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Room Temperature Hydrosilylation of Silicon Nanocrystals with Bifunctional Terminal Alkenes

Yixuan Yu, Colin M. Hessel, Timothy Bogart, Matthew G. Panthani, Michael R. Rasch, and Brian A. Korgel*

Department of Chemical Engineering, Texas Materials Institute, and Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712-1062, USA

Abstract

H-terminated Si nanocrystals undergo room temperature hydrosilylation with bifunctional alkenes with distal polar moieties—ethyl-, methyl-ester or carboxylic acids—without the aid of light or added catalyst. The passivated Si nanocrystals exhibit bright photoluminescence (PL) and disperse in polar solvents, including water. We propose a reaction mechanism in which ester or carboxylic acid groups facilitate direct nucleophilic attack of the highly curved Si surface of the nanocrystals by the alkene.

Keywords

Room temperature hydrosilylation; Silicon nanocrystal; Bifunctional alkene; Monolayers; Surface passivation

1. INTRODUCTION

Silicon (Si) nanocrystals exhibit bright photoluminescence (PL) with size-tunable color over much of the visible to near-infrared spectrum.^{1–4} Since Si is susceptible to oxidation, surface passivation is needed to prevent corrosion and stabilize the PL, which can be provided by Si-C bonded organic capping ligands. One approach to obtain these is by synthesis of H-terminated Si nanocrystals followed by hydrosilylation.^{1–7} Bifunctional alkenes can also be grafted by hydrosilylation to expose distal functional groups needed for aqueous dispersibility and for tethering biological molecules for medical applications,⁶ such as propionic acid,⁸ acrylic acid,⁹ and allylamine.¹⁰ Here, we report that H-terminated Si nanocrystals undergo *room temperature* hydrosilylation in the presence of ω -ester-terminated and ω -acid-terminated alkenes without photoexcitation or added catalyst and that these nanocrystals can be dispersed in polar and aqueous solvents and retain their photoluminescence.

Hydrosilylation reactions on silicon (Si) surfaces have been widely studied since 1993 when Linford and Chidsey showed that alkenes can insert into surface Si-H and yield Si-C bonded alkyl groups.¹¹ This reaction involves silyl radicals that can be created using a radical initiator, catalyst, heat, or light.^{12,13} Hydrosilylation on Si surfaces can also be promoted with Grignard¹⁴ or alkyllithium reagents,¹⁵ or catalyzed with Lewis acid¹⁶ or Pt

*Corresponding Author: (T) +1-512-471-5633; (F) +1-512-471-7060; korgel@che.utexas.edu.

Supporting Information.

TGA data, results for exposure of HF-terminated Si nanocrystals to undecanoic acid and a mixture of undecanoic acid and octane, dispersion stability in water and NaCl solution. This material is free of charge via the Internet at <http://pubs.acs.org>.

complexes,¹⁷ and direct nucleophilic attack of Si-H may also be possible.¹⁸ Hydrosilylation with ω -ester-terminated alkenes has also been accomplished on Si (100) surfaces heated to 200°C¹⁹ and on porous silicon heated to 85°C²⁰ or exposed to UV light.^{21,22} Alkene esters²³ and 10-undecenoic acid²⁴ have also been attached to Si nanocrystals by heating to 135–140°C or stirring under intense white light (250 W). However, room temperature hydrosilylation of a Si surface without catalyst or photoinitiation has not been reported.

Room temperature hydrosilylation was carried out by exposing hydrogen-terminated Si nanocrystals to either ω -ester-terminated (alkene-COOR) or ω -acid-terminated alkenes (alkene-COOH). The nanocrystals, ranging between 2 and 8 nm in diameter, were obtained using methods initially developed by Hessel and Veinot⁵ in which a wet HF etch is used to liberate Si nanocrystals from an oxide matrix material produced by hydrogen silsesquioxane (HSQ) decomposition. Both ester and carboxylic acid groups were found to facilitate direct nucleophilic attack by the alkene to yield Si-C bonded capping ligands. Neither the ester nor the acid form stable bonds to the surface but are needed to promote the hydrosilylation reaction.

