Tuning Wettability by Controlled Roughness and Surface Modification Using Core-Shell Particles

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INTRODUCTION

Wetting and non-wetting phenomena are ubiquitous in the natural and technological worlds, and their understanding has been the subject of intensive investigations over the past decades. Examples include droplet spreading on solids such as a spraying of paint, penetration of ink in paper, and liquid absorbency or repellency of fabrics. Recent applications, such as microfluidic technologies and the regulation of the hydrophobic interactions for the protein adsorption, reflects the continuous interests in wetting phenomena. Numerous surface modification techniques are used to control wettability and adhesion of polymer surfaces. A promising strategy to regulate wetting behavior is the combination of the surface patterning and the chemical surface modification. Recently, we reported a route to fabricate two-level structured self-adaptive surfaces of polymer materials [1]. The first level of structure was built by a rough polymer film that consists of needle-like structures of micrometer size. The second level of structure was formed by the nanoscopic self-assembled domains of a demixed polymer brush irreversibly grafted onto the needles. The large scale surface structure enabled us to reversibly tune the wettability upon exposure to different solvents over a wide range. It was found that the wettability, evaluated in terms of the contact angle hysteresis, was strongly dependent on the shape and size of the features [2]. Here we present the alternate strategy to fabricate patterned surfaces with specifically designed surface roughness using core-shell particles. The surface morphology and roughness is built by self-assembled submicrometer- and micrometer-sized monodisperse core-shell particles forming ordered films on silicon wafer substrates. The shell of the particles is made from hydrophobic polymer brushes covalently grafted to the particles.

EXPERIMENTAL

The “grafting to” method was used to anchor soft polymer chains to the hard silica core particles and the smooth silicon wafer substrate providing surfaces with solvent, mechanical and thermal resistance. Glycidoxypropyltrimethoxysilane (GPS) was chemisorbed from 2% toluene solution to provide high concentration of epoxy groups on the surface of silica particles. Afterwards, mixture of modified particles and monocarboxyterminated polystyrene (PS Mn = 45 900, Mw = 48 400) of random copolymer of polystyrene and hexafluoropolystyrene (FPS Mn = 40 000) was annealed at 150°C to produce a dense layer of grafted polymer on the surface. [3] The amount of grafted polymer determined by IR spectroscopy corresponds to the 3.5 – 4.0 nm of the layer thickness.

The layer of hexagonally packed particles of small size (0.2 – 2.3 μm) was prepared by a vertical deposition technique from toluene suspensions at 70°C. [4] The particles of the size larger than 3 μm were deposited via sedimentation on the slightly inclined silica wafer modified with a thin layer of the grafted polymer. The quality of the layers was controlled by optical, scanning force (SFM) and scanning electron (SEM) microscopy.

SURFACE MORPHOLOGY

The monodisperse particles pack in a close dense hexagonal array (Figure 1). The triangle connecting the contact points of adjacent spheres is taken as a elementary cell of the layer (Figure 2a). A 3D image of this cell is presented in Figure 2b. We used two models to estimate the surface roughness of the layer. According to the *Model 1* the effective surface roughness is determined by semispheres giving the value of route-mean-square (rms) roughness equals to *0.29 R*. In the *Model 2* the effective surface roughness is determined by both the upper semi-spheres the cylindrical pores. In this case rms = *0.54 R*. The calculated ratio between the intrinsic surface of the layer of the beads and the surface of plane of the layer (r_s) is 1.9 independently on the particle size.

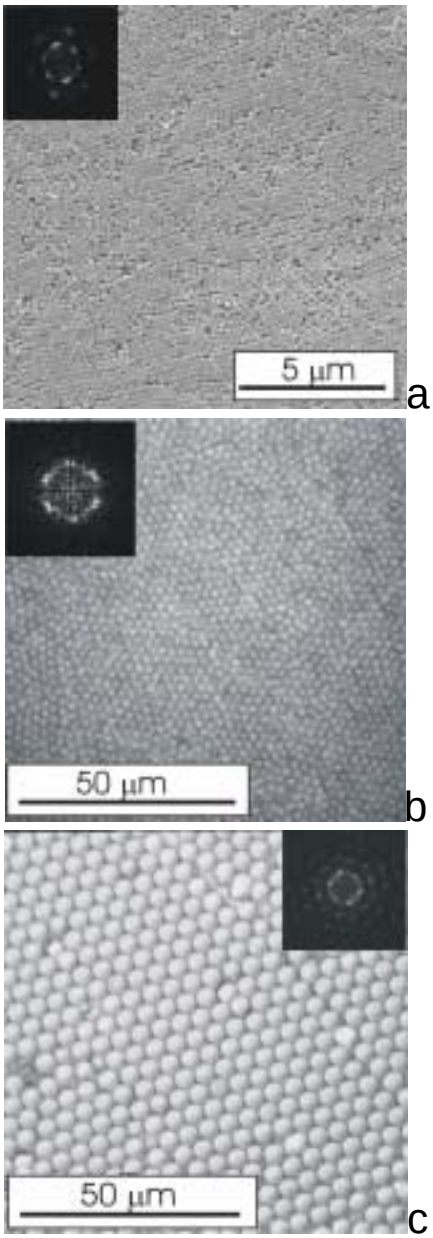

Figure 1. SEM image of 200 nm particles (a) and optical microscopy images of 2.3 (b) and 5 μm particles (c).

