Influence of some system parameters on silica surface patterns by sol-gel phase separation method

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Abstract. We have studied the effect of different coating methods and precursor compositions on the size, surface density and shape of round surface structures prepared by phase separation-based surface patterning method with potential application in preparing superhydrophobic optically functional structural coatings. Increase in solvent polarity resulted in larger micro- and nanosize surface features. Variation in precursor concentration and extent of initial polymerization were shown to result in different surface densities and geometries of formed features. The effect of different surface patterns on wettability was evaluated by WCA measurements.

1. Introduction

Sol-gel method offers a variety of well established, facile and versatile technologies for flexible design of materials for a wide range of applications, including optical devices [1], sensors [2], biomaterials [3], coatings [4]. In addition to the possibility of preparing different pure [5], doped [6, 7], mixed oxides [8] and hybrids [8, 9] at relatively low temperatures, sol-gel also enables in-situ control over the nano- and microstructure of prepared materials during transition from sol to gel [10]. Micro- and nanostructure of surfaces has a critical role in the design of superhydrophobic coatings [11] and sol-gel has been applied in phase separation based strategies [12, 13] to achieve suitable micro- and nanoroughness. In the case of self-cleaning windows, optical properties of obtained hydrophobic surfaces are also a concern [14]. Sol-gel-based methods that are simple and can be applied on industrial scale have been used to prepare films that, when coupled with low-surface energy, can have water contact angles as high as 167° [15]. Nevertheless, such film coatings can compromise the transparency of the glass due to numerous reflections and refractive surfaces. We have reported a strategy based on phase separation in silicon alkoxide solutions that results in a single layer of round surface features [16]. This method also holds considerable potential in designing optically functional coatings, as each surface feature can be designed to act as a micro-lens. We hereby present our results on the variation of several system parameters such as extent of precursor concentration, pre-polymerization and solvent polarity on the formation of round silica surface features. The results demonstrate the potential of the method for the development of single-step coating technology for structural coatings with simultaneous optical and superhydrophobic functionality.

2. Experimental

Patterned structures were prepared from solutions of partially hydrolyzed tetraethylorthosilicate (TEOS) in different solvents. All chemicals were purchased from Sigma-Aldrich. Conventional acidcatalyzed hydrolysis and polymerization of TEOS was carried to prepare sols. TEOS was mixed with solvent on a magnetic stirrer, followed by the addition of water containing 3.5 % nitric acid to initiate hydrolysis. Obtained solution was stirred for 1 h before coating on soda lime glass slides (2.5 x 2.5 cm) by spin coating or spraying. Glass slides were pre-cleaned with acetone in ultrasonic bath, rinsed with methanol and dried with gaseous nitrogen. For investigating the impact of solvent type, sol concentration and water-alkoxide molar ratio on silica structures, different process parameters were applied. Solvent ratios (solvent:TEOS) 1, 5, 9, 13 and 17 (S) as well as water-alkoxide molar ratios 0.4, 0.8, 1.2, 1.6, 2 and 4 (R) were tested with solvents propanol, ethanol and methanol. During synthesis relative humidity of surrounding environment was fixed at 15 % to 20 % at temperatures 22-23 °C. All samples were subsequently heated at 200°C for 20 h to transform gel material into oxide.

Scanning electron microscope (SEM) graphs of silica domes were acquired with Tescan VEGA II SBU with accelerating voltage of 10 kV. The samples were previously sputter coated with a 5 nm layer of gold using a SC7640 Auto/Manual High Resolution Sputter Coater. To estimate surface hydrophobicity water contact angle (WCA) measurements were performed. A water droplet of 4 µl volume was placed at the surface and measured at three different spots using Canon EO5 650D with objective Canon MP65 and GIMP for measuring WCA from images.