2. EXPERIMENTAL DETAILS

Materials

FOx®-16, 10-undecenoic acid (98%), methyl 10-undecenoate (96%), ethyl 10-undecenoate (97%), undecanoic acid (97%), and 1-octene (98%) were purchased from Sigma-Aldrich. Ethanol, toluene, hexanes, chloroform, and hydrochloric acid (HCl, 37.5%) were from Fisher Scientific. Hydrofluoric acid (HF, 48%) was obtained from EMD chemicals. Deionized (DI) water was obtained using a Barnstead Nanopure Filtration System (17 M Ω resistance).

Preparation of hydride-terminated Si nanocrystals

Hydrogen-passivated nanocrystals were synthesized as described previously.¹ Hydrogen silsesquioxane (HSQ) was heated to 1100–1300°C for 1 hour under forming gas flow. Higher temperature produces larger nanocrystals. The product was ground with agate mortar and pestle for 10 min and shaken in a wrist-action shaker for 10 hours with 3 mm borosilicate glass beads. 300 mg of the ground powder were etched in 1 ml 25% HCl and 10 ml 40% HF in dark for 4–6 hours. Nanocrystals were isolated by centrifugation at 8000 rpm for 5 minutes and rinsed once with DI water, twice with ethanol, and once with chloroform.

Passivation of Si nanocrystals with ω -ester-terminated or ω -acid-terminated alkenes

The Si nanocrystals isolated from the HF etching procedure were dispersed in 6 mL of methyl 10-undecenoate, ethyl 10-undecenoate, or 10-undecenoic acid. Methyl 10-undecenoate and ethyl 10-undecenoate dispersions were deoxygenated by four freeze-pump-thawed cycles and then stirred under nitrogen flow for 20 hours at room temperature (~20°C); 10-undecenoic acid dispersions were stirred at 30°C since the melting point of 10-undecenoic acid is approximately 26°C. Poorly capped nanocrystals were separated by precipitation by centrifugation at 8000 rpm for 5 minutes and discarded. Ligand-stabilized nanocrystals that remained dispersed in the supernatant were then precipitated with hexanes and isolated by centrifugation.

Nanocrystals capped with methyl 10-undecenoate or ethyl 10-undecenoate were purified by dispersing in 1:1 v/v ethanol:toluene and washing three times by solvent/antisolvent precipitation with 1:1 v/v ethanol:toluene and hexanes. Nanocrystals capped with 10-undecenoic acid were purified by dispersing in ethanol and purified by precipitation with

hexanes. Ester-terminated Si nanocrystals were redispersed in 1:1 v/v ethanol:toluene and acid-terminated nanocrystals were redispersed in ethanol.

Acid-terminated nanocrystals were transferred to water by repeated dilution of ethanol dispersions using 50 kDa molecular weight cut off centrifugal filters and pH 7 DI water.

Si nanocrystal passivation with mixed alkene and acid/ester at room temperature

Passivation experiments were also carried out using mixtures of alkene and acid or ester as controls. Hydride-terminated Si nanocrystals (6 mg) were dispersed in 12 ml of 1-octene and 1 ml of undecanoic acid. The dispersions were deoxygenated by three freeze-pump-thaw cycles and stirred under nitrogen flow for 12, 24, or 120 hours at room temperature. Poorly capped nanocrystals were precipitated by centrifugation at 8000 rpm for 5 minutes and discarded. The remaining nanocrystals in the supernatant were then precipitated with ethanol and isolated by centrifugation. The ligand-stabilized nanocrystals were purified by dispersing in toluene and washing three times by precipitation with ethanol.

Hydrosilylation yield determination

The yield of nanocrystals obtained after hydrosilylation was determined by measuring the weight fraction of starting H-terminated Si nanocrystals retained after purifying the hydrosilylated nanocrystals. Typically, 520 mg of oxide-embedded Si nanocrystals were HF-etched and divided into four samples of equal weight. Three of the samples were passivated at 30°C with 10-undecenoic acid, methyl 10-undecenoate, and ethyl 10-undecenoate and then purified and dried. The remaining sample was used to determine the mass of starting material. The weight fraction of capping ligand in the hydrosilylated samples was determined by thermal gravimetric analysis (TGA, Mettler Toledo TGA-1). TGA measurements were made using 1 mg of nanocrystals dried into a 70 μ L alumina crucible (Mettler Toledo), heated from 40°C to 800°C at 20°C/minute under 50 mL/min air flow.

