

Amino-functionalized monolayers covalently grafted to silica-based substrates as a robust primer anchorage in aqueous media

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ABSTRACT

Controlling surface coverage and stability of supported aminoalkylsilane monolayers on silica-based substrates still remains a challenge for the development of biosensors and nanomaterials. We have developed protocols using simple surface chemistry and self-assembly from solution without stringent deposition conditions to covalently attach monolayers of 11-aminoundecyltriethoxysilane (AUTES) onto mica and silica substrates. The resulting self-assembled monolayers (SAMs) exhibited excellent hydrolytic stability. The long alkyl chain together with the large grafting density and homogeneity enhanced the monolayer stability by preventing the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bonds from hydrolysis over a wide range of pH values (2–10) for long time periods (up to 8 days). The control over the surface density of amino groups was achieved and the reactivity of the amino SAMs was confirmed by covalently attaching carboxyl-functionalized nanoparticles on the SAMs. The immobilized nanoparticles exhibited the same hydrolytic stability as that of the SAMs. The AUTES SAMs prepared in this study exhibited the best hydrolytic stability of similar systems reported so far.

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1. Introduction

Alkylsilane self-assembled monolayers (SAMs) on silica-based substrates have useful applications in materials science and engineering [1] for sensing [2,3], surface coating [4], medical devices [5], micro- and nano-fabrication technologies [6]. More specifically, aminoalkylsilane monolayers are suitable surfaces for immobilizing chemical and biological entities such as proteins [7], oligonucleotides [8], polymers [9], nanoparticles (NPs) [10,11], cells [12] through chemical or physical attachment [13–17]. Surface density of amino groups is an important parameter as it determines the quantity, conformation and physico-chemical properties of immobilized systems. For most applications, such immobilization must be robust enough to resist cleavage or detachment under variable environmental conditions. Alkylsilanes, including aminoalkylsilanes can be covalently attached on silica-based substrates via

$\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bonds using vapor or liquid phase [18]. The most common aminoalkylsilane SAMs are made of short alkyl chains such as 3-aminopropyltriethoxysilane (APTES) [7,18–22], 3-aminopropyltrimethylethoxysilane (APDMES) [18–20], and 3-aminopropyl-diisopropylethoxysilane (APDIPES) [19]. The resulting SAMs usually exhibit good thermal stability in air [21] and organic solvents [21,22]. Unfortunately, the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bonds are very susceptible to hydrolysis and therefore, the SAMs can detach from the surface at high pH and with added salt [20,23–26]. In addition, the terminal amino groups can condensate on the surface and catalyze the hydrolysis of the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bonds, making the hydrolytic stability of aminoalkylsilanes SAMs more challenging than alkylsilane SAMs [20,23,27]. However, it has been shown that a pH lower than the pK_a value of the amino groups disfavors the amino catalyzed hydrolysis of the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bond [27]. The sensitivity of $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bond to hydrolysis has limited the use of aminoalkylsilane-based SAMs in aqueous media [20,23,27].

The nature of silane functionality also influences the stability of the SAMs [23]. The trimethoxy- and triethoxy-silanes provide multiple points of attachment so that they can react with the surface as well as with adjacent aminoalkylsilanes forming a reticulated SAM as illustrates in Fig. 1. This reticulation is known to enhance the

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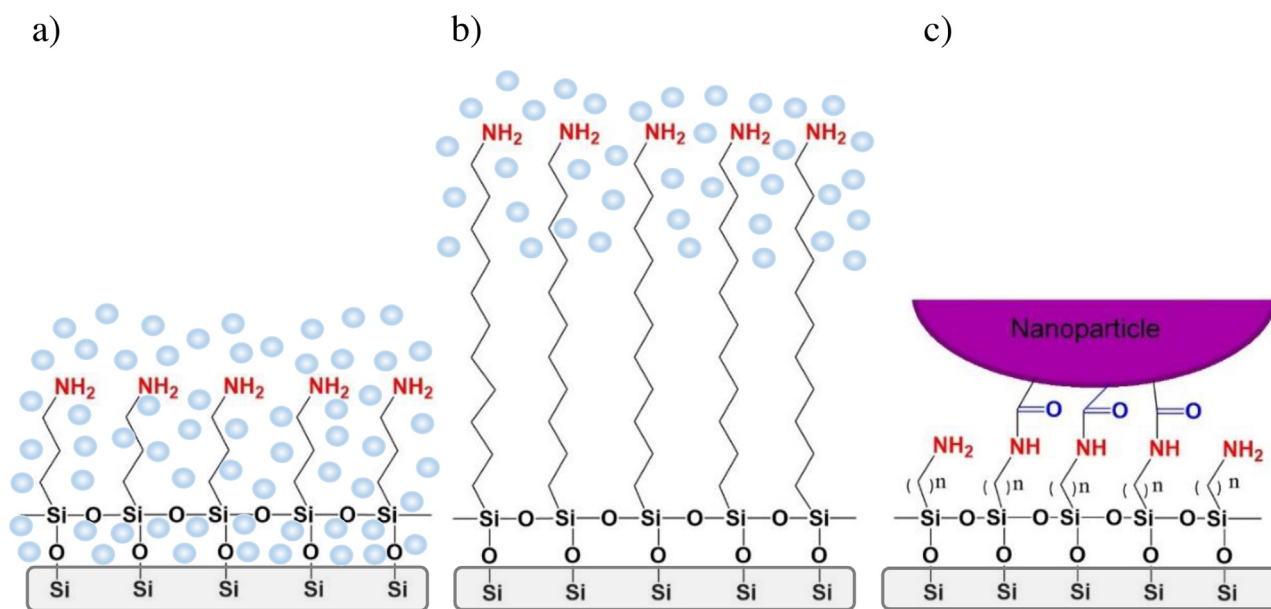