3. Results and discussion

In this study we examined the influence of reaction parameters such as solvent type, sol concentration and water-alkoxide molar ratio on sol-gel phase separation process and subsequent formation of surface features. Mostly, we obtained symmetric round surface structures with diameter ranging from 200 nm to 20 µm. Sol-gel phase separation is known to start with the nucleation of isolated domains of separated phase, droplets of either solvent-rich or solvent-poor phase inside continuous solution phase domain [12]. The process then proceeds to formation of bi-continuous two-phase system with a large phase interface. In most cases where porous oxides are prepared, this kind of structure is also preserved by optimized speed of solvent evaporation. In our case the volatile solvent is optimized to evaporate before the evolution of continuous organosilica-rich phase (explained in figure 1). Nucleation is followed by growth of the droplets and gradual diminishing of solvent-rich phase due to solvent evaporation. In most cases we observed the formation of isolated round surface features formed from the droplets on the surface after partial flattening of not fully gelled silica-forming precursor.

As expected, different coating methods, such as spin-coating and spraying, lead to qualitatively different results. Spin-coating is more sensitive to variations in precursor compositions, results in sharper change in the size of surface features. During the spin-coating most of the material, which is applied on the surface, spins off the surface, and the thickness of the precursor layer in which the phase separation occurs, depends on the viscosity. The latter is influenced by both solvent concentration and extent of precursor polymerization. With spraying, the domes tend to be larger in diameter and height due to the larger thickness of precursor left on the surface. The amount of precursor that stays on the substrate is also less influenced by the viscosity of the precursor. Additionally, as observed, some of the surface features formed in case of spray coating were less flattened, in some cases not even to half-sphere geometry. That is the result of

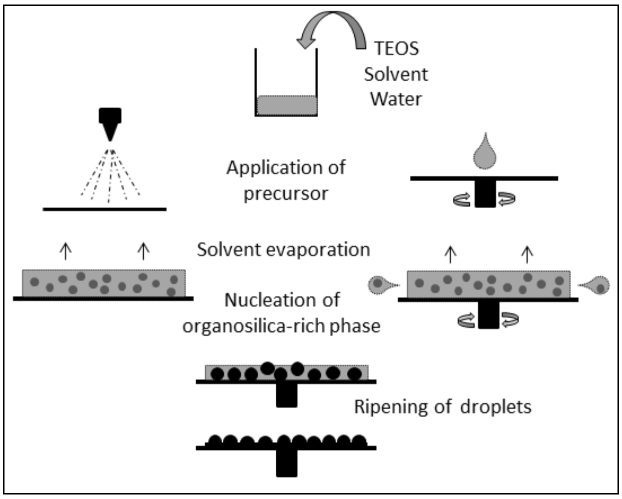

Figure 1. Schematic illustration of used coating processes and formation of surface patterns.

solvent evaporation from the coated layer being slow enough compared to gelling, so that the viscosity of the silica-forming phase preserves the droplet shape once the solvent has fully evaporated.

Varying parameters did not lead to clear linear changes in size and shape. Nevertheless, increase in solvent polarity (propanol < ethanol < methanol) and volatility led to increase in the diameter of the surface features, which varied from about 200 nm to 20 µm. At the same time, the used solvents acted differently in response to varying sol concentration and water-alkoxide molar ratio.

Varying amount of added propanol resulted in decrease in the surface density of structures from 200 to 5 domes per 100 μm^2 as propanol concentration increased due to the lower material amount, which has stayed on the substrate during spin-coating (figure 2a-d). However, dome diameter was not significantly affected and remained about 200 nm. By spraying, there was no such variation in density. As propanol has comparatively low polarity among used solvents, phase separation has not occurred completely, resulting in formed surface featured being covered by thin film layer. As R was varied, there was not noticeable change in dome size or density.

