

Interfacial modification of silica surfaces through γ -isocyanatopropyl triethoxy silane–amine coupling reactions[☆]

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Abstract

The development of robust, cost-effective methods to modify surfaces and interfaces without the specialized synthesis of unique coupling agents could provide readily accessible routes to optimize and tailor interfacial properties. We demonstrate that γ -isocyanatopropyl triethoxysilane (ISO) provides a convenient route to functionalize silica surfaces through coupling reactions with readily available reagents. ISO coupling agents layers (CALs) can be prepared from toluene with triethylamine (TEA), but the coupling reaction of an amine to the ISO CAL does not proceed. We use near edge X-ray absorption fine structure (NEXAFS), time-of-flight secondary ion mass spectrometry (TOF-SIMS) and sessile drop contact angle to demonstrate the isocyanate layer is not degraded under coupling conditions. Access to silanes with chemical functionality is possible with ISO by performing the coupling reaction in solution and then depositing the product onto the surface. Two model CAL surfaces are prepared to demonstrate the ease and robust nature of this procedure. The surfaces prepared using this method are the ISO reacted with octadecylamine to produce a hydrocarbon surface of similar quality to octadecyl trichlorosilane (OTS) CALs and with 9-aminofluorene (AFL), an aromatic amine functionality whose silane is otherwise unavailable commercially.

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1. Introduction

Silane coupling agents have long provided a simple route to control the chemical and physical properties of surfaces and interfaces. Their use is ubiquitous in technologies from microelectronics to medical implants that rely on surface coatings created from silanes. Silane coupling agents have been developed to passivate and functionalize metal oxides for applications such as improving adhesion [1], controlling the fouling properties of surfaces [2,3], chemical sensors [4],

molecular and organic electronics, and reagents for performing reactions [5,6]. For some applications, commercially available silane coupling agents may not provide the chemical functionality of interest. For example, in the field of organic electronics or molecular electronics, specific surface groups to direct crystallization or maximize electronic transport require custom synthesis. The isocyanate species in ISO could form the foundation for a general strategy to prepare a diversity of chemical surfaces because it can undergo a wide variety of coupling reactions.

The reaction of an isocyanate with a nucleophile, such as an alcohol, thiol or amine is well documented [7,8]. The advantage of this chemistry is the commercial availability of many different types of nucleophiles and the high reactivity of the isocyanate with amines or alcohols. The isocyanate/amine system, in particular, provides rapid and quantitative reaction between the two species. Given the commercial availability of γ -isocyanatopropyl triethoxy silane (ISO) and many amines to

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choose from, this system is seemingly ideal for a general strategy to modify surfaces. However, few studies have considered isocyanate surfaces as a starting point to access diverse surface chemistries [9–12].

Several studies have used isocyanate coupling reactions to modify polymer interfaces [13], or for polymer layer by layer assembly [14,15]. It is recognized that isocyanate CALs are difficult to prepare, leading to their limited use [10]. Recently, an isocyanate based trichlorosilane was synthesized and coupled with hydrazines, amines and alcohols [10]. The researchers proposed that a decyl carbon spacer between the ISO and the silane was required to create densely packed, well-ordered monolayers that, in turn, would increase the effectiveness of the ISO-amine reaction. However, the synthesis of this trichlorosilane requires many steps to prepare and its starting materials are not commercially available.

Here we prepare CALs with different functional moieties using commercially available γ -isocyanatopropyl triethoxysilane and amines. Evidence of surface bound isocyanates and near monolayer surface coverage is provided by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, contact angle goniometry, ellipsometry, and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Aqueous solutions to couple amines to the ISO surface were avoided to prevent any degradation of the isocyanate and due to the limited solubility of the octadecyl amine in water. We show that the surface coupling reaction of octadecylamine (ODA) to the ISO surface in several organic solvents of different dielectric constant results in analytically undetectable quantities of ODA grafted to the surface, but the surface bound isocyanates remain undegraded. An alternative to surface coupling is demonstrated by the successful preparation of silane CALs with ODA and fluorene moieties grafted to silicon oxide surfaces.

2. Materials and methods¹

All solvents were purchased from Sigma Aldrich (Milwaukee, Wisconsin) unless otherwise noted. Single side polished silicon [1 0 0] wafers (Silicon Inc., Boise, Idaho) were washed with isopropanol and blown dry before cleaning with exposure to ultra violet (UV) ozone to remove any adsorbed organics.

2.1. Self-assembled monolayer preparation

2.1.1. γ -Isocyanatopropyl triethoxysilane

Clean silicon oxide wafers were subjected to a mixture of chloroform (or toluene) (25 mL), TEA (8.3 mg) and γ -isocyanatopropyl triethoxysilane (Gelest, Morrisville, PA) (3.2 mL) for 1.5 h. After deposition, the surface was rinsed with both toluene and chloroform, and then dried with a stream of nitrogen. Surface coupling reaction were performed by

placing the isocyanate bearing silicon wafer in a solution of amine (0.02 mol/L) dissolved in 25 ml dry chloroform for 24 h followed by chloroform and methanol washings (3×10 mL), then the surface was dried with nitrogen. Degradation reactions were performed by treating ISO surfaces with a hydrochloric acid solution (5 mol/L in water) for 2 h to hydrolyze the isocyanate for further characterization. The surfaces were washed with water and blown dry with nitrogen.

