Organic trihydridosilanes can be grafted to hydrogen-terminated porous Si nanostructures with no catalyst. The reaction proceeds efficiently at 80 °C, and it shows little sensitivity to air or water impurities. The modified surfaces are stable to corrosive aqueous solutions and common organic solvents. Octadecylsilane $H_2Si(CH_2)_17CH_3$ and functional silanes $H_2Si(CH_2)_nBr$, $H_2Si(CH_2)_3CH=CH_2$, and $H_2Si(CH_2)_n(CF_3)_2CF_3$ are readily grafted. When performed on a mesoporous Si wafer, the perfluoro reagent yields a superhydrophobic surface (contact angle 151°). The bromo-derivative is converted to azide, amine, or alkyne functional surfaces via standard transformations, and the utility of the method is demonstrated by loading of the antibiotic ciprofloxacin (35% by mass). When intrinsically photoluminescent porous Si films or nanoparticles are used, photoluminescence is retained in the grafted products, indicating that the chemistry does not introduce substantial nonradiative surface traps.

Extensive effort has been expended on stabilizing the surface of silicon to improve its suitability for various energy, electronics, sensor, and biological applications. The hydrosilylation reaction developed by Buriak, Boukherroub, and many others has been a mainstay in the field because of the ease with which functional species can be incorporated into the surface and the relatively low hydrolytic reactivity of the resulting Si–C bonds. The hydrosilylation reaction involves coupling of surface Si–H species to alkene or alkyne moieties on the organic reagent, and it requires scrupulous exclusion of air and water to avoid oxidative side reactions with Si–H. An alternative to hydrosilylation is dehydrogenative coupling, where a hydridosilane ($RSiH_2$) instead of an alkene (RCH=CH$_2$) is coupled to the surface Si–H species (Scheme 1). An advantage of this approach is that the high reactivity of the silane reagent with trace oxygen and water can be expected to reduce the possibility of oxidative side reactions with the Si-H surface. Buriak and co-workers reported the first grafting reaction of hydridosilanes with porous Si surfaces using early transition metal catalysts to effect the transformation. The presence of these highly reactive catalysts led to oxidative side reactions, and the utility of the method was not fully realized. More recently, Veinot and co-workers demonstrated coupling of organosilanes to hydrogen-terminated Si nanoparticles catalyzed by the rhodium complex known as Wilkinson’s catalyst. Following the report of non-catalyzed dehydrogenative coupling of organosilanes to various surfaces including silicon, in this work we find that the reaction proceeds under mild thermal conditions on pSi surfaces without any added catalyst to generate stable, functional coatings, with minimal oxidation, and with retention of the electronic quality of the original Si-H surface.

The silicon nanostructures used in this work were prepared in the form of porous Si (pSi) films or nanoparticles by electrochemical etching of silicon wafers in aqueous ethanolic HF (see Supporting Information for detailed experimental conditions). The electrochemical etch gener-
a mesoporous silicon skeleton terminated on the surface with hydrogen atoms. We first investigated the reaction of a pSi film with octadecylsilane, H₃Si(CH₂)₁₇CH₃ (“H₃Si-(C₁₈₃)”). After heating to 80 °C in the presence of the neat silane reagent and workup involving thorough rinsing of the sample (Figure S1 in the Supporting Information), infrared, Raman, and contact angle measurements (Figure 1) were indicative of extensive surface grafting. The modified porous layer was significantly more hydrophobic than the pSi starting material or the non-porous Si substrate (Figure 1d and Figure S2), and the infrared spectrum of the as-prepared pSi sample (Figure S4) was significantly more hydrophobic than the pSi starting material or the non-porous Si substrate (Figure S4).

The Raman spectrum of pSi–Si(C₁₈₃) (Figure 1b) showed that the crystallinity of the material was retained (Si lattice mode at 515 cm⁻¹), and scanning electron microscope (SEM) images (Figure 1c) demonstrated that the open pore structure was preserved. Optical porosity measurements indicated that the grafting reaction decreased the open porosity of the pSi samples somewhat (Figure S3 and Table S1).

