Communications to the Editor

A New Route to Covalently Attached Monolayers: Reaction of Hydridosilanes with Titanium and Other Metal Surfaces

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We report the reaction of hydridosilanes with titanium surfaces (eq 1; a monohydridosilane is shown as an example). The products are monolayers that are covalently attached to the surface by Ti−

$$TiO_2-OH + R_3Si-H \rightarrow TiO_2-OSiR_3 + H_2 \qquad (1)$$
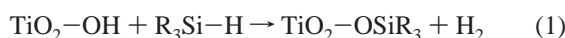
O−Si bonds with surface densities as high as those of self-assembled monolayers (SAMs).[2] Thiols can be used on gold substrates and functional silanes with readily hydrolyzable groups (most often chloro or alkoxy) can be used on different forms of SiO_2, but if there is a need to modify other materials, however, there are simply not available techniques.

The chemistry that we describe is more general in several respects than the results reported here. First, the reaction also works well with a range of other metal oxide surfaces. Second, we have studied a variety of titania surfaces and all react unexceptionally. We discuss here primarily only data obtained using Si-supported titanium (∼100 Å of Ti evaporated and deposited on polished Si wafers) and fumed titania (BET nitrogen surface area is 50 m²/g).

Table 1 shows carbon analysis data for several samples of fumed titania (50 m²/g) that were allowed to react with various hydridosilanes in heptane solution (∼5 wt % hydridosilane) at 65−70 °C (unless indicated otherwise) for various extents of time. Several aspects of these data warrant comment. (1) These reactions are thermally activated and require long reaction times to achieve maximum bonding density. The reaction of *n*-octylsilane proceeds to ∼60% conversion at room temperature after 30 min, but requires hours at elevated temperature to achieve maximum bonding density. (2) The maximum bonding density for *n*-alkylsilane-derived monolayers is ∼5 chains/nm² (∼20 Å²/chain); this is similar to the density of SAMs of alkane thiols on gold[3], SAMs of alkyltrichlorosilanes on silica,[4] and Langmuir−Blodgett monolayers of fatty molecules.[5] (3) Dialkyl- and trialkylsilanes show dramatically decreased coverage relative to the monoalkyl-silanes due to sterics. The *n*-octadecyldimethylsilane monolayer has ∼1/3 the bonding density of the *n*-octadecylsilane monolayer. This trend is also observed in the series of phenylsilane, diphenylsilane, and triphenylsilane monolayers.

Figure 1 shows transmission infrared spectra of *n*-octylsilane and a sample of titania that was reacted with octylsilane. The obvious peaks at 2150 (ν_{Si-H}) and 925 cm⁻¹ (δ_{Si-H}) present in the starting material are absent in the product, indicating the quantitative conversion of Si−H bonds to Si−O bonds. The broad

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(4) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.
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Table 1. Bonding Density Data for Hydridosilane-Modified Titania[a]

hydridosilane	reaction time (h)	bonding density (groups/nm²)[b]	Si−H bonds reacted per silane[c]
n-C₈H₁₇SiH₃	0.5[d]	3.01 ± 0.05	3.2
n-C₈H₁₇SiH₃	48	5.21 ± 0.05	2.8
n-C₁₈H₃₇SiH₃	1[d]	1.96 ± 0.05	3.0
n-C₁₈H₃₇SiH₃	48	5.15 ± 0.05	2.7
n-C₁₈H₃₇SiH₃	120	5.05 ± 0.05	2.7
n-C₁₈H₃₇SiH₃	48[e]	3.21 ± 0.05	2.1
n-C₁₈H₃₇SiMe₂H	120	1.52 ± 0.05	0.8
(*iso*-C₃H₇)₃SiH	24	1.15 ± 0.2	1.0
C₆H₅SiH₃	24	3.61 ± 0.05	
(C₆H₅)₂SiH₂	24	1.85 ± 0.05	
(C₆H₅)₃SiH	24	0.85±0.05	