HF etch of 10-undecenoic acid-capped Si nanocrystals

2.5 mg of Si nanocrystals capped with 10-undecenoic acid were dispersed in 5 mL of 48% HF and 5 mL of ethanol, and stirred in the dark for 30 minutes. HF was removed by centrifugation at 3000 rpm with a 50 kDa molecular weight cut off centrifugal filter to collect the nanocrystals. During the centrifugation step, the volume of the retentate is reduced from 10 mL to 1 mL. DI-H₂O is then added to the retentate to a volume of 10 mL, followed by another centrifugation. This dilution/centrifugation process was repeated five times. The nanocrystals were then redispersed in ethanol, transferred to a glass centrifuge tube, and purified by precipitation with hexanes.

Materials Characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained on a Thermo Mattson Infinity Gold FTIR spectrometer equipped with a Spectra-Tech Thermal ARK attenuated total reflectance module. A background measurement was taken after purging with N₂ for 30 minutes before loading the sample into the ARK attenuated total reflectance module. Nanocrystals dispersed in a solvent (i.e. ethanol, toluene) with concentration of 1 mg/ml were drop cast onto the crystal plate of the ARK module and dried with N₂. Measurements were made by acquiring 128 scans at a resolution of 4 cm⁻¹. The average transmittance is reported with background subtraction.

Transmission electron microscopy (TEM) images were acquired digitally using either a FEI Tecnai Biotwin TEM operated at 80 kV accelerating voltage or with a JEOL 2010F TEM operated at 200kV. Nanocrystals were drop cast onto plasma-treated (5 min) 200 mesh carbon-coated copper grids for imaging (Electron Microscopy Science). The TEM samples

were then heated at 200°C under forming gas for 3 hr. For highest TEM resolution, nanocrystals were drop cast onto graphene TEM substrates prepared on lacey carbon-coated copper grids (Electron Microscopy Sciences) by dropping 3 μ L of ethanol dispersion of graphene (0.1 mg/mL).

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra in the UV-visible wavelength range were acquired on a Varian Cary Eclipse fluorescence spectrophotometer and in the UV-visible-NIR wavelength range on a Fluorolog-3 spectrophotometer (Horiba Jobin Yvon) with InGaAs photomultiplier tube for visible detection and a Hamamatsu H10330-45 detector for NIR detection. UV-visible absorbance spectroscopy was performed on a Varian Cary 50 Bio ultraviolet-visible (UV-vis) spectrophotometer. PL quantum yields were estimated relative to Rhodamine 101 in anhydrous ethanol.

X-ray diffraction (XRD) was performed using a Rigaku R-Axis Spider Diffractometer with an image plate detector and a graphite monochromator using Cu K α radiation ($\lambda=0.15418$ nm). The instrument was controlled by Rapid/XRD diffractometer control software (version 2.3.8, Rigaku Americas Corp.) Nanocrystals were placed onto a nylon loop and mineral oil was applied to secure the sample if necessary. Two-dimensional diffraction data were collected for 10 min while rotating the sample stage at 5° per minute. 2D diffraction data were radially integrated with 2DP Spider software (version 1.0, Rigaku Americas Corp.)

Small angle X-ray scattering (SAXS) data were obtained for solvent-dispersed Si nanocrystals. Measurements were performed on a Molecular Metrology system using a rotating copper anode X-ray source (Bruker Nonius FR591, $\lambda=0.154$ nm) operating at 3.0 kW, and a 2D multiwire gas-filled detector (Molecular Metrology, Inc.). Si nanocrystals passivated with methyl 10-undecenoate and 10-undecenoic acid were dispersed in 1:1 v/v ethanol:toluene and pure ethanol, respectively. Measurements were conducted using 200 μ L of nanocrystal solution (5 mg Si nanocrystals/mL). Datasqueeze (JDK 1.6.0_21) was used to convert 2D intensity profile to 1D plot. SAXS data are reported with the solvent background subtracted.