Because oxidation of pSi (to pSiO₂) involves a large volume expansion in the pore walls, oxidizing conditions can close the pores and trap material such that it cannot be readily washed out. Thus we performed tests to determine if the organosilane was chemically bonded to the pSi surface, rather than merely physically trapped in the pores. Thorough rinsing of the samples in an aqueous solution of HF-containing ethanol has become a standard test to determine if a species is grafted via Si–C bonds, because HF attacks and dissolves Si–O bonds much more rapidly than Si–Si or Si–C bonds. Treatment of the octadecylsilane-grafted pSi product with aqueous ethanolic HF resulted in no change in the FTIR features associated with the SiH₃ bonds, because HF attacks and dissolves Si–O bonds much more rapidly than Si–Si or Si–C bonds. Treatment of the octadecylsilane-grafted pSi product with aqueous ethanolic HF resulted in no change in the FTIR features associated with the SiH₃ bonds, because HF attacks and dissolves Si–O bonds much more rapidly than Si–Si or Si–C bonds. Treatment of the octadecylsilane-grafted pSi product with aqueous ethanolic HF resulted in no change in the FTIR features associated with the SiH₃ bonds, because HF attacks and dissolves Si–O bonds much more rapidly than Si–Si or Si–C bonds.
coverage that it protects this subsurface oxide from attack by aqueous ethanolic HF.

Based on infrared and contact angle measurements, the optimal temperature to form pSi-Si(C$_{18}$) was determined to be 80°C (Figure S5a). This temperature is substantially lower than the >100°C temperatures typically employed when thermal hydrosilylation is used to attach alkenes to pSi surfaces$^{[12,10]}$ and it minimizes side-reactions that can occur in the presence of adventitious oxygen or water. Control experiments performed in the absence of silane reagent indicated little oxidation of the pSi substrate at 80°C, while at 120°C, pSi surface oxidation was more substantial (Figure S5b). An additional control reaction determined that octadecylsilane did not react in the absence of pSi under the reaction conditions (80°C, 24 h), i.e., the reagent does not undergo a dehydrogenative coupling reaction with itself (by NMR, Figure S6). The optimal reaction time for the reaction at 80°C was determined to be 24 h, though surface grafting was apparent after 1 h (Figure S7). Based on contact angle and infrared measurements, the degree of surface coverage was readily tunable by adjustment of the reaction time between 1–24 h.

The dehydrocoupling reaction is remarkably tolerant of water and air; the reaction was found to proceed as well in air as in argon ambient, and introduction of up to 10% (by volume) water to the reaction mixture did not adversely affect the grafting reaction (Figure S8), although formation of silicon oxide as a side-product was observed by FTIR in all the reactions. As expected for a Si–C modified surface$^{[2a,11]}$, the organosilane-grafted pSi-Si(C$_{18}$) product displayed substantial stability toward harsh conditions such as heat (120°C), light (224 mW cm$^{-2}$), or strongly oxidative (1 M H$_2$O$_2$) or acidic (1 M HCl) conditions (Figure S9).

The dehydrocoupling reaction was also found to proceed on pSi nanoparticles. Porous silicon nanoparticles (pSiNPs) were prepared by ultrasonic fracture of a free-standing pSi film as previously described$^{[12]}$, except that the ultrasonication step was performed with the film immersed in neat hydrosilane reagent. This directly generated a homogeneous distribution of hydrophobic particles of average hydrodynamic size 160 nm (Figure S10). For either the pSi film or pSi nanoparticle grafting reactions, we believe the probable mechanism for these reactions to be a combination of dehydrogenative coupling and dissociative adsorption on the strained hydrogenated silicon surface as indicated in Scheme 1, although detailed mechanistic studies were not performed.