[a] Reaction in heptane solution at 65−70 °C using fumed titania. [b] Calculated from the carbon concentration and the titania surface area. [c] Calculated from the hydrogen volume and the carbon concentration. [d] Reaction at room temperature. [e] The titania in this sample had been heated at 120 °C at reduced pressure prior to reaction.
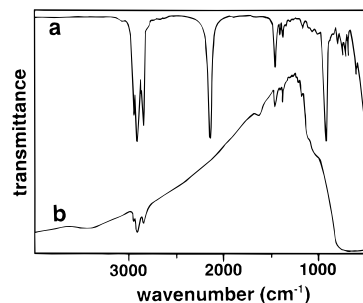

Figure 1. Transmission infrared spectra of (a) *n*-octylsilane and (b) a pressed pellet of fumed titania that had been reacted with *n*-octylsilane in heptane at 65−70 °C for 48 h.

absorbance from 1100 to 1000 cm⁻¹ indicates the formation of Si−O−Ti bonds (and perhaps Si−O−Si bonds). The hydrocarbon stretching (2950−2850 cm⁻¹) and bending (1475−1375 cm⁻¹) vibrations indicate the presence of octyl groups on the titania surface. These changes are consistent with covalent attachment of *n*-octylsilane moieties to the TiO₂ surface. Spectra of other hydridosilane-treated titania surfaces are similar: no residual Si−H bonds, Ti−O−Si bonds, and characteristic alkyl and aryl group absorbances. We note that *n*-octadecylsilane-modified surfaces show no Si−H bonds at any stage of reaction (even at low bonding density) and this argues for 3 bonds between silicon and surface titanols being the principal mode of bonding.

The volume of hydrogen gas produced as a byproduct was determined for several reactions. Table 1 shows the number of Si−H groups that react (determined from the volume of hydrogen liberated) per silane molecule that is incorporated in the mono-layers (determined from carbon analysis). The data for the *n*-octadecyl monolayers indicate that ∼3 molecules of hydrogen are released at early reaction times that produce incomplete monolayers and that this value decreases to ∼2.7 at later reaction times that produce more dense monolayers. Dehydration of the titania by heating in a vacuum causes a reproducible decrease in the bonding density of attached silanes.

XPS data of single surfaces also reflect monolayer formation, with bonding density and thickness values that depend on the sterics of the hydridosilane. After silanization, the titania surfaces
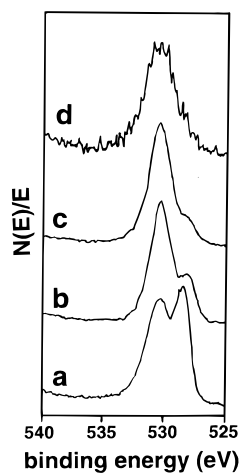
Figure 2. XPS spectra (O$_{1s}$ region) of (a) silicon-supported titanium and monolayers prepared on this substrate by reaction with (b) *n*-octadecyl-dimethylsilane, (c) *n*-octylsilane, and (d) *n*-octadecylsilane in heptane at 65−70 °C for 48 h.

all exhibit a Si$_{2p}$ peak (~102 eV) in the spectra and the Ti$_{2p}$ intensity (~460 eV) is attenuated due to the overlayer. The O$_{1s}$ spectra are sensitive to the monolayer thickness. Figure 2 shows O$_{1s}$ spectra for a bare titania surface (supported on silicon) and several titania-supported monolayers. The lower binding energy peak is due to oxygen bonded to two titaniums and the higher binding energy peak is due to surface oxygen species. The relative intensities of these peaks indicate the thickness of the overlayer that attenuates the Ti−O−Ti signal. The *n*-octadecylsilane-derived monolayer almost completely attenuates the substrate signal (hence the noise in Figure 2d) and thinner monolayers attenuate it to a lesser extent. Table 2 shows the thicknesses of monolayers that were determined using the attenuation of the Ti$_{2p}$ signal and eq 2,[6] where N_o and N are the intensity of the Ti$_{2p}$ peak for bare titania and monolayer samples, respectively, θ is the take-off angle

$$\text{thickness} = \ln(N_o/N)/\lambda\,\sin\theta \qquad (2)$$

and λ is the Ti$_{2p}$ photoelectron mean free path. A literature value[7] of $\lambda = 20$ Å was assumed for these calculations.