2.1.2. Reactions of γ -isocyanatopropyl triethoxysilane

A mixture of chloroform (17 mL), γ -isocyanatopropyl triethoxysilane (3.2 mL) and octadecylamine (or 9-aminofluorene) (0.0900 g) were left to stand unmixed for 24 h. A clean silicon oxide wafer piece (3×0.75) cm was placed in this solution with TEA (8.3 mg) and the solution was allowed to react for 1.5 h at room temperature. The resulting surface was washed with chloroform and methanol and then blown dry with nitrogen.

2.2. Contact angle goniometry

Sessile drop contact angle measurements were made with a First Ten Angstrom FTA125 contact angle analyzer. Ultrapure water (18.2Ω cm) and hexadecane solvents were used to calculate surface energies based on the Li and Neumann equation of state for interfacial tensions of hydrophobic surfaces [16].

2.3. Spectroscopic ellipsometry

Ellipsometric data at a single angle (30° from the surface normal plane) from surface modified single side polished Si wafers were obtained with an M-2000 series spectroscopic ellipsometer (J.A. Woollam Co., Inc., Lincoln, NE). The oxide thickness was determined from freshly UVO-cleaned reference films by using a three-phase model (air, SiO₂, Si) and the SiO₂ index of refraction reported by Brixner [17]. The organic film thickness was determined from a four-phase model (air, organic, SiO₂, Si), fixing the oxide thickness at the reference film value, and assuming an index of 1.5 for the organic layer.

2.4. Time of flight secondary ion mass spectrometry

Time-of-flight secondary ion mass spectrometer experiments were performed on an Ion-TOF IV (Münster, Germany) time-of-flight secondary ion mass spectrometer equipped with a 10 keV Cs⁺ primary ion beam source which bombarded the surface at an incident angle of 45° to the surface normal. For each sample, five positive and five negative mass spectra were acquired. The target current was maintained at ≈ 2 pA pulsed current with a pulse width of 1 ns and a 150 μ s cycle time (≈ 6666 Hz frequency). Each spectrum was averaged over 120 s count time with a raster size of $\approx 200 \mu\text{m} \times 200 \mu\text{m}$. These conditions resulted in Cs⁺ ion doses that were well below the static SIMS limit of 10^{13} ions/cm². Both positive and negative secondary ions were extracted from the sample into a reflection-type time of flight mass spectrometer. The secondary ions were then detected by a microchannel plate detector with

¹ Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.

post acceleration energy of 10 kV. A low energy electron flood gun was utilized for sample charge neutralization in the positive mode.

2.5. Near-edge X-ray absorption fine structure spectroscopy

NEXAFS measurements were conducted at the U7A beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. The experimental conditions have been described elsewhere [18]. The spectra were collected with the incident beam at the magic angle (54.7°) to the sample to remove any polarization dependence. For the NEXAFS spectra in this paper, the experimental standard uncertainty in the peak position is ± 0.15 eV. The relative uncertainty in the NEXAFS intensity is less than $\pm 2\%$ as determined by multiple scans on a sample.

In a NEXAFS experiment, soft X-rays are absorbed when the incident radiation is at the correct energy to excite a core shell electron to an unoccupied molecular orbital. Because of the well-defined energy gap associated with a core shell to unoccupied orbital transition, NEXAFS measurements are sensitive to the bonding characteristics of the atom with a discrete peak for each chemical bonding environment. A $K\alpha$ auger electron is emitted (for carbon and nitrogen) when the excited core electron from the irradiated sample decays. Only the electrons emitted near the surface (within 1–6 nm of the surface for carbon K-edge electron yield spectra) of the film surface have enough kinetic energy to escape the surface potential.

3. Results and discussion

To investigate the feasibility of using ISO CALs to functionalize silica surfaces, we present results in three sections: characterization of an ISO CAL surface, investigation of the surface coupling of an amine to the ISO CAL, and the formation of a CAL from the product of the coupling of the ISO and an amine in solution. In the first section, we determine conditions for ISO deposition that provide near monolayer coverage while avoiding side reactions that may destroy the isocyanate functionality. Next, we use octadecylamine (ODA) to investigate the ISO-amine surface coupling reaction. If the reaction proceeds to completion, the result should be a highly functionalized surface with wetting properties similar to that of an octadecyl trichlorosilane monolayer. Finally, we demonstrate an alternative approach to modifying surfaces by coupling the ISO and amine in solution and then depositing the reaction product onto silica surfaces as a CAL. These two approaches to functionalize silicon substrates with ISO are schematically illustrated in Fig. 1 for clarity.

