**Surface Modification**

**Thermally Induced Silane Dehydrocoupling on Silicon Nanostructures**

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**Abstract:** 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 \( H_2Si(CH_2)_{17}CH_3 \) and functional silanes \( H_2Si(CH_2)_{17}Br, H_2Si(CH_2)CH=CH_2, \) and \( H_2Si(CH_2)_{17}(CF_2)_{2}CF_3 \) 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 alkyn 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.

**Scheme 1.** Proposed dehydrogenative coupling reactions between trihydridosilanes and hydrogenated silicon in the presence of air.

**Communications**

with the Si–C grafted aliphatic. For example, the C-Si-H band in silacyclohexane[6] appears as a strong band at 865 cm\(^{-1}\), and the SiH\(_3\) wag in diethylsilane[7] appears as a very strong band at 840 cm\(^{-1}\). A sharp band appeared in the spectrum of the as-prepared pSi starting material at 907 cm\(^{-1}\), assigned to the SiH\(_2\) scissor mode \(\delta(\text{Si–H})\), and in the octadecylsilane starting material the corresponding SiH\(_{2}\) deformation mode[8] \(\delta(\text{Si–H})\) appeared at 922 cm\(^{-1}\).

The Raman spectrum of pSi–Si(C\(_{18}\)) (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 pSiO\(_2\)) 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.[9] 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.[1c,2a] Treatment of the octadecylsilane-grafted pSi product with aqueous ethanolic HF resulted in no change in the FTIR features associated with the surface modification (Figure 1a) and elemental analysis by energy-dispersive X-ray (EDS) analysis revealed strong carbon and oxygen signals (Table S2). By contrast, a control sample consisting of thermally oxidized pSi subjected to the same dehydrogenative coupling conditions and then treated with HF resulted in complete removal of the FTIR signatures of the octadecylsilane reagent (Figure S4). Therefore we conclude that the grafting reaction on hydrogen-terminated pSi results in organosilane covalently bonded to the pSi surface. The silicon oxide observed in the FTIR and EDS measurements is presumably beneath this grafted layer, 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.
coverage that it protects this sub-surface oxide from attack by aqueous ethanolic HF.

Based on infrared and contact angle measurements, the optimal temperature to form pSi–Si(C18) 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,[12a,12c] 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–Si modified surface,[12a,12c] the organosilane-grafted pSi–Si(C18) product displayed substantial stability toward harsh conditions such as heat (120 °C), light (224 mW cm⁻²), or strongly oxidative (1 M H₂O₂) 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,[12c] 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 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 S11).[14] Chemical reactions with this type of surface often lead to loss of photoluminescence due to the generation of non-radiative carrier traps.[14] However, some reactions—in particular oxidation[15] and hydrocarbon grafting[16,17]—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(C18) 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–SiO₂ 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.[13] By contrast, the coupling product pSi–Si(C18) retained its photoluminescence and large contact angle.
We found the reaction (ii) in Figure 3 and Figure S17. This derivative reacted with the alkyne moiety in tetrahydrofuran yields pSi-Si(C$_3$Br$_4$N) with (4-(1,2,4,5-Tetrazin-3-yl)phenyl)methanamine hydrochloride by electrostatic interaction. The reaction of pSi-Si(C$_3$Br$_4$N) readily underwent the Staudinger reaction (catalyzed "click" reaction) in either aqueous (iv) or methanol buffer (v) with PPh$_3$/Cs$_2$CO$_3$ and sodium azide (NaN$_3$) respectively (left side). The reaction of pSi-Si(C$_3$Br$_4$N) with NaN$_3$ proceeds smoothly (reaction (i) in Figure 3 and Figure S17), and the reaction product pSi-Si(C$_3$Br$_4$N)$_2$ readily underwent the Staudinger reaction (reaction (ii) in Figure 3 and Figure S17). This primary amine-terminal product is a useful starting point for many bioconjugation reactions, and it also provides a hydrophilic surface that is positively charged at physiologic pH, which enables electrostatic loading of various negatively charged drugs. As an example of this latter feature, we loaded the antibiotic drug ciprofloxacin 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$_3$Br$_4$N)$_2$ 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 more hydrophobic fluorescein molecule (contact angle 140°) with 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).

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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(C6H5)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 (H,SiR) 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.

Acknowledgements

This work was supported by the National Science Foundation under Grant No. DMR-1210417 and by the Defense Advanced Research Projects Agency (DARPA) under Cooperative Agreement HR0011-13-2-0017. The content of the work does not necessarily reflect the position or the policy of the Government. K.H.A. acknowledges support from S. Korean Grant No. GRL 2014K1A1A2064569.

Keywords: mesoporous materials · photoluminescence · porous silicon · quantum dots · surface chemistry

How to cite: Angew. Chem. Int. Ed. 2016, 55, 6423–6427
Angew. Chem. 2016, 128, 6533–6537
