

Tuning the hydrophobic properties of silica particles by surface silanization using mixed self-assembled monolayers

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Abstract

Here we describe a novel method of preparing hydrophobic silica particles (100–150 nm; water contact angle of dropcasted film ranging from 60° to 168°) by surface functionalization using different alkyltrichlorosilanes. During their preparation, the molecular surface roughness is also concurrently engineered facilitating a change in both the surface chemical composition and the geometrical microstructure to generate hierarchical structures. The water contact angle has been measured on drop-cast film surface. The enhancement in the water contact angle on 3D (curved) SAMs in comparison to that on 2D (planar) surface is discussed using the Cassie–Baxter equation. These silica particles can be utilized for many potential applications including selective adsorbents and catalysts, chromatographic supports and separators in microfluidic devices. © 2007 Elsevier Inc. All rights reserved.

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1. Introduction

In recent years, the use of self-assembled monolayers (SAMs) to impart a desired function to a surface has received extensive attention due to its ease of manipulation of surface energy, and thereby also of such properties like adhesion, lubrication, corrosion and anti-stiction [1]. It is well known that the water contact angle (CA) (θ), $\theta < 90^\circ$ and $\theta > 90^\circ$ can indicate surface ‘hydrophilicity’ or ‘hydrophobicity,’ respectively, and when it is above 150°, the word ‘superhydrophobic’ is sometimes used. Nature exhibits this phenomenon in ‘lotus leaf effect’ to harness the roll-off action for self-cleaning of leaves which has been attributed to a combined micro and nanoscale morphology of its surface [2–5]. In brief, the surface of the lotus leaf is textured with micron-sized hills and valleys (bumps) that are decorated with nanometer sized particles of a hydrophobic wax like material, which prevents the penetration of the water into valleys [6–20]. As a result, water cannot wet the surface and therefore forms nearly spherical water droplets, leading to superhydrophobicity. Achieving superhydrophobicity is of

great current interest in view of its diverse applications such as selective adsorbents and catalysts, chromatographic supports, adhesives in paints, fabrics and low-friction surfaces and separators in microfluidic devices [6–8].

Artificial superhydrophobic surfaces have been prepared using various strategies including the generation of rough surfaces first and then modification with low surface energy molecules or roughening the surface of hydrophobic materials and creating well-ordered structures using micromachining and etching [5–12]. Various methods have recently been proposed to create superhydrophobic surfaces, including electrochemical deposition, plasma fluorination, sol–gel, UV irradiation, etc. It is well known that, the wetting property of a solid surface is governed by both its chemical composition and geometric microstructure [12–25]. In addition, a few methods have been reported to make the superhydrophobic coating on silica particles by forming polyelectrolyte multilayer films by layer-by-layer process, or by forming the film of silica particles on substrate by Langmuir–Blodgett (LB) technique and subsequent formation of a alkylsilane SAM for fabricating hydrophobic surfaces. It is well known that, the wetting property of a solid surface is governed by both its chemical composition and geometric microstructure [12–37].

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In this work, we report the enhancement in the hydrophobicity of the SAM formed on the curved surface (silica particles). Our strategy is to optimize the hydrophobicity of silica particles (~100 nm) using different organosilane molecules (as the chemical compositions determine the surface free energy) and thus have greater influence on wettability. Further, for contact angle measurements we have chosen drop cast films of such functionalized spheres, which automatically render hierarchical micro–nano roughness by their coating on a smooth silicon surface. The molecules employed are: octadecyltrichlorosilane (OTS), octyltrichlorosilane (OTCS), 3-aminopropyltrimethoxysilane (APTMS), 3-[tris-(trimethylsilyloxy)-silyl]-propyl methacrylate (MSMA), poly-(MSMA), dodecyltrichlorosilane (DTS), and decyltrichlorosilane (DTCS). Characterization data obtained using CA measurements, FTIR spectroscopy and SEM have been discussed to illustrate the reasons for this superhydrophobic behavior.