3.1. Isocyanate surface

ISO surfaces were prepared following a known method of depositing alkoxy silanes onto glass and colloidal silica with a slight modification. Walba and coworkers deposited octadecyl triethoxy silane (OTE) on float glass by adsorption in toluene with a catalytic amount of butyl amine [19]. For the systems studied here, we use TEA because the isocyanate is reactive

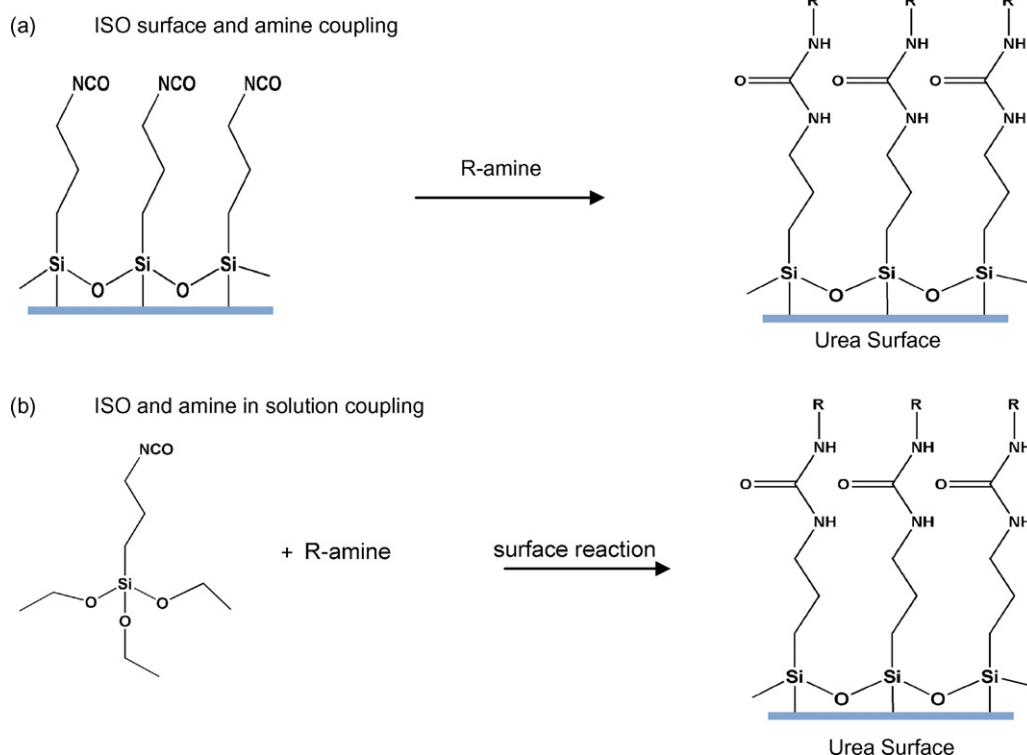


Fig. 1. Preparation of functionalized surfaces with isocyanate/amine/urea chemistry with two different approaches. (a) Schematic of surface coupling reaction pathway, (b) schematic of the solution coupling approach.

with primary amines such as butylamine. The amine in the reaction mixture promotes the silanol-triethoxy silane reaction by making the surface silanols more nucleophilic and provides a proton that facilitates the loss of ethanol during the surface condensation reaction. Although TEA will not provide a proton during the condensation reaction, it can hydrogen bond with the silanol surface and promote a smaller catalytic effect [20]. Here, the TEA-toluene method consistently formed surfaces with a water contact angle of 67° (see Supplemental section S1). However, surfaces with a consistent water contact angle could not be prepared when chloroform was used as a deposition solvent instead of toluene (vide infra). The thickness of the toluene-TEA deposited isocyanate layer was $5.0 \pm 0.2 \text{ \AA}$ thick as measured by ellipsometry. If we assume an all *trans* extended aliphatic chain of six carbons (estimating $\text{N}=\text{C}=\text{O}$ as three carbons) without defects, the thickness is approximately 9 \AA [21,22]. Given that the silane only contains three carbons, the chains are most likely disordered and not extended, therefore 5 \AA is reasonable.

The chemical structure of the ISO monolayers deposited from chloroform and toluene was measured with NEXAFS. Fig. 2a and b show the carbon and nitrogen NEXAFS spectra for chloroform and toluene deposited solutions and an oxide reference. The carbon K-edge spectrum and nitrogen K-edge spectrum from the oxide reference includes $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ and $1s \rightarrow \pi_{\text{N}=\text{N}}^*$ excitations from adventitious hydrocarbon and adsorbed nitrogen from exposure to the laboratory atmosphere. The most striking difference between the chloroform and toluene prepared surfaces, in the carbon K-edge spectra (Fig. 2a), was the lack of a $1s \rightarrow \pi_{\text{C}=\text{O}}^*$ transition occurring at 289.6 eV from the chloroform deposited silane. The NEXAFS nitrogen edge (Fig. 2b) data show a large $1s \rightarrow \pi_{\text{C}=\text{N}}^*$ peak at 402.2 eV indicating C=N bonds present after toluene deposition but absent after chloroform deposition. The NEXAFS data suggest a lack of isocyanate functionality on the chloroform deposited surface or that the coverage of silane was incomplete. Notably, the carbon-nitrogen (π^* peak at 402.2 and σ^* peak at 406.1 eV) (Fig. 2b) content was also lower in the chloroform case than the toluene deposited surface implying lower coverage and poor deposition.