X-ray photoelectron spectroscopy (XPS) was performed using a commercial X-ray photoelectron spectrometer (Kratos Axis Ultra), utilizing a monochromatic Al K α X-ray source ($h\nu=1486.5$ eV), hybrid optics (employing a magnetic and electrostatic lens simultaneously) and a multi-channel plate detector coupled to a hemispherical analyzer. Si nanocrystal films were drop-cast onto indium tin oxide coated glass slides and were secured on the experimental tray using double-sided Cu tape. The photoelectron take-off angle was normal to the surface of the sample and 45° with respect to the X-ray beam. All spectra were recorded using a single sweep and an aperture slot of 300 μ m by 700 μ m. High-resolution spectra were collected with 20 eV pass energy. Spectra were collected at 0.1 eV intervals and 1500 ms integration time through a tungsten coil set at 4.8 V bias with respect to the sample. The pressure in the analysis chamber was typically 3×10^{-9} Torr during data acquisition. Sample charging was corrected by shifting the Si⁰ 2p^{3/2} to a binding energy of 99.3 eV. Background subtraction was done using a Shirley background model.²⁶ The Si⁰ 2p^{3/2} and Si⁰ 2p^{1/2} peaks were fit with Voigt profiles (30% Gaussian character) centered at 99.3 and 99.8 eV, respectively, maintaining the appropriate intensity ratio of 2:1 corresponding to the spin-orbit splitting ratio for p-orbitals. Peak contributions from Si¹⁺, Si²⁺, Si³⁺, Si⁴⁺, and Si-C were fit using Voigt profiles centered at 100.4 eV, 101.5 eV, 102.6 eV, and 103.7 eV, and 102.0 eV, respectively.

3. RESULTS AND DISCUSSION

Si Nanocrystal Passivation with Ethyl 10-Undecenoate

Room temperature addition of relatively size-monodisperse, freshly HF-etched Si nanocrystals to the ω -ester-terminated alkene, ethyl 10-undecenoate, under air-free conditions yields a yellow (2–5 nm diameter) or yellowish-brown (8 nm diameter) optically clear dispersion after about 20 hours. The nanocrystals can then be precipitated with non-polar organic solvent and redispersed in a mixture of ethanol and toluene. TEM (Figure 1) showed that these nanocrystals are not aggregated and have similar size as the starting material. XRD (Figure 1) verified that the passivated nanocrystals remain crystalline, with diamond cubic Si peaks of width consistent with the sizes measured by TEM. Higher yields of smaller nanocrystals are obtained after purification, indicating that there is a size-dependence for the passivation reaction. The ethyl 10-undecenoate passivated nanocrystals were also found to be luminescent as shown in Figure 1 with size-dependent PL consistent with previous studies of alkene-passivated Si nanocrystals.¹

Hydrosilylation with Methyl 10-Undecenoate and 10-Undecenoic Acid

Room temperature addition of H-terminated Si nanocrystals to the ω -methyl ester- and ω -acid-terminated alkenes, methyl 10-undecenoate and 10-undecenoic acid, also gave optically clear dispersions. Figure 2 shows photographs of the Si nanocrystal dispersions before and after passivation, along with absorbance, PLE and PL spectra. Like the nanocrystals passivated with ethyl 10-undecenoate, the nanocrystals do not disperse in non-polar solvents. The acid- and ester-terminated nanocrystals exhibited orange PL with quantum yields of about 7%, similar to hydrophobic hydrosilylated Si nanocrystals in this size range.^{1,6,8,22} The nanocrystals passivated with undecenoic acid could also be transferred to water by repeated dilution of ethanol dispersions using 50 kDa molecular weight cut off centrifugal filters and pH 7 DI water. These nanocrystals could be dispersed in pure water or in NaCl solutions (See Supporting Information).