2. Experimental

2.1. Materials

n-Octadecyltrichlorosilane (C₁₈, OTS) (95%), octyltrichlorosilane (C₈, OTCS), dodecyltrichlorosilane (C₁₂, DDS), decyltrichlorosilane (C₁₀, DCS), 4-aminopropyltrimethoxysilane (APTMS), 4-[tris-(trimethylsilyloxy)-silyl]-propyl methacrylate (MSMA) and tetraethyl orthosilicate (TEOS) were obtained from Aldrich, while toluene (99.5%), ethanol (99.5%) and ammonia were purchased from Qualigens. Commercially available *n*-type, one-side polished, silicon wafers of (100) orientation with 0.001–0.007 Ω cm resistivity were used as substrates. These silicon wafers (1 × 1 cm²) were rinsed with deionized water (18 MΩ cm), sonicated in ethanol and dried under a flow of nitrogen. These wafers were soaked in 1:10 HF:H₂O solution for 40 s to remove a native SiO₂ layer and further immersed in a *piranha* solution (7:3 concentration H₂SO₄:H₂O₂) for 40 min at 80 °C to grow a fresh oxide layer, followed by rinsing with deionized water, dried in a stream of nitrogen and used for further experiments.

Silica particles were prepared by using the well-known Stober's method as reported elsewhere [38]. In brief, 1.3 ml TEOS was added into 5 ml ethanol and stirred for 10 min. To this solution, 3 ml ammonia in 22.7 ml of ethanol was added drop-by-drop and stirred for 2 h to get silica particles. These particles were washed several times and dried under nitrogen atmosphere, redispersed in ethanol and refluxed for 2 h to get monodispersed silica particles.

2.2. Silanization

2.2.1. Monolayer formation

Prior to silanization, silica particles were dried for 10 h at 150 °C under nitrogen atmosphere and were used immediately. In a typical synthesis procedure, 25 mg silica particles (100–150 nm) were dispersed in dry toluene and stirred for 30 min. To the above mixture 10 ml, 1% OTS (w/w) solution in toluene

was added drop wise, and in order to ensure a complete monolayer formation of OTS on silica, the mixture was refluxed for 24 h under nitrogen atmosphere. This solution was then allowed to stand for few hours, filtered and washed several times with toluene and ethanol in order to remove unreacted OTS. This (OTS-silica) was subsequently dried in a vacuum oven at 60–70 °C for 4 h and used for further characterization. Similarly, the silanization was carried out by changing the % of OTS (w/w) in toluene (i.e., 5, 10, 15, 20, and 25) and also by using different silane reagents such as APTMS, MSMA, OTS, OTCS, DTS, and DTCS. In each case 10% silane (w/w) in toluene was used for surface modification. Fig. 1 shows a schematic of typical terminal groups and their arrangements, in which the silane molecules are linked to silica surface through Si–O–Si linkage with different terminal functional group, which determines its wettability.

2.2.2. Mixed monolayer formation

Mixed monolayers of APTMS:OTS (1:1) and OTS:OTCS (1:1). To form a mixed monolayers, silane reagents were mixed in toluene (APTMS and OTS; 1:1 w/w) and then added drop wise on to the silica particles dispersed in toluene.

2.2.3. Polymerization of MSMA monomer

Polymerization of MSMA monomer (*in situ*): 25 mg silica particles were dispersed in dry toluene and stirred for 30 min. To this solution 2.5 mg 5-(trimethoxysilyl) propyl methacrylate monomer, 1 ml triethyl amine (as a catalysts) and azobis isobutyronitrile (AIBN, as an initiator) were added and the mixture was refluxed for 24 h under nitrogen atmosphere. Subsequently this mixture was cooled, allowed to stand for few hours, filtered and washed several times with toluene and ethanol in order to remove excess of monomer and the resultant poly(MSMA) silica was used for further characterization.

2.3. Characterization

Scanning electron microscopic (SEM) measurements were carried out on a Leico stereoscan model 450 instrument equipped with Phoenix energy dispersive analysis of X-ray (EDAX) attachment. Transmission electron microscopic (TEM) measurements were carried out a JEOL 1200 EX TEM operated at an accelerating voltage of 120 kV. The bare silica and modified-silica particles were dispersed in the appropriate (e.g., toluene) solvent and drop/spin casted to form a film on Si substrate, which was dried at 100 °C for an hour. The water sessile drop contact angle (CA) measurements were carried out on thus prepared substrate on GBX-model 'Digidrop' CA meter. CA was calculated by measuring the angle at three different locations. The modified-silica particles were made in the form of pellet after mixing with spectroscopic grade KBr and the FTIR spectra were recorded using a Perkin Elmer 1615 spectrometer in a diffuse reflectance mode (DRIFT). Thermogravimetric analysis was carried out on a Seiko thermal analyzer model No. TCA/DIA-32. Thermal stability of OTS-silica was studied by CA measurements after annealing Si substrate in nitrogen for 5 min at different temperatures.

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