The chemical functionality for each of the substrates was also measured with TOF-SIMS, a surface sensitive technique that can identify specific ion fragments that are characteristic of functional groups on a sample. A representative sample of the negative ion mass fragments from three of the surfaces studied is available in the Supplemental section (S3). We identified two key fragments in the negative ion mass spectra to analyze the state of the surface bound isocyanate. The fragments were at a mass to charge ratio (m/z) of 26, a fragment from a CN^- ion, and at a mass to charge ratio of $m/z = 42$, a fragment indicative of an NCO^- or isocyanate ion. Fig. 3 is a bar chart of the CN^- and NCO^- ions on each substrate normalized to the total intensity of fragments from each surface [23]. The use of a normalized intensity accounts for any systematic variations caused by differences in sample thickness or capacitance. The intensity of the isocyanate fragment indicates that both chloroform and toluene deposited surfaces contain about the

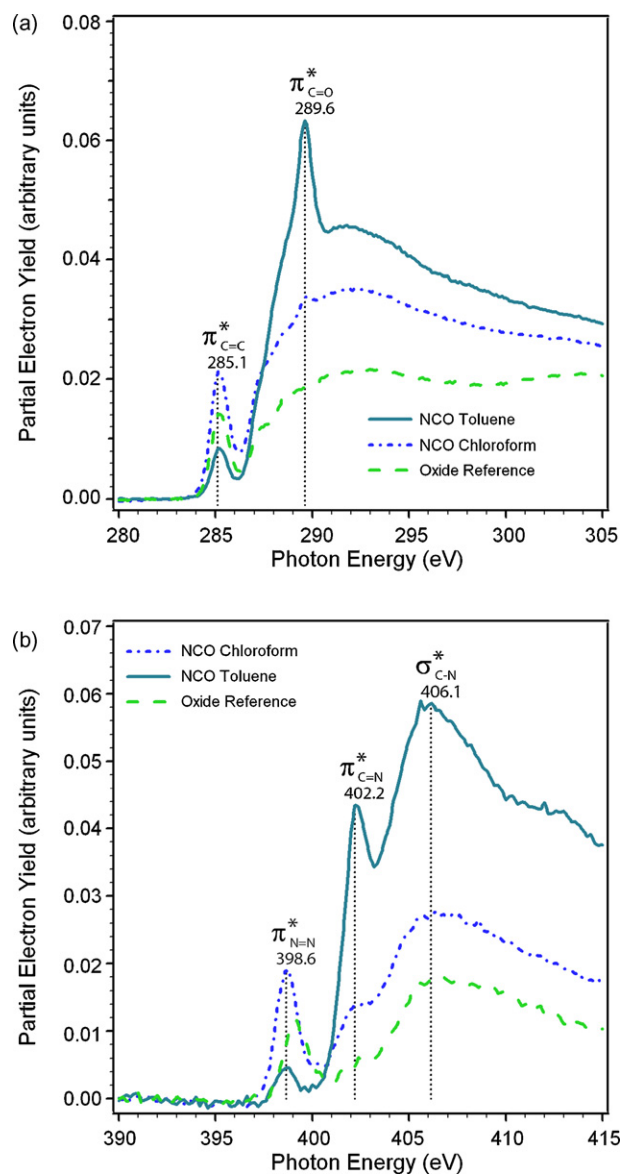


Fig. 2. NEXAFS spectra (a) carbon edge, (b) nitrogen edge of chloroform and toluene deposited isocyanate surfaces and an oxide reference.

same fraction of isocyanate functionality. However, the NEXAFS and TOF-SIMS data both indicate that the surface coverage of ISO surfaces deposited from toluene is higher than that of ISO surfaces deposited from chloroform.

3.2. Surface coupling an amine to ISO CAL

After the silane deposition was optimized, isocyanate surfaces were prepared for modification with octadecylamine (ODA). This amine was chosen because the formation of a successful CAL can be assessed by comparison of hydrocarbon CALs such as OTS [21,22]. We evaluate the success of the ODA coupling through contact angle measurements and ellipsometry. Table 1 shows a list of solvents and conditions used to perform the ODA-ISO surface reaction. Several organic solvents were chosen to explore the effect of dielectric constant on the coupling reaction, but ODA has limited solubility in

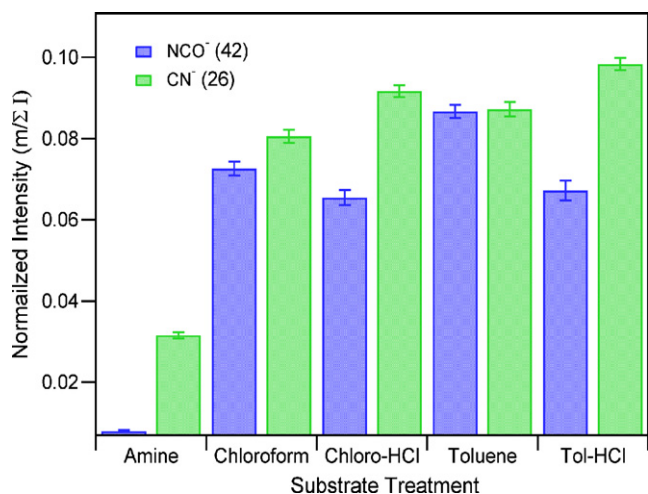


Fig. 3. NEXAFS carbon edge spectra of (a) chloroform, (b) toluene deposited, and HCl treated surfaces. The γ -aminopropyl silane surfaces are included for a reference.

