International Conference on Solid State Physics 2013 (ICSSP’13)

Colloidal route to bio-inspired hierarchical superhydrophobic substrates

Muhammad A. Raza a*,1, Harold J.W. Zandvliet b, Bene Poelsema b and E. Stefan Kooij b*2

aCentre of Excellence in Solid State Physics, University of the Punjab, QAC, Lahore-54590, Pakistan
bPhysics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Abstract

Inspired by biomaterials such as the Lotus leaf and rose petals, we present a facile, inexpensive bottom-up colloidal route to prepare superhydrophobic surfaces with hierarchical roughness. Spin coating is used to assemble silica microspheres into multilayered arrays, which are subsequently decorated with gold nanoparticles. The surface chemistry of the silica and gold is modified by adsorption of fluoroalkylsilane and dodecanethiol, respectively. The wetting properties, both static and dynamic, of surfaces in relation to the morphology of the substrates are addressed.

© 2015 Elsevier Ltd. All rights reserved.
Selection and Peer-review under responsibility of the Committee Members of International Conference on Solid State Physics 2013 (ICSSP’13)

Keywords: Superhydrophobic substrates; Colloidal route; Silica; Gold nanoparticles; Wetting properties

* Corresponding author. E-mail address: akramraza.cssp@pu.edu.pk
1. Introduction

The variety in wetting properties of naturally occurring surfaces is due the diversity in microstructure of their surfaces, as revealed by microscopic examination [1,2]. Naturally occurring superhydrophobic surfaces can be divided into two categories on the basis of liquid surface adhesion: (i) non-sticky surfaces, with large water contact angles (typically CA> 150°) and low sliding angle (SA< 10°), such as the Lotus leaf [1] and water strider legs [3]; and (ii) sticky surfaces, with large water contact angles (CA> 150°) and large sliding angles (SA> 10°); an example of the latter type of surface are rose petals (Rosea Rehd) [4,5].

It is well established that by controlling the roughness and interfacial chemistry, artificial surfaces with various wetting behaviour can be manufactured. Here we demonstrate how colloidal gold nanoparticles and silica microparticles can be used in a bottom-up approach. The hierarchical architecture is achieved by self-assembled arrays of particles with dimensions varying from micrometers into the low-nanometer range. The largest length scale is provided by (multi-)layers of silica spheres (130-850nm) , which are decorated with 13-45nm gold particles. The chemistry of the structured surfaces is modified by functionalizing the gold nanoparticles and silica spheres with dodecanethiol and fluoroalkylsilanes, respectively.

2. Experimental details

The various steps in the bottom-up assembly of hierarchical (and flat) substrates are schematically shown in Fig. 1. Silica sphere arrays (130-850nm diameter) were deposited on silicon substrates by spin-coating [6,7]. To enable deposition of gold nanoparticles on flat or hemispherical surfaces, the silica was functionalized with mercaptopropyl-trimethoxysilane (MPTMS); thiol end groups provide a large affinity for irreversible adsorption of the citrate-stabilized gold nanoparticles (13-45nm diameter) [8,9]. After the colloidal assembly the exposed silica surfaces were functionalized with perfluorooctyltriethoxysilane (PFOTS) to ensure sufficient stability of the substrates and also to lower the surface energy. Finally, gold nanoparticles were hydrophobized by derivatization with dodecanethiol (DDT).

![Fig. 1. Schematic representation of the preparation steps of flat (right) and hierarchical (left) hydrophobic substrates. Silica surfaces (spin coated microsphere arrays) were functionalized with MPTMS, followed by gold nanoparticle deposition. Finally, the surfaces were hydrophobized with PFOTS and DDT.](image-url)
The superstructure morphology was assessed by helium ion microscopy. Contact angle measurements were performed using the sessile drop method under ambient conditions at room temperature. Advancing and receding contact angles were determined by increasing or decreasing the droplet volume while it was in contact with the surface; sliding angles were determined by tilting the sample holder. Typically, 4-10μl water droplets were used; contact angle values were determined by the average of at least five independent measurements.