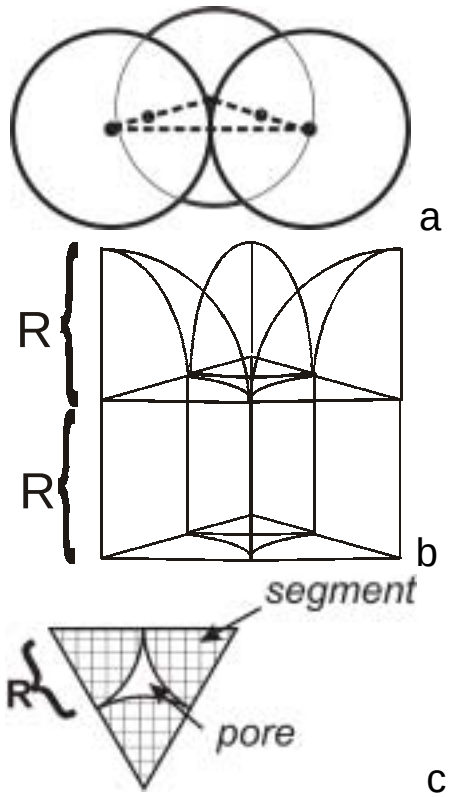

Figure 2. Scheme of the elementary cell of a hexagonally packed array of spherical particles.

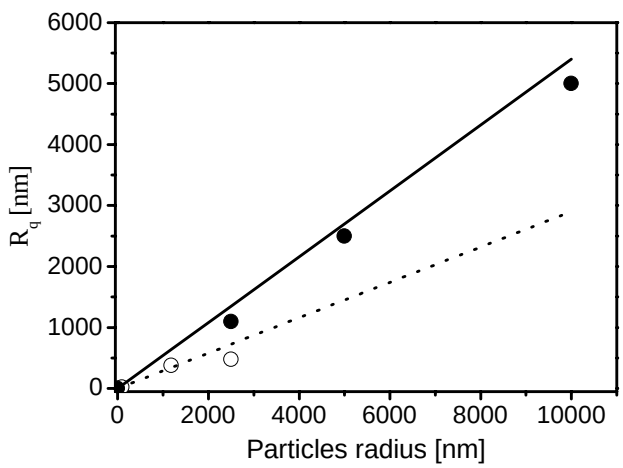

Figure 3. Experimental rms roughness (R_q) (– - SFM, ! - optical profilometer) and theoretically calculated plots using Model 1 (dashed line) and Model 2 (solid line).

Figure 3 compares the experimental data presented in terms of rms roughness (obtained using SFM and optical profilometer) with the roughness calculated from the models. We found that SFM data are in good correlation with the first model. That is because of the limited penetration of the tip into the porous layer. The data obtained with the optical method correlate with the second model.

WETTING BEHAVIOR

The influence of the particle dimension and the chemistry of the shell polymer on the wetting behavior of the hexagonally packed particle arrays is shown in terms of advancing (θ_a) and receding (θ_r) water contact angles in Fig. 4. As compared to the smooth surfaces (which are hydrophobic surfaces with surface free energies of 28 mJ/m^2 for PS brushes and 25 mJ/m^2 for FPS brushes, respectively), the contact angle hysteresis was increased on the patterned surfaces due to the crease of θ_a and the decrease of θ_r. This behavior is expected for a "homogeneous wetting regime" on a rough surface[5]. In the case of FPS the hysteresis was smaller on the patterned surfaces. For both polymers, the effect of the increasing vertical roughness was similar: θ_a was almost independent on roughness, while θ_r increases until the particle diameter approaches the value of 5 μm, and then decreases again. The results demonstrate still quite large hysteresis. Further investigations are presently carried out to explain this effect.

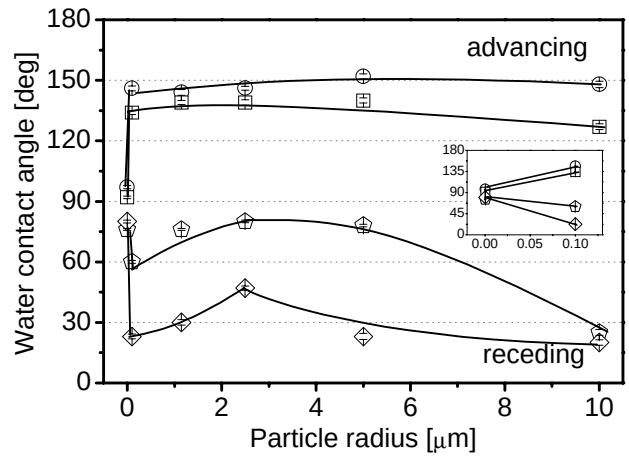

Figure 4. Water contact angle vs. particle diameter for different shell polymers PS (∀ - advancing, M - receding) and FPS (– - advancing, - receding)

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