Table 1
Optimization conditions for the reaction of ODA with γ -isocyanatopropyl silane surfaces

Solvent	Thickness (± 0.2 Å)	Dielectric constant of solvent
ISO TEA	5.03	—
Toluene (5×10^{-3} mol/L)	5.40	2.4
Toluene (5×10^{-5} mol/L)	5.61	2.4
Toluene (100 °C) (5×10^{-3} mol/L)	5.31	2.4
Cyclopentanone	5.81	2.3
Chloroform	5.72	4.8
Chloroform (100 °C)	5.78	4.8
Ethyl acetate	5.64	6.0
CHCl ₃ –DMF (9:1)	5.55	≈7.9

The reported thickness is only the organic layer thickness. The native oxides were about 1.5 nm in all cases. Water contact angle of all surfaces was 70° before and after ODA reaction.

many common solvents limiting the number of choices (for information see [Supplementary material \(S2\)](#)). The influence of ODA concentration on surface coupling yield was also explored.

The contact angles and film thickness of isocyanate surfaces exposed to ODA in different solvents and at different concentrations did not change from those of the ISO only surface. The water contact angle remained approximately 70° rather than changing to values near 110° as expected for a well-packed OTS and the CAL thickness remained approximately 5 Å rather than 24.7 Å expected from an OTS monolayer [22]. These results suggest that ODA did not react with the ISO surface. The lack of any surface reaction, even under these presumably favorable conditions, could be due to chemical degradation of the isocyanate during or after the deposition process, but this is unlikely. Alternatively, the short aliphatic carbon segment between the silicon atom and the isocyanate group in the ISO molecule could prevent access of the amine to the isocyanate group.

We tested the degradation of surface bound isocyanates by analyzing NEXAFS and TOF-SIMS data from the as deposited

ISO surfaces and from ISO surfaces treated with an acid solution, 5 mol/L HCl in water. Acid treatment can transform an ISO to an amine group through the loss of CO₂. NEXAFS and TOF-SIMS data from the acid treated surfaces are compared to those of a known amino CAL prepared to evaluate the initial degree of ISO species on the surface. The γ -aminopropyl triethoxy silane surface was prepared as a reference by deposition from ethanol with a drop of acetic acid to catalyze hydrolysis of the silane. The ISO samples were cut in half with one half saved as a control, and the other half exposed to HCl solution to verify that the surfaces degraded.

When the toluene and chloroform deposited ISO surfaces were treated with 5 mol/L HCl, the toluene surfaces decreased in contact angle from 70° to 18° and the area under the peak of the $\pi_{C=O}^*$ in the carbon edge NEXAFS spectrum is decreased substantially (Fig. 4). The NEXAFS spectrum of the HCl degraded surface deposited from chloroform is similar to the