To test the effect of the surface grafting reaction on the intrinsic photoluminescence of quantum-confined pSi$^{[13]}$, we prepared luminescent pSi from n-type silicon wafers. The n-type preparation displays strong photoluminescence (PL) immediately after electrochemical etching (Figure 2a and Figure S1)$^{[14]}$. Chemical reactions with this type of surface often lead to loss of photoluminescence due to the generation of non-radiative carrier traps$^{[15]}$. However, some reactions—in particular oxidation$^{[16]}$ and hydrocarbon grafting$^{[2b,16]}$—have been found to passivate the surface and preserve photoluminescence from pSi. Similar to these surface-passivating reactions, the octadecylsilane dehydrocoupling reaction was found to preserve photoluminescence (Figure 2 and Figure S11). The pSi–Si(C$_{18}$) coupling product displayed a strongly hydrophobic character similar to the hydride-terminated pSi starting material. However, consistent with prior observations$^{[17]}$, hydride-terminated pSi slowly lost photoluminescence intensity and became more hydrophilic when submerged in water (Figure 2). Thermally oxidized (Si–SiO$_2$ core–shell) pSi samples displayed similar degradation of photoluminescence. This behavior results from oxidation and dissolution of the quantum-confined silicon nanostructures in the sample$^{[18]}$. By contrast, the coupling product pSi–Si(C$_{18}$) retained its photoluminescence and large contact angle.

**Figure 2.** Dehydrocoupling reaction preserves the intrinsic photoluminescence of pSi. a) Photoluminescence (PL) images ($\lambda_{em}$ = 385 nm) of as-etched pSi (pSi), thermally oxidized pSi (pSi-oxi), and coupling product pSi–Si–(CH$_2$)$_3$–CH$_3$ (pSi–Si(C$_{18}$)). All display room-temperature PL. The pSi and pSi–Si(C$_{18}$) samples are hydrophobic and added water does not wet the surface. The pSi-oxi sample (thermally oxidized at 80°C for 24 h) is hydrophilic and PL is quenched by water. b) The integrated PL intensity ($\lambda_{em}$ = 500–950 nm) from the indicated samples as a function of time submerged in water. c) Water contact angle of each sample, as indicated, at day 0 and day 5. Water contact angle standard error is ±5° from 3 replicate measurements.
Figure 3. Summary of the reactions of functional hydridosilanes with pSi, and subsequent modification chemistry performed on the products. The coupling reactions of pSi chips with the functional hydridosilane reagents H$_2$Si(CH$_3$)$_3$Br, H$_2$Si(CH$_3$)$_2$CH=$CH$CH$_3$, and H$_2$Si(CH$_3$)$_2$CF$_3$ generate the grafted products pSi-Si(C$_1$)-Br, pSi-Si(C$_1$)-CH$_2$CH$_3$, and pSi-Si(C$_1$)-CF$_3$, respectively, (left side). The chips containing the products pSi-Si(C$_1$)-Br and pSi-Si(C$_1$)-CH$_2$CH$_3$ were subjected to subsequent chemical reactions: i) Reaction of pSi-Si(C$_1$)-Br with NaN$_3$ generates pSi-Si(C$_1$)-N$_3$. ii) Ultrasonic irradiation of pSi-Si(C$_1$)-N$_3$ with PPh$_3$ in tetrahydrofuran yields pSi-Si(C$_1$)-NH$_3$ (Staudinger reaction). iii) Reaction of pSi-Si(C$_1$)-Br with propargylamine in the presence of Cu$^{2+}$ and sodium ascorbate generates pSi-Si(C$_1$)-(1H,1,2,3-triazol-4-yl)CH$_2$NH$_3$ (catalyzed “click” reaction) in either aqueous or dimethylsulfoxide (v) solvents. iv) Ultrasonic irradiation of pSi-Si(C$_1$)-CH$_2$CH$_3$ with (4-(1,2,4,5-Tetrazin-3-yl)phenyl)methanamine hydrochloride yields pSi-Si(C$_1$)-6-phenyl-1,4-dihydropyridazine-CH$_2$NH$_3$ (uncatalyzed “click” reaction).

(> 140°) even after 9 days of immersion in aerated water. This behavior is similar to the behavior of luminescent pSi after it has been grafted with alkyl species by hydrosilylation.[22,23] However, as with p-type pSi, the dehydrocoupling reaction on n-type pSi showed substantially superior tolerance to air and water impurities compared with the hydrosilylation reaction (Figure S12).