Figure 3 shows TEM images and SAXS data for Si nanocrystals capped with methyl 10-undecenoate and 10-undecenoic acid. The average nanocrystal diameter was determined from SAXS (Figures 3B and 3D) by assuming a dilute dispersion of non-interacting spherical particles:^{6, 27}

$$I(q) \propto \int_0^\infty N(R)P(qR)R^6 dR. \quad (1)$$

q is the scattering vector, $q(4\pi/\lambda)\sin(\theta/2)$, with scattering angle θ ; $P(qR)$ is the form factor for a solid homogeneous sphere of radius R ,

$$P(qR) = \left[3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right]^2; \quad (2)$$

and the average radius $\bar{R}$, and standard deviation δ , of the dispersion are obtained by assuming a Gaussian size distribution,

$$N(R) = \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{(R - \bar{R})^2}{2\delta^2} \right] \quad (3)$$

Fits of Eqns (1–3) to the SAXS data in Figures 3B and 3D gave average diameters of 2.3 ± 0.6 nm and 2.3 ± 0.9 nm for the Si nanocrystals passivated with methyl 10-undecenoate and 10-undecenoic acid, respectively. The nanocrystals used for these passivation experiments were obtained from the same batch of HF-etched nanocrystals. These data indicate that there is little change in size during the passivation reactions. The nanocrystals also remain crystalline diamond cubic Si—Figure 3E shows some high resolution TEM images of crystalline Si nanocrystals passivated with 10-undecenoic acid.

FTIR Analysis

FTIR spectra confirmed that passivation by the ω -ester-terminated (alkene-COOR) and ω -acid-terminated alkenes (alkene-COOH) occurs by hydrosilylation to create Si-C bonding and leave the polar functional groups (i.e., ester or acid) exposed on the nanocrystal periphery, which is consistent with their dispersibility in polar solvents. Figure 4 shows ATR-FTIR spectra of Si nanocrystals after passivation with methyl 10-undecanoate, ethyl 10-undecenoate and 10-undecenoic acid. The characteristic signatures of the vinyl group (i.e., sp^2 C-H_x stretching at 3076 cm^{-1} , strong deformation vibrations of sp^2 C-H at 990 cm^{-1} and 907 cm^{-1} , and C=C stretching at 1640 cm^{-1}) subside after hydrosilylation, while the peaks associated with C-H_x stretching, -CH₂- scissor vibration, C-O stretching, and C=O stretching remain. The polar functional groups remain intact and exposed to the solvent, as expected based on the observed dispersibility in polar solvents. Similar FTIR spectra have been reported for other Si substrates after thermal and photoinduced hydrosilylation of ω -ester-terminated and ω -acid-terminated olefins.^{19–22}

Further Verification of Si-C Bonding of Ligands

Reaction between hydride-terminated Si nanocrystals and undecanoic acid (no terminal alkene) did not yield passivated nanocrystals. FTIR spectra of the brown precipitate obtained from the reaction (Figure 5C) showed Si-H stretching at 2100 cm^{-1} and deformation at 910 cm^{-1} , and Si-O stretching between 1000 cm^{-1} and 1100 cm^{-1} , characteristic of ligand-free hydride-terminated Si nanocrystals.^{6,28} Neither ester or carboxylic acid functional groups formed stable bonds with the Si-H terminated surfaces.

An additional experiment was performed to further verify that ligands were Si-C and not Si-O-C bonded to the nanocrystal surface. An HF etch was performed on Si nanocrystals passivated with 10-undecenoic acid. HF would cleave and remove any Si-O bonded ligands and remove the capping ligands, but would not affect any Si-C bonded ligands. FTIR spectra of the nanocrystals isolated after 30 minutes of exposure to HF were similar (Figure 6B) to the material prior to the etch. The only noticeable difference was a stronger Si-H stretch (2100 cm^{-1}) and weaker Si-O stretch (1000 cm^{-1} – 1100 cm^{-1}), indicating that the ligands were still bound to the nanocrystals, but that the residual oxidized surface was partly transformed to hydride-terminated surface, due to HF. This is not unexpected, as all passivated nanocrystals had some oxidation and incomplete elimination of hydride species evident in the FTIR spectra (Figure 4 for example), that is probably due to steric hindrance between neighboring capping ligands that prevents Si-C termination of all surface Si atoms.