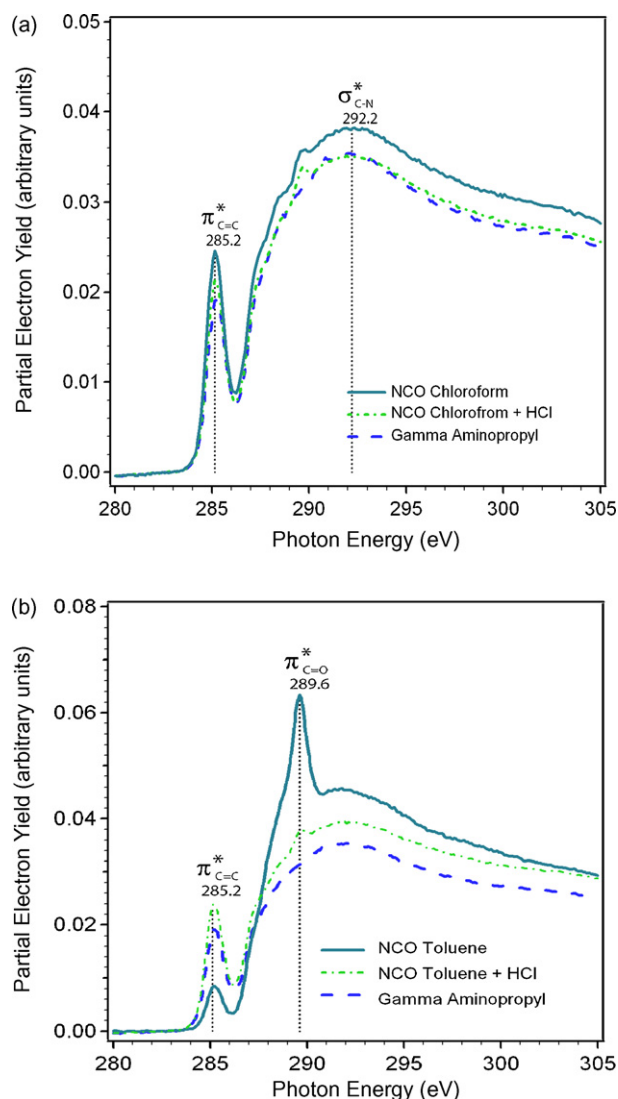


Fig. 4. Normalized peak intensity of the $m/z = 26$ (CN⁻) and $m/z = 42$ (NCO⁻) negative mass fragments for the five surfaces (γ -aminopropyl silane, chloroform deposited γ -isocyanatopropyl silane, chloroform–HCl degraded, toluene deposited, toluene–HCl degraded). Error bars are standard uncertainty from four measurements.

NEXAFS spectrum from the γ -aminopropyl silane reference surface indicating substantial degradation of the surface bound isocyanates. Even before acid exposure, the isocyanate surface deposited from chloroform revealed a surface chemistry similar to the γ -aminopropyl silane reference surface. Treatment of chloroform surface with HCl did not substantially alter the surface chemistry detected in NEXAFS spectra. The NEXAFS results suggest that the ISO CAL deposited from chloroform could be chemically degraded during deposition and the surfaces have a very low surface coverage of isocyanates.

TOF-SIMS spectra show that the ISO CALs deposited from both toluene and chloroform both show a decrease in the ISO peak ($m/z = 42$) and an increase in the CN^- peak ($m/z = 26$) after treatment with HCl. For reference, the γ -aminopropyl silane had small amount of ($m/z = 42$) material present while toluene surfaces resulted in the most intense ($m/z = 42$) peak (Fig. 3). These results confirm the decomposition of surface isocyanates upon exposure to the HCl solution and thus, the presence of ISO functionality of the CALs deposited from toluene and chloroform. However, the surface coverage is lower when isocyanate surfaces were deposited from chloroform.

The failure of the surface coupling reaction between ODA and the ISO CAL is not due to a lack of surface bound isocyanates. Extreme conditions were required to degrade the intact isocyanates from the chloroform and toluene deposited surfaces. More likely, these results suggest that the isocyanates are not accessible to the incoming amines due to either a steric barrier or a random orientation of isocyanate moieties. This hypothesis is consistent with those of Ardes-Guisot et al., who synthesized 10-isocyanatodecyl trichlorosilane (ICT) and performed surface reactions of amines, alcohols and hydrazines with the surface tethered isocyanate [10]. The (ICT) has a long surface tethering group that apparently forms a more reactive isocyanate surface. When dodecylamine was reacted with the ICT surface, water contact angles of 92° were obtained, which is less than the contact angle of 110° expected for a well-packed OTS layer but is substantially greater than the water contact angles obtained from the ODA-ISO surface coupling approach [22].

3.3. Amine coupling in solution

As an alternative to the reaction between surface bound isocyanates and ODA, we performed the ISO-amine coupling reaction in solution to mitigate any steric limitations due to limited freedom of diffusion and rotation of a surface bound isocyanate. In this approach, γ -isocyanatopropyl triethoxysilane was reacted with ODA in chloroform, followed by CAL formation from the reaction product. Again, ODA provides a good reference to the extent of functionality imparted to the surface because well-packed surfaces should have contact angles approaching that of OTS.

We performed the coupling reaction in chloroform because ODA has poor solubility in toluene. Fourier transform infrared (FTIR) spectroscopy measurements, in solution, confirm the conversion of the isocyanate to urea (data not shown) after a 12 h reaction. Surfaces were prepared by allowing the reaction

product to deposit onto silicon oxide for 1.5 h. Surfaces prepared by varying the ODA-ISO solution coupling time increased in water contact angle from 84° for 0.5 h to 104° for 120 h. Fig. 5b shows the dependence of surface energy on coupling time for a constant deposition time of 1.5 h. For long solution reaction times, the ODA surface energy approaches that of octadecyl trichlorosilane monolayers and is higher than that obtained by Ardes-Guisot et al. [10]. The NEXAFS spectra confirm the increase in surface coverage by increasing the solution reaction time. Fig. 5a shows stacked carbon edge NEXAFS spectra of a series of ODA surfaces prepared by varying the solution coupling time while keeping the deposition