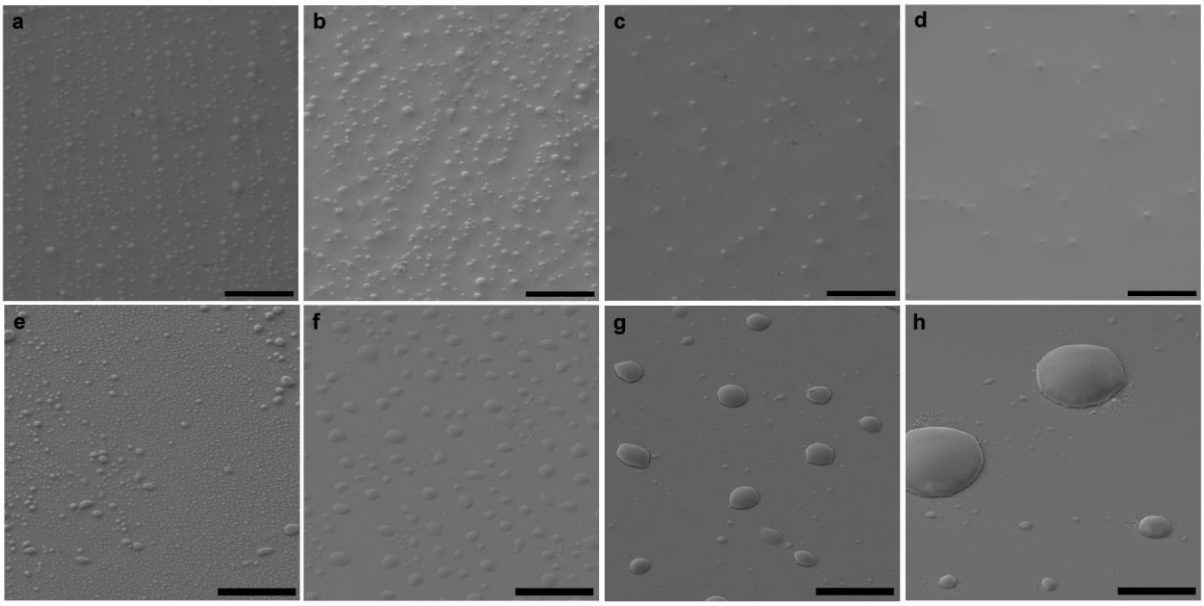

Figure 2. SEM images of series with variation of concentration in propanol (a – d) and methanol (e – h) solutions. Scale bars correspond to 5 µm (a – d) and 20 µm (e – h).

When using ethanol as a solvent, the difference in coating method was clearly seen. Silica structures via spraying were larger in diameter and height compared to the spun films. For example, TEOS:solvent ratio 1:9 with R = 1.2 led to size change of about 10 times (figure 3a,b). Increasing R led to slight increase in the surface density of the structures. With R = 1.6, the most spherical shape features were observed (figure 3c).

Methanol behaved differently as a solvent compared to propanol and ethanol that were relatively similar tendencies. Methanol is the most polar of the three, leading to fast complete phase separation but is also the most volatile so TEOS component has not polymerized significantly by the time the

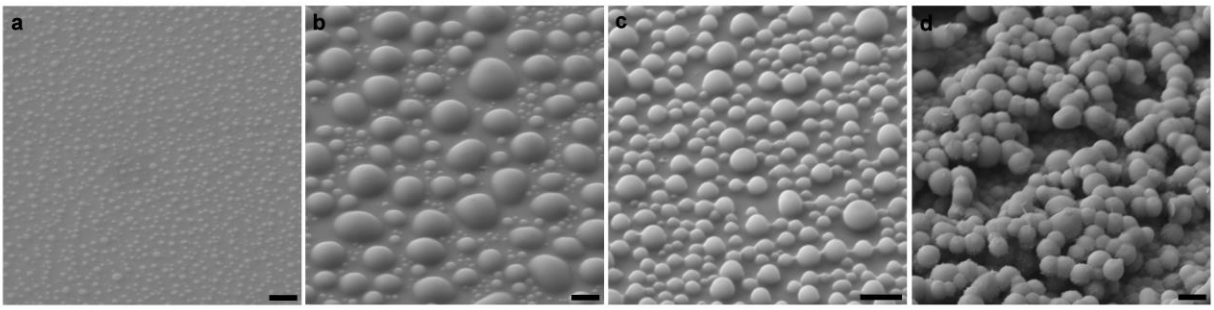

Figure 3. SEM images of silica domes from different series: spin-coated (a) and sprayed (b) structures with ethanol, S = 9, R = 1.2; sprayed structures with ethanol, S = 9, R = 1.6 (c); sprayed structures with ethanol, S = 1, R = 1.2 (d). Scale bars correspond to 2 µm.

solvent has fully evaporated and the still liquid droplets can merge on the substrate. For that reason relatively large surface features or even films were formed by spraying. As TEOS:methanol ratio was varied, spin-coating led to increasing domes as solvent concentration increased (figure 2e-h). Solvent ratio S = 17 also resulted in continuous film.