Fig. 1. Schematic representation of (a) APTES SAMs immersed in water (b) AUTES SAMs immersed in water and (c) carboxyl-functionalized NPs covalently attached to amino SAMs, with $n = 3$ or 11 . The longer alkyl chains of AUTES compared to APTES act as a hydrophobic barrier protecting the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bond from hydrolysis.

stability of SAMs but can also lead to buckling and to the formation of aggregates and/or multilayers [23]. Heterogeneous layers are particularly favored with trimethoxysilanes whose reticulation is fast whereas more homogeneous SAMs are usually obtained with triethoxysilanes, which slowly reticulate.

Changing the surface chemistry can improve the robustness of supported SAMs on silica-based surfaces. Different chemical bonds have been used to attach SAMs on silica surfaces including (i) $\text{Si}_{\text{surface}}-\text{C}_{\text{adsorbate}}$ (on oxide-free silicon substrates) using 10-carboxydecyl [28], 1-octadecene [29] or 1-octadecyne [29] (ii) $\text{Si}_{\text{surface}}-\text{O}-\text{C}_{\text{adsorbate}}$ using aminoalcohol [28], 1-octadecene [29] or 1-octadecyne [29] and (iii) $\text{Si}_{\text{surface}}-\text{O}-\text{P}_{\text{adsorbate}}$ using 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid [30]. Most of them have shown enhanced stability compared to SAMs attached via $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bonds. However, these studies did not investigate systematically amino-functionalized SAMs, whose amino groups can catalyze the hydrolysis of the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bond as previously mentioned. Increasing the length of the alkyl chain to improve stability of alkylsilane SAMs is less constraining than changing the surface chemistry and was shown to improve the stability by providing a hydrophobic spacer, which prevents water penetration into the SAMs and subsequent hydrolysis of the $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{surface}}$ bond [21,25,26]. In addition, long alkyl chains prevent the condensation of the amino groups on the surface and promote well-packed, homogeneous and smooth SAMs [25,26,31]. Long aminoalkylsilanes such as 11-aminoundecyltriethoxysilane (AUTES) and 11-aminoundecyltrimethoxysilane (AUTMS) have indeed been studied to functionalize substrates for developing biosensors [26] and microelectromechanical systems (MEMS) [32]. However, the experimental conditions used for these studies gave rise to multilayers, which were investigated in restricted environmental conditions, i.e., in air or water for relatively short time periods (2 h). Given the importance in improving the stability of SAMs on silica-based substrates, a systematic evaluation of the hydrolytic stability is very much in need by controlling the grafting density, homogeneity and environmental conditions to provide reliable and reproducible devices in various applications.

We chose to use SAMs made of AUTES to study systematically the hydrolytic stability, reactivity and grafting density on silica-

based substrates over extended time periods (up to 8 days) under various conditions. In addition, the reactivity of the primary amine at the outermost layer of the SAMs was investigated by attaching carboxyl-functionalized NPs. The hydrolytic stability of these immobilized systems was also investigated under the same conditions.

2. Materials and methods

Ruby mica sheets were purchased from S & J Trading Inc. (Glen Oaks, NY, USA). Plasma Prep II from SPI Supplies was used to activate freshly cleaved mica surfaces using argon (5.0 grade). Milli-Q quality water was obtained from a Millipore Gradient A10 purification system (resistance $18.2 \text{ M}\Omega \text{ cm}$, $\text{TOC} < 3 \text{ ppb}$). Silicon wafers were obtained from University Wafer Co (100 mm diameter, boron-doped (100) orientation, one side polished). Styrene, divinylbenzene (DVB), acrylic acid (AA), potassium persulfate (KPS), 3-aminopropyltriethoxysilane (APTES), *N*-(3-dimethylaminopropyl)-*N'*-ethyl-carbodiimide (EDC), *N*-hydroxysuccinimide (NHS), hydrochloric acid, sodium hydroxide, 4-nitrobenzaldehyde (4-NBA), Trizma base, ethylenediaminetetraacetic acid (EDTA), citric acid, sodium bicarbonate, dodecyltrichlorosilane and sulfate modified polystyrene fluorescent orange nanoparticles (sulfate-modified polystyrene NPs of 100 nm diameter) were purchased from Sigma-Aldrich. 11-aminoundecyltriethoxysilane (AUTES) was purchased from Gelest Inc. Styrene, anhydrous DVB and AA were distilled under reduced pressure. KPS was used without further purification.

2.1. Carboxyl-functionalized nanoparticle synthesis

Carboxyl-functionalized NPs are composed of polystyrene core and poly(acrylic acid) shell. The NPs were synthesized by surfactant-free emulsion polymerization with KPS as the initiator [33]. 3.25 g of styrene, 0.16 g of DVB and 0.45 g of AA were dissolved in 200 mL of Milli-Q water in a 500 mL three-neck flask equipped with a reflux condenser. The system was degassed with nitrogen for 30 min while being stirred at a speed of 350 rpm. 1.35 g of the initiator were then added with 20 mL of water and the flask was heated

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