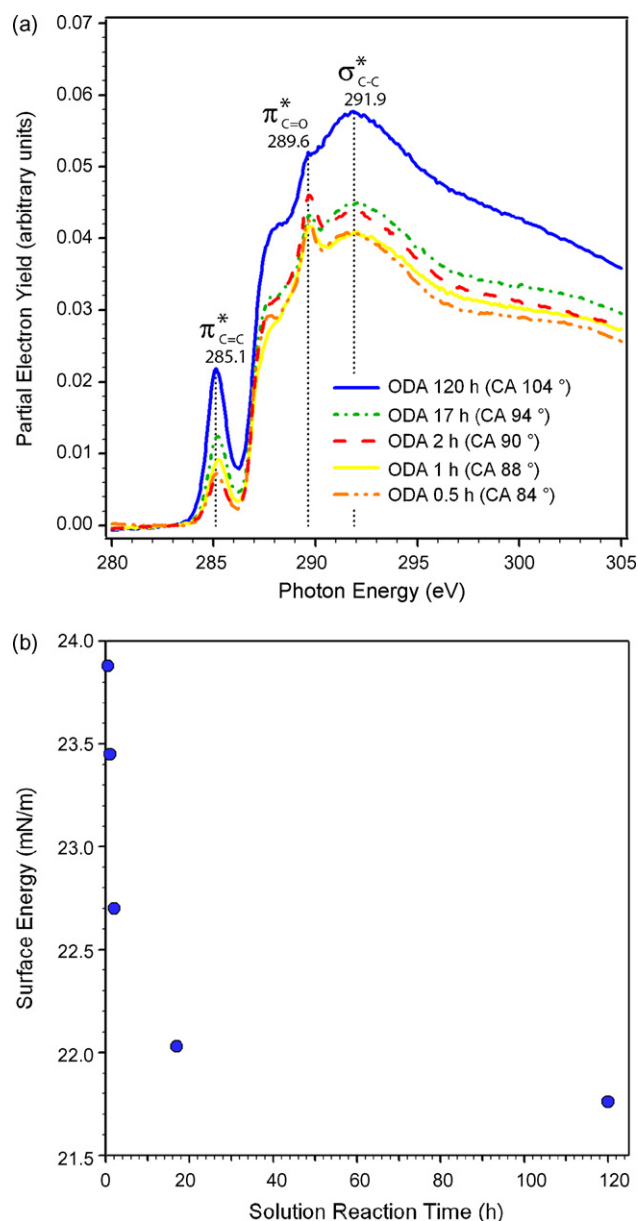


Fig. 5. (a) A series of carbon edge NEXAFS spectra and their corresponding water contact angles of surfaces functionalized with 1-(3-(triethoxysilyl)propyl)-3-octadecylurea (the product of the reaction between ODA and ISO) for different solution reaction times at a constant deposition time of 1.5 h. (b) Solution reaction time of ODA and ISO versus surface energy for a 1.5 h deposition time.

time constant at 1.5 h. Increases in partial electron yield are evident for $1s \rightarrow \pi_{C=O}^*$ and $1s \rightarrow \pi_{C=C}^*$ with increasing solution reaction time. The film thickness of the ODA monolayer is $28.0 \pm 1.4 \text{ \AA}$ at the longest solution reaction time. The ideal thickness of a 24-carbon chain with no tilt is approximately 32 \AA as calculated from Wassermann's equation [22]. The solution reaction plus deposition time needed to reach full coverage of the ODA-ISO silane is substantially longer than the 1.5 h deposition times reported for OTE prepared from toluene-butyl amine solution [19]. The long solution reaction time we observe to reach high coverage of ODA-ISO might be the result of a lack of water in the system due to chloroform as the solvent. A trace amount of water in the solvent is known to catalyze the hydrolysis of the triethoxy silane to a silanol thereby increasing the absorption and surface condensation with surface silanols. Another reason for the long reaction times could be the result of a competitive adsorption processes with the excess ODA remaining from the solution coupling at shorter reaction times; amines can hydrogen bond with free surface silanols. A competitive adsorption process might cause the silane to take longer to diffuse and displace the adsorbed ODA interacting with the surface silanols resulting in slower deposition. Purification of the solution reaction product could lead to both an increased coverage and faster adsorption kinetics. Indeed, when we purified the product of the ODA-ISO reaction, by passing it through a short silica gel column (chloroform + 5 vol.% methanol previously passivated with hexamethyldisilazane) to remove excess amine, we obtained reproducible 104° water contact angle surfaces after a 1.5 h deposition. The best yield of the urea product was obtained from a 36 h solution reaction followed by purification. Comparing unpurified silane to purified silane deposited surfaces for a 17 h solution coupling and 1.5 h deposition time, the difference in water contact angle is 10° ($94\text{--}104^\circ$). It should be noted, we only attempted reactions conditions with non-protic solvents. One of the reviewers of this paper pointed out that an apolar protic cosolvent, such as an alcohol, may enhance the rate of reaction of isocyanates to amines thereby alleviating the need for purification.

The versatility and ease of introducing functional groups to the isocyanate using the solution coupling approach described above is demonstrated by preparing a fluorene urea CAL (FLU). Fluorene is not commercially available as a silane and is of interest for emerging applications such as organic light emitting diodes and organic field effect transistors. In addition, the 9-aminofluorene (AFL) is a polycyclic aromatic primary amine, and shows the robust nature of the amine-ISO solution coupling/deposition approach. The FLU silane was prepared through coupling in solution as described above for the ODA silane. One might expect lower yields of AFL-ISO reaction compared to the aliphatic amine of ODA because the aromatic amine should be less nucleophilic.

