



Kinetic studies of attachment and re-orientation of octyltriethoxysilane for formation of self-assembled monolayer on a silica substrate



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ABSTRACT

The present study deals with kinetic studies of the chemical modification for synthesizing a hydrophobic silica surface. Surface silanization (modification) via formation of Self-Assembled Monolayer (SAM) using a short chain triethoxyoctylsilane (TEOS) was carried out under inert atmosphere at room temperature. Fourier transmission infrared (FTIR) spectroscopy, water contact angle (WCA) and atomic force microscopy (AFM) were employed to investigate surface modification. FTIR analysis in the range from 900–1200 cm^{-1} and 2850–3000 cm^{-1} confirmed surface modification and re-orientation of the attached molecules. Kinetic studies of TEOS SAM formation were fitted by Exponential Association function. Kinetic fitting of FTIR data in the range from 900–1200 cm^{-1} revealed a very fast attachment of TEOS molecules resulting in total surface coverage within 16 min whereas re-orientation rate was slow and continued till 512 min. Further, change in orientation from lying-down to standing-up state was supported by contact angle analysis. AFM images initially showed small islands of ~20 nm, which in-fill with time indicating formation of a smooth monolayer. Our findings indicate that formation of octyl SAM is fast process and completes within 8.5 h in contrary to reported 24 h in conventional SAM formation protocols. The kinetic fitting data can be explored to design a nanopatterned surface for a specific application.

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1. Introduction

Silanization is becoming one of the most widely used functionalization techniques for modifying silica surfaces with free chemical groups via self-assembled monolayers (SAMs). It is often used to modify the physical and chemical properties of surfaces without affecting bulk properties of materials. These modified surfaces find wide applications in surface science, microfluidic systems for nano/biosensors, surface patterning, drug delivery, immobilization of biomolecules, and many other fields [1–6]. Organosilanes are among the widely used organic molecules that can modify intrinsic properties of silica substrates by forming self-assembly via covalent linkage. An organosilane molecule basically consists of 3 parts (i) surface-reactive head group (-OR), which covalently attaches to surface silanol groups (-SiOH) via siloxane (Si-O-Si) bond formation, (ii) alkyl chain, serves as hydrocarbon chain spacer and (iii) terminal group (X) that imparts functionality to a silica surface. Although this process seems to be a simple reaction, but the actual process is very complex due to complications of uncontrolled reactions and its

sensitivity to reaction conditions such as temperature, moisture percentage, type of solvent, reaction time, concentration and solution age [2,7–10]. Zisman et al. reported the existence of threshold temperature (T_c) above which the formation of SAM gets completely inhibited. T_c is an intrinsic property of a silane molecule below which ordered monolayer formation takes place. The rate of SAM formation was found to decrease with decrease in reaction temperature but resulted in a highly ordered and closely packed self-assembly [11]. Excess moisture may result in polymerization of silane molecules in solution and polysiloxane deposition on the surface [6]. Solvent such as anhydrous toluene, which has trace amount of water and can extract water molecules from surface. This enhances the monolayer formation rate. SAMs formation kinetics very much depends on adsorbate concentration. Concentration and reaction time are inversely related to each other as reaction time decreases with increase in adsorbate concentration [12].

Hydrophobicity to the silica surfaces for applications like protein immobilization [13,14] can be imparted by functionalising them via hydrophobic carbon chain. Octadecyltrichlorosilane (OTS) and octadecyltrimethoxysilane (OTMS) are widely used alkylsilane for synthesising hydrophobic surfaces with 18 carbon atom hydrocarbon chain present between terminal and head group [15–17]. Among other amphiphilic molecules, fluoro-alkyl-substituted silanes also favour this property of hydrophobicity. They are even more potential reagents

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for producing hydrophobicity (water contact angle, $\theta = 119.4 \pm 0.7^\circ$) than OTS ($\theta \approx 110^\circ$) on silica surfaces [18,19].

Attenuated total reflection-infrared spectroscopy (ATR-IR), water contact angle, ellipsometry, atomic force microscopy (AFM), quartz crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS) had been used till date for studying kinetics of surface modification by formation of monolayer films [7,19–23]. Kinetic studies of monolayer formation by AFM have revealed small islands of hydrophobic SAM that in-fill to produce smooth surface with nanoscale roughness, as indicated by the reduction in average roughness (R_a) value [8, 20,24]. In spite of huge efforts made in studying mechanisms and kinetics of SAM formation using silanization, there still exist huge discrepancies among scientific community. Moreover, very few researchers among them have focused on the rearrangement/reorientation upon increase in surface density of attached molecules. This could possibly be due to structural phase transitions or crystallization of alkyl chains resulting molecular reorientation [18,25,26]. Godin et al. [27] and Schreiber et al. [28] observed fast attachment of alkanethiols molecules on gold surface in the initial lower coverage stage, where molecules remain in the lying down phase having their alkyl chains lying parallel to the gold surface. In the second stage, which is quite slower process, molecules undergo transition at higher coverage into standing up phase, indicating SAM formation via two different time constants. Yang et al. [8] reported poor ordering of monolayers of organosilanes with short carbon chain (propyl) whereas SAMs of longer carbon chain (octadecyl and decyl) formed comparatively more ordered monolayers. Growth kinetics of the octadecyl and decyl silanes showed Langmuir like kinetics and undergoes phase transition process from lying-down to standing-up phase at higher coverage density.