Etching the Si nanocrystals passivated with 10-undecenoic acid for even longer—for 6 hours—led to nanocrystals that no longer dispersed in ethanol. However, the ligands are still observed in the FTIR spectra (Figure 6C), with strong C-H stretch (2800 cm^{-1} – 3000 cm^{-1}) and C=O stretch (1710 cm^{-1}). Furthermore, there is no Si-O stretch (1000 cm^{-1} – 1100 cm^{-1}). The C=O stretch of “neat” 10-undecenoic acid (Figure 6E) occurs as a single peak between 1690 cm^{-1} and 1720 cm^{-1} , while the C=O stretch of 10-undecenoic acid bound to the Si nanocrystals appeared as a doublet (Figure 6D). The C=C stretch at 1640 cm^{-1} of “neat” 10-undecenoic acid is also not present in the nanocrystal spectra, further indicating that the C-H

and C=O signals in the FTIR spectra correspond to bound ligand. The change in dispersibility therefore appears to result from increased surface hydrogenation or hydrogenation of the acid group, but FTIR shows that the ligands are clearly still attached to the nanocrystals after the long HF etch, confirming Si-C bonding to the surface.

XPS Analysis

XPS also confirmed Si-C bonding of the ligands to the nanocrystals. Figure 7 shows XPS data of Si nanocrystals passivated with ethyl 10-undecenoate, methyl 10-undecenoate, and 10-undecenoic acid. Si⁰ peak contributions (Si⁰ 2p^{3/2} at 99.8 eV and Si⁰ 2p^{1/2} at 99.3 eV) are clearly present. Si-C ligand bonding results in a peak at 101.9 eV,⁶ which is prominent for example in spectra for Si nanocrystals hydrosilylated with dodecene (Figure 7D) and absent from spectra of hydride-terminated Si nanocrystals (Figure 7F). The Si-C feature is present in the spectra for Si nanocrystals passivated with ethyl 10-undecenoate, methyl 10-undecenoate, and 10-undecenoic acid. XPS also showed evidence of some surface oxidation, as peak contributions from Si⁴⁺ (103.7 eV), Si³⁺ (102.6 eV), and Si¹⁺ (100.5 eV) species are also present. It should be noted however that the extent of oxidation is relatively minor. For instance, there is very little Si⁴⁺ species present, which is dominant in HF-etched Si nanocrystals exposed to air without surface passivation and especially the oxide-embedded nanocrystals.

Reaction Mechanism

The passivation reaction was found to depend on nanocrystal size and the functional group. Figure 8 lists the yield of nanocrystals with three different sizes obtained after passivation with ethyl 10-undecenoate, methyl 10-undecenoate and 10-undecenoic acid. Ethyl 10-undecenoate provided the most effective room temperature passivation, and the smallest nanocrystals were found to be most reactive.

To gain a better understanding of the reaction mechanism and the role of the ester and acid functional groups in the hydrosilylation reaction, various control experiments were carried out. Room temperature passivation did not occur with alkene (dodecene), ester (methyl 10-undecanoate) or acid (10-undecanoic acid). Alkene-ketones also did not lead to passivation.

The ester (or carboxyl) segment of the bifunctional ligands catalyzes hydrosilylation, most likely by a mechanism in which the nucleophilic carbonyl group of the ester (acid) coordinates to the oxophilic Si surface and enhances the reactivity of the Si-H to the alkene end of another independent reactant molecule. Upon coordination, the Si-H bond lengthens, increases in hydridic character, and becomes more nucleophilic toward alkenes. When in close proximity, the electron deficient C=C accepts H⁻ from surface to facilitate Si-C bond formation, as illustrated in Figure 9A. Unlike radical-initiated hydrosilylation that propagates across the Si surface,^{11,12} this single-step reaction must occur repeatedly for complete surface passivation, similar to Lewis acid catalyzed hydrosilylation reactions.

