acetylene on freshly etched porous Si) as a functional and stable nanomaterial. The surface modification chemistry described here provides a means to attach molecules to a stable porous silicon-based matrix using conventional bioconjugate methods.

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