Table 2 also shows water and hexadecane contact angle data for a number of monolayers. The *n*-octylsilane- and *n*-octadec-ylsilane-derived monolayers exhibit water contact angles that are as high as the best self-assembled, most close-packed monolay-ers.[2,4] The hexadecane contact angles, however, are surprising low and indicate penetration of the probe fluid into the mono-layers, arguing that they are less ordered than SAMs prepared from alkylthiols and alkyltrichlorosilanes. We note that the hysteresis in the water contact angle data for *n*-octylsilane- and

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Table 2.   Contact Angle and Monolayer Thickness Data for Titanium-Supported Monolayers[a]

hydridosilane	water (deg) θ_A	water (deg) θ_B	hexadecane (deg) θ_A	hexadecane (deg) θ_B	monolayer thickness (Å)[b]
none (TiO$_2$)	spreads		spreads		
(*i*-C$_3$H$_7$)$_3$SiH	107	60	15	5	11.1
(*n*-C$_3$H$_7$)$_3$SiH	100	69	10	0	10.2
(*t*-C$_4$H$_9$)SiMe$_2$H	104	97	20	10	4.0
n-C$_8$H$_{17}$SiH$_3$[c]	113[c]	96[c]	10[c]	0[c]	16.3
n-C$_{18}$H$_{37}$SiH$_3$[c]	117[c]	100[c]	33[c]	20[c]	22.6
n-C$_{18}$H$_{37}$SiMe$_2$H[c]	95[c]	67[c]	10[c]	0[c]	12.3
C$_6$H$_5$SiH$_3$	98	70	spreads		8.9
(C$_6$H$_5$)$_2$SiH$_2$	71	40	spreads		9.7
(C$_6$H$_5$)$_3$SiH	64	31	spreads		4.9

[a] Reaction in heptane solution at 65−70 °C for 48 h using silicon-supported titanium, unless indicated otherwise. [b] Determined by XPS using the attenuation of the Ti$_{2p}$ photoelectron line. [c] These monolayers were prepared on single-crystal rutile.

Table 3.   Reaction of Octadecylsilane with Various Metal Foils[a]

sample	XPS atomic composition[b]	water contact angle (deg) θ_A	water contact angle (deg) θ_R
Ni−C18	C$_{14}$O$_5$SiNi$_{0.1}$	109	71
Cr−C18	C$_{16}$O$_4$SiCr$_{0.2}$	105	90
Fe−C18	C$_{14}$O$_4$SiFe$_{0.2}$	126	93
Mo−C18	C$_{15}$O$_3$SiMo$_{0.1}$	116	95
Nb−C18	C$_{18}$O$_6$SiNb$_{0.4}$	105	85
Zr−C18	C$_{20}$O$_7$SiZr$_{0.5}$	124	90
W−C18	C$_{15}$O$_5$SiW$_{0.3}$	100	82

[a] Reaction in heptane solution at 65−70 °C for 48 h. [b] Determined using 15° takeoff angle data.

n-octadecylsilane-derived monolayers is high (17°), but not far from that reported for supported monolayers[4,5] (10−15°). The data for the series of phenyl, diphenyl, and triphenyl monolayers reflect their relative bonding density (Table 1) and the exposure of residual titanols to the probe fluid.

Table 3 shows some of our early XPS and water contact angle data on a variety of metal foil surfaces containing native oxide coatings that were treated with *n*-octadecylsilane. These surfaces are rougher than the titanium surfaces we described above and the contact angle data reflect this in high hysteresis values. All of the surfaces, however, are extremely hydrophobic indicating close-packed monolayer formation. We note that the XPS atomic composition of the outermost surface layer is almost independent of the nature of the metal, also arguing for dense monolayer formation.

Supporting Information Available: Preparation of hydridosilane-modified fumed titania (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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