Due to disparity among different researchers about the time constant in SAM formation kinetics, we studied SAM formation of triethoxyoctylsilane (TEOS) on a silica substrate to determine time constant for molecular attachment and re-orientation. TEOS is less reported octylsilane for preparing hydrophobic surface in spite of providing good hydrophobicity. It has 8 carbon chain attached to the head group that provides hydrophobicity to the surface. Previously, we have reported effect of TEOS on surface chemistry for modulating protein adsorption and insulin aggregation [29–31]. In this work, we have studied the kinetics of TEOS SAM formation on a silica substrate by FTIR, contact angle and AFM. To our best knowledge, kinetics of octylsilane SAM formation on a silica substrate has been reported for the first time by this piece of work. It will be an important research path in terms of stating the initial growth kinetics of octylsilane on a silica substrate for various applications like bio/nanosensors, preparing protective coatings, drug delivery, and microfluidics etc. [2,32,33]. The data obtained from all three studies were used for determining rate kinetics of molecular attachment and further re-orientation on a silica substrate.

2. Material and methods

Triethoxy(octyl)silane (TEOS) (cat. no. 440213) and anhydrous toluene (cat. no. 244511) were purchased from Sigma Aldrich, India. Methanol, toluene, glass wool were procured from Himedia, India. P doped silicon wafers (100) were purchased from Macwin, India. Mili-Q water (18 M Ω) was used throughout the work.

2.1. Surface modification

Silicon wafers used for surface modification were cut using glass cutter into 1 cm² size square chips. These chips were washed in three steps using well established protocol mentioned in our previous reports [29]. Briefly, silicon chips were sonicated for 1 h in a piranha solution prepared freshly by mixing sulfuric acid and 30% hydrogen peroxide (H₂O₂) in 7:3 v/v. In later steps, these chips were sonicated for 30 min each in ammonia solution (Water: H₂O₂:NH₃ = 5:1:1 v/v) and in HCl solution (Water: H₂O₂:HCl = 3:1:1 v/v). Chips were washed with

plenty of water after every step. Finally, washed chips were sonicated in acetone for 5 min before overnight drying in hot air oven at 75 °C. Glass wool was also washed using the above mentioned cleaning protocol.

Dried surfaces were modified by dipping them in 1% (v/v) TEOS solution in anhydrous toluene under nitrogen atmosphere at 22(\pm 2) °C in a glove bag. Surfaces were incubated for different time periods and later washed and dried according to our reported method [29].

2.2. Fourier transformation infrared (FTIR) spectroscopy

FTIR analysis was carried out at room temperature using Nicolet iS10, Thermo Smart Omni-Transmission instrument at a scanning speed of 15 scans per second with resolution 2 cm⁻¹. Samples were prepared by making KBr pellet containing 5% cleaned glass wool. 10 μ l of 1% TEOS solution (conc. 31.8 mM) in anhydrous toluene was dropped on pellet and left for reaction. The samples were scanned after different time periods (0, 0.5, 1, 2, 4, 8, 16, 32, 60 and 90 min). KBr pellet without glass wool was used as control. Experiments were triplicated for calculating the standard deviation.

2.3. Water contact angle (WCA)

WCA was measured using sessile drop method as reported previously by our group [29,31]. Contact angle was recorder at three different spots on the same sample using Drop Shape Analyzer-DSA25 (Make: Kruss GmbH-Germany). Surfaces analysed were modified by forming SAMs of octylsilane by incubating chips in 1% TEOS (v/v) solution in anhydrous toluene for different time periods (0, 1, 2, 4, 8, 16, 32, 60, 90 min, 8.5, 17 and 24 h).

2.4. Atomic force microscopy (AFM)

AFM analysis of modified surfaces (reaction time) were carried out in non-contact mode under clean room conditions at room temperature using Agilent model no. 5500 series with silicon nitride tip of <10 nm radius (Nanosensor, Model: PPPNCH). The roughness parameter ($R_a = \sum_{i=1}^n |z_i|$) where z_i is the height of surface features) was determined using the Gwyddion software (covered by GNU General Public License). The frequency of texture on surface is described in terms of roughness factor (R_f), which is defined as the ratio of actual surface area to projected surface area. R_f was calculated using the method described in our previous reports [29,34]. Briefly, we assumed surfaces with spherical texture with average wavelength, λ_a and average height, R_a . Profile perimeter, P , is calculated by fitting a circle to the profile arc. R_f is calculated as P^2/L^2 , where P is the profile perimeter and L is the length of scanned area. AFM images were recorded for each sample of at least three different preparations.

2.5. Ellipsometry

The thickness of octyl SAM on surface modified for 24 h was analysed using SEMILAB, Spectroscopic Ellipsometry Analyzer - SEA instrument (Model: GESSE). The instrument was equipped with HeNe laser (632.8 nm) which was focused on sample at an angle of incidence of 70° and the data fitting was carried out using optical constants, $n = 3.871$, $k = 0.0158$ for Si substrate and $n = 1.521$, $k = 0$ for TEOS film [35,36].

3. Results and discussion

3.1. FTIR spectroscopy

In the present study, we focused on determining the effect of different silanization time intervals on the growth of TEOS SAM on a silica

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