3. Morphology and wetting of hierarchical substrates

Microscopy images of different substrates are compiled in Fig. 2; sessile drops (insets) are used to assess the wettability. Flat silicon substrates, as well as pristine silica sphere arrays exhibit very small contact angles. After coating the flat or hemispherical surfaces with PFOTS (middle panels) the morphology remains essentially unchanged; close examination reveals PFOTS-bridges between touching spheres. The wettability is modified considerably. The flat surface exhibits contact angles of approximately 110°, while the silica sphere arrays show even larger contact angles. This can be understood by considering the roughness induced by the silica spheres; the droplets are in a mixed state, i.e. partially wetting the spheres [7,10]. In the right panels of Fig. 2 the flat surface and silica arrays after deposition of gold nanoparticles are shown. In both cases, nanoparticles are randomly distributed. Nevertheless, there is clearly a minimum distance separating the nanoentities, arising from the surface charge of the particles [11].

![Microscopy images of substrate morphology](image)

**Fig. 2.** (left) Microscopy images of the substrate morphology: (a,b) Flat oxide-covered silicon surfaces before and after PFOTS treatment. (d,e) Silica sphere (440nm) arrays before and after PFOTS derivatization. (c,f) Gold nanoparticles (50nm) on flat silicon and on silica sphere arrays. The wettability results (insets) show that superhydrophobicity is achieved on hierarchical structures. (right) Top panel: Dynamic advancing and receding contact angles (up and down triangles, resp.) as a function of the static contact angle. The dashed line has a slope of 1. Bottom panel: Sliding angle as a function of the SCA. Results are shown for 440nm silica spheres, decorated with gold nanoparticles with diameters in the range 13-45nm.

Results of static, advancing and receding contact angles as well as sliding angle measurements on surfaces consisting of 440nm silica spheres decorated with various gold nanoparticles are summarized in Fig. 2(right). From the absolute value of the contact angles, the contact angle hysteresis (difference between advancing and receding CAs) and the sliding angles, we conclude that superhydrophobicity is only achieved in the case of hierarchical surface roughness. Only on silica sphere arrays decorated by gold nanoparticles do we observe CA>150°, reduced hysteresis and SA<5°, characteristic for superhydrophobic substrates. Although a detailed characterization of the wetting mechanism on these hierarchical surfaces lies outside the scope of this work, we assume that the droplets on the substrates with hierarchical roughness are neither in the Wenzel nor Cassie-Baxter state. Most likely they reside in a mixed state as presented by Bormashenko et al. [12]: the droplets partially wet the smaller nanoparticles, while...
entrapping air between the larger silica spheres. As described in previous literature reports, this is a prerequisite for pushing out the liquid into the suspended Cassie-Baxter state, therewith considerably reducing the contact angle hysteresis and thus giving rise to superhydrophobic wetting characteristics [9,12–15].

4. Self-cleaning property

The ‘fakir’ state of droplets and also impurities, such as dust particles, on top of the hierarchical structures of superhydrophobic surfaces leads to a very small contact area and low adhesion force between particles and surface [1]. When a droplet rolls over such a surface, dust particles are picked up. Strong capillary forces between particles and droplet compete with the weak adhesion (Van der Waals) interaction with the substrate. In Fig. 3 this self-cleaning by a water droplet on a slightly tilted superhydrophobic substrate is shown.

Fig. 3. Sequential photographs of self-cleaning by a water droplet (10μl) on an inclined superhydrophobic substrate. The objects to the right of the needle are dust particles, which are removed by the moving droplet.

Acknowledgements

Acknowledgements and Reference heading should be left justified, bold, with the first letter capitalized but have no numbers. Text below continues as normal. One of the authors (M.A. Raza) acknowledges support from the Higher Education Commission of Pakistan†.

References


† Partly reprinted from J. Colloid Interface Sci., 385/1, M.A. Raza, E.S. Kooij, A. van Silfhout H.J.W. Zandvliet, B. Poelsema, A colloidal route to fabricate hierarchical sticky and non-sticky substrates, 73-80, Copyright (2012), with permission from Elsevier