The mechanism of ligand attachment has similarities to Lewis acid (LA) catalyzed hydrosilylation Si-H surfaces with unsaturated carbon-carbon bonds.¹⁶ Lewis acids such as Et₂AlCl catalyze hydrosilylation reactions by forming electropositive adducts with alkenes or alkynes that readily insert into Si-H bonds via attack at the electropositive carbon by H⁻.^{16,29} In other words, the Lewis acid makes the alkene a stronger electrophile. In the case of the ester and carboxylic acid functional groups, the carbonyl activates the Si-H bond. Coordination of the electron rich carbonyl group to the Si surface enhances the nucleophilicity of the Si-H bond enough to facilitate H⁻ attack at the unsaturated carbon-carbon bond. Our observations show the extent of the catalytic effect increases with increasing electron density at the carbonyl oxygen (C=O). The hydrosilylation efficiency—

evaluated by determining the weight fraction of passivated Si nanocrystals recovered after purification—was observed to follow the trend of alkene-ethyl ester > alkene-methyl ester > alkene-carboxylic acid (See Supporting Information). Light was also found to play no role, as reactions performed under room light and in the dark yielded similar results. These findings are consistent with the mechanism in Figure 1A. Illustrated in Figure 9B, esters have stronger resonance forms than carboxylic acids due to the electron donating character of alkyl groups and correspondingly have greater electron density on the carbonyl oxygen.³⁰ Also consistent with the proposed mechanism, attempts to add alkene-ketones to the surface led to no hydrosilylation and surface passivation. Without oxygen adjacent to the carbonyl to contribute to a resonance form, the ketone cannot activate Si-H bonds as needed for hydrosilylation.

Liu *et al.*^{31,32} or Zaborovskiy *et al.*³³ recently proposed a mechanism for attachment of bifunctional alkyne-esters to tris(trimethylsilyl)silane involving a radical chain mechanism initiated by reaction of adventitious oxygen with Si-H bonds to form silyl and hydroperoxyl radicals. In the case of the Si nanocrystals, if adventitious oxygen created silyl radicals then hydrosilylation would be expected with 1-octene at room temperature, which is not observed. On the other hand, through the exactly same procedure, reaction in a mixture of undecanoic acid (no terminal alkene) and 1-octene, however, did lead to a yellow transparent solution of passivated Si nanocrystals with orange PL, demonstrating the catalytic hydrosilylation of terminal alkenes by carbonyl functional groups. FTIR (Figure 5D) revealed strong C-H stretching at 2800 cm⁻¹–3000 cm⁻¹, but negligible C=O stretching (1710 cm⁻¹), indicating the Si nanocrystal was passivated with 1-octene at room temperature, with the presence of undecanoic acid.

4. CONCLUSIONS

Bifunctional alkenes with distal polar moieties—either ethyl-, methyl-ester or carboxylic acids—undergo room temperature hydrosilylation with 2–8 nm diameter H-terminated Si nanocrystals without photoexcitation or added catalyst. The polar ester or carboxylic acid functional group promotes addition across the terminal alkene to yield hydrophilic Si nanocrystals. The Si nanocrystals still exhibit bright PL when dispersed in polar solvents, including water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

TEM images of Si nanocrystals with (A) 2.5 nm, (B) 5.5 nm, and (C) 8.0 nm diameter after room temperature passivation with ethyl 10-undecenoate. Insets: Photographs of nanocrystals dispersed in 1:1 v/v ethanol:toluene. (D) High resolution TEM image of a 10-undecenoic acid-capped Si nanocrystal. The 0.202 nm lattice spacing corresponds to the (220) d-spacing of diamond cubic Si. (E) XRD of the ethyl 10-undecenoate-capped Si nanocrystals imaged in (a–c). A diffraction pattern of 2.5 nm diameter Si nanocrystals embedded in oxide and a reference pattern for diamond cubic Si ((PDF # 027–1402, $a=b=c=5.431$ Å) are also provided. The diameters were determined by TEM. (F) PL ($\lambda_{\text{exc}}=400$ nm) from ethyl 10-undecenoate-capped Si nanocrystals dispersed in 1:1 v/v

ethanol:toluene. The PL intensities are normalized—the larger nanocrystals have lower PL quantum yield.