Although the chemical stability imparted by Si-C-grafted organic species on pSi surfaces is required for many applications, perhaps the most important feature of grafting reactions is their ability to yield functional surfaces.[24] We found the organosilane dehydrocoupling reaction to be tolerant of functional groups and demonstrated several key functionalization reactions on pSi surfaces, summarized in Figure 3. In particular, functional hydridosilanes containing bromo and alkene terminal groups were successfully grafted, and the strongly hydrophobic perfluorocarbon hydridosilane was also grafted. The functional groups on the silane reagent retained their integrity, and the perfluorocarbon product displayed superhydrophobic behavior, with a water contact angle of 150° (Figure S13 and S14). As with the octadecylsilane derivative, these surface chemistries were not removed with aggressive rinsing in organic solvent or in aqueous ethanolic HF (Figure S15), establishing the Si–Si and Si–C bonding motif of the surface grafting reaction.

To test its suitability for further organic functionalization reactions, the pSi-Si(C$_1$)-Br derivative was subjected to various common temperature–time–solvent combinations (dimethyl formamide, dimethyl sulfoxide, dichloromethane, and tetrahydrofuran) and it demonstrated high durability (Figure S16). The substitution reaction of pSi-Si(C$_1$)-Br with sodium azide (NaN$_3$) proceeded smoothly (reaction (i) in Figure 3 and Figure S17), and the reaction product pSi-Si(C$_1$)-N$_3$ readily underwent the Staudinger reaction[19] with triphenylphosphine (PPh$_3$) to generate a terminal amine, pSi-Si(C$_1$)-NH$_3$ (reaction (ii) in Figure 3 and Figure S17). This primary amine-terminal product is a useful starting point for many bioconjugation reactions,[20] and it also provides a hydrophilic surface that is positively charged at physiological pH, which enables electrostatic loading of many negatively charged drugs. As an exemplar of this feature, we loaded the antibiotic drug ciprofloxacin[21] by electrostatic means into the amine-functionalized surface. Up to 35 ± 3 % by mass of the drug could be loaded into the porous matrix at pH 7 (Figure S18).

To demonstrate the ability to functionalize the pSi-Si(C$_1$)-NH$_3$ derivative by chemical bond formation, the material was reacted with fluorescein isothiocyanate (FITC), which resulted in conjugation of the fluorescent molecule to the surface via an amide bond. After workup, the sample displayed the bright green fluorescence spectrum characteristic of fluorescein, and infrared measurements confirmed the integrity of the attachment chemistry (Figure S19). The water contact angle increased substantially upon fluorescein conjugation, indicative of replacement of the highly hydrophilic amine species (contact angle 16°) with the more hydrophobic fluorescein molecule (contact angle 72°).

The bromo derivative pSi-Si(C$_1$)-Br underwent a nucleophilic substitution reaction with the amine of propargylamine (reaction (iii) in Figure 3 and Figure S20), while the azide on the pSi-Si(C$_1$)-N$_3$ derivative reacted with the alkyne moiety
of propargylamine in a copper-catalyzed “click” reaction[22] (reaction (iv) and (v) in Figure 3 and Figure S17). Because residual metals can be problematic for therapeutic applications of nanomaterials, we also demonstrated the catalyst-free “click” reaction: tetrazine(phenyl)methanamine hydrochloride with the pSi-Si(CH₂)₂-CH=CH₂ derivative (reaction (vi) in Figure 3, Figure S21 and Figure S22). This tetrazine-alkene “click” reaction proceeds without added catalyst.[23] These reactions all occurred under mild conditions, and they were characterized by infrared spectroscopy, water contact angle measurements, and optical absorbance.

In summary, dehydrogenative coupling of hydrido-organosilanes (H₂SiR) provides a mild, efficient, and experimentally convenient means to attach Si–C bonded species to hydrogen-terminated Si surfaces. The method is tolerant of terminal -Br and -alkene substituents, allowing entry into a range of useful functional nanomaterials and nanoparticles. The chemistry proceeds via Si–Si bond formation, which yields chemically stable surface that preserve photoluminescence from quantum-confined Si domain in the porous Si matrix.

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