The solution coupling method was used to functionalize the surfaces with AFL and produced surfaces with water contact angles of about 70° . Surfaces of similar quality were produced regardless of whether the urea fluorene silane was purified before deposition or not. Fig. 6 shows the NEXAFS spectra

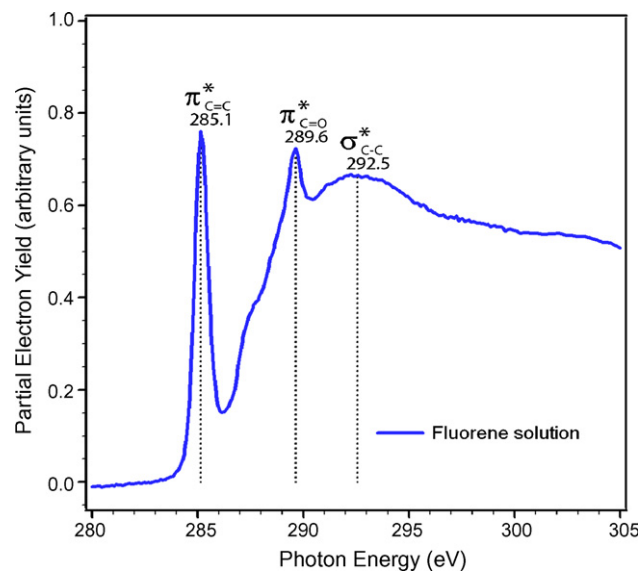


Fig. 6. Carbon edge NEXAFS spectra of fluorene surfaces prepared from solution coupling for a 1.5 h surface deposition.

from the solution coupled fluorene. The enhanced peak area of the $1s \rightarrow \pi_{C=C}^*$ for the solution coupled approach shows good coverage of the fluorene species prepared by the solution coupling method. The high coverage of FLU is consistent with the previous finding for ODA surface.

Given the solution coupling approach succeeds at creating functionalized surfaces of both ODA and FLU, something other than isocyanate degradation is limiting the surface reaction of the amine and isocyanate. Zhang and Srinivasan have shown that reducing the orientation distribution of surface bound amines could nearly double their reaction yield with cyclic anhydrides [24]. We suggest the free amine and bound isocyanate are unable to get in close enough proximity to react.

The isocyanate system used here seems to inhibit the surface coupling reaction to such an extent that no reaction takes place. This lack of reaction is surprising given that a silane with a similar carbon linker (propyl) but containing an amine (γ -aminopropyl triethoxy silane) terminal group, instead of an isocyanate, will react with a cyclic anhydride in partial functionalization of the surface (up to 60%) [24]. To increase the yield of the anhydride to the surface bound amine, Zhang and Srinivasan prepared a surface of the rigid aminophenyl triethoxy silane and were able to obtain nearly quantitative reaction of the surface amines with the cyclic anhydrides.

The free amine concentration at the surface of the aromatic amino CAL was much greater than that of the aliphatic amino CAL due to minimized steric interactions. Steric hindrance of the coupling reaction is more of a concern with bulkier functional groups such as isocyanates and with systems for less reactive functionalities. The past results of Zhang and Srinivasan suggest that factors contributing to low surface reaction in our surface coupling approach are the orientation distribution of isocyanates presented at the air interface and the steric hindrance of the adsorbing/reacting amine.

4. Conclusions

γ -Isocyanatopropyl triethoxysilane monolayers surfaces were successfully prepared from toluene-TEA solutions. Choice of deposition solvent affects the coverage and to a lesser the extent of degradation on the surface. Additionally, TOF-SIMS and NEXAFS indicate that ISO surfaces prepared from toluene are of greater coverage and retain more isocyanate functionality than surfaces prepared from chloroform solutions. Hydrochloric acid degradation studies confirm the existence and degradation of isocyanate species on both toluene and chloroform prepared ISO surfaces. Minimal direct coupling of amines to toluene prepared isocyanate surfaces occurred during surface coupling reactions and we hypothesize this is due to a combination of contributions from steric limitations of the ODA amine adsorbing, the orientation distribution of the isocyanates exposed to the air interface under the reaction conditions tried, and sluggish reaction kinetics. However, a solution coupling approach that involved reacting the isocyanate with octadecylamine and then depositing the CAL, resulted in high water contact angle surfaces approaching those from OTS functionalization. Purification of the silane reduces the need for long solution reaction time of the amine and isocyanate before deposition. We demonstrated the ease of this approach and generality of the amine-isocyanate reaction by preparing a commercially unavailable silane with a pendent fluorene in just one-step. These results suggest that when designing a multi-component surface coupling strategy, the reaction kinetics should be fast and near quantitative to prevent problems with adsorption, and the reactants should have minimal steric interactions near their reactive sites to maximize the yield of the surface functionality.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apsusc.2007.07.170](https://doi.org/10.1016/j.apsusc.2007.07.170)

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