Figure 2.

Absorbance (green dotted curve), PLE ($\lambda_{em}=650$ nm; blue dashed curve) and PL ($\lambda_{exc}=325$ nm; red solid curve) spectra of 2.3 nm diameter Si nanocrystals passivated at room temperature with (A) methyl 10-undecenoate (“Si-ester”) dispersed in 1:1 v/v ethanol:toluene and (B) 10-undecenoic acid (“Si-acid”) dispersed in ethanol. (Bottom) Photographs of nanocrystal dispersions before (turbid) and after (optically clear) ligand passivation under room and UV (365 nm) light to show the nanocrystal fluorescence.

Figure 3.

TEM images and SAXS measurements of Si nanocrystals passivated at room temperature with (A,B) methyl 10-undecenoate and (C,D) 10-undecenoic acid. In (B) and (D), the green circles are experimental data and the blue line is a fit of Eqns (1–3), which give average diameters of 2.3 ± 0.6 nm and 2.3 ± 0.9 nm, respectively. (E) High resolution TEM images of the Si nanocrystals passivated with 10-undecenoic acid; 0.202 nm lattice spacing is consistent with (220) d-spacing of diamond cubic Si.

Figure 4.

ATR-FTIR spectra of (A) methyl 10-undecenoate-capped, (B) ethyl 10-undecenoate-capped, and (C) 10-undecenoic acid-capped Si nanocrystals compared to pure “neat” methyl 10-undecenoate, ethyl 10-undecenoate, and 10-undecenoic acid.

Figure 5.

ATR-FTIR spectra of pure (A) undecanoic acid and (B) 1-octene compared to the (C) precipitate obtained after adding H-terminated Si nanocrystals to undecanoic acid, and the (D) Si nanocrystals that remained dispersed after passivation in a mixture of 1-octene and undecanoic acid.

Figure 6.

ATR-FTIR spectra of (A) 10-undecenoic acid-capped Si nanocrystal before HF etch, (B) 10-undecenoic acid-capped Si nanocrystal being etched in HF for 30 minutes, and (C) 10-undecenoic acid-capped Si nanocrystal being etched in HF for 6 hours, (D) zoomed-in spectra between 1800 cm^{-1} and 1600 cm^{-1} of 10-undecenoic acid-capped Si nanocrystal being etched in HF for 6 hours, (E) zoomed-in spectra between 1800 cm^{-1} and 1600 cm^{-1} of “neat” 10-undecenoic acid.

Figure 7.

XPS of Si nanocrystals passivated with (A) ethyl 10-undecenoate, (B) methyl 10-undecenoate, (C) 10-undecenoic acid. XPS data are also shown for (D) Si nanocrystals capped with 1-dodecene by a typical high temperature hydrosilylation procedure (See Ref. 1 for example); (E) dodecene-capped Si nanocrystals after 3 weeks of exposure to air; (F) HF-etched Si nanocrystals exposed to air for 5 days; and (G) oxide-embedded Si nanocrystals obtained from HSQ thermal decomposition. Data (o) are fit (black line) to separate peak contributions from Si^0 $2p_{3/2}$, Si^0 $2p_{1/2}$, Si^{1+} , Si^{2+} , Si^{3+} , Si^{4+} , and Si-C signals (color lines).

Hydrosilylation Yield

2.5 nm	20 %	66 %	100 %
5.5 nm	< 5 %	23 %	51 %
8.0 nm	none	< 5 %	23 %

Figure 8.

Yield of nanocrystals obtained after hydrosilylation with 10-undecenoic acid, methyl 10-undecenoate, and ethyl 10-undecenoate. Nanocrystals with three different average diameters were tested. (See Supporting Information for TGA data)

Figure 9.

(A) Mechanistic illustration of methyl 10-undecenoate attachment to the Si nanocrystal surface. The catalyst molecule is shown in its resonance form to emphasize the regions of electrostatic interaction. (B) Relative resonance strengths of 10-undecenoic acid, methyl 10-undecenoate, and ethyl 10-undecenoate.