In most cases WCAs of samples prepared by spraying were higher compared to the spin-coated surfaces. Sprayed coatings with S = 1 and R = 1.2 in ethanol were estimated to have the highest hydrophobicity, with WCA about 131° (figure 3d). However, these cases may be classified as porous films. In case of surfaces patterned with round surface features, 88° WCA was achieved in case of S=9, R=1.6 in ethanol. It is important to point out that the achieved shift towards hydrophobicity is the effect of surface structure only, the surface energy resulting from surface chemistry of prepared substrates is relatively high. To demonstrate that, a film was prepared in a similar fashion using aged TEOS solution in which no phase separation occurred and a smooth film with no detectable roughness was obtained. The WCA was estimated to be 25° in case of that reference sample.

4. Conclusions

Using different coating methods and suitable precursor compositions in sol-gel phase separation surface patterning can be used for preparing round silica surface features with different size, surface density and geometry. Different solvents, concentrations and initial extent of precursor polymerization were used in spray- and spin-coating. Obtained results provide first proof of controllability and potential of phase separation-based surface patterning method in the development of optically functional superhydrophobic structural surface coatings.

Acknowledgments

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References

[1] Sanchez C, Lebeau B, Chaput F and Boilot JP 2003 *Advanced Materials* **15** 1969.
[2] Jeronimo PCA, Araujo AN and Montenegro MCBSM 2007 *Talanta* **72** 13.
[3] Avnir D, Coradin T, Lev O and Livage J 2006 *Journal of Materials Chemistry* **16** 1013.
[4] Purcar V, Stamatin I, Cinteza O, Petcu C, Raditoiu V, Ghiurea M, Miclaus T and Andronie A 2012 *Surface & Coatings Technology* **206** 4449.
[5] Francis LF 1997 *Materials and Manufacturing Processes* **12** 963.
[6] Paerna R, Joost U, Nommiste E, Kaeaembre T, Kikas A, Kuusik I, Kink I, Hirsimaki M and Kisand V 2012 *Physica Status Solidi a-Applications and Materials Science* **209** 953.
[7] Kiisk V, Kangur T, Paalo M, Taette T, Lange S, Pikker S and Sildos I 2011 *Materials Chemistry and Physics* **130** 293.
[8] Timusk M, Jaervekuelg M, Salundi A, Lohmus R, Leinberg S, Kink I and Saal K 2012 *Journal of Materials Research* **27** 1257.
[9] Paalo M, Taette T, Hussainov M, Hanschmidt K, Lobjakas M, Lohmus A, Maeeorg U, Kink I and Iop 2012. Preparation and Characterization of CNT/TiO2 Based Transparent Fiber Electrodes. *International Conference on Functional Materials and Nanotechnologies.*
[10] Saal K, Taette T, Jaervekuelg M, Reedo V, Lohmus A and Kink I 2011 *International Journal of Materials & Product Technology* **40** 2.
[11] Yan YY, Gao N and Barthlott W 2011 *Advances in Colloid and Interface Science* **169** 80.
[12] Nakanishi K and Tanaka N 2007 *Accounts of Chemical Research* **40** 863.
[13] Kajihara K, Kuwatani S, Maehana R and Kanamura K 2009 *Bulletin of the Chemical Society of Japan* **82** 1470.

[14] Ganbavle VV, Bangi UKH, Latthe SS, Mahadik SA and Rao AV 2011 *Surface & Coatings Technology* **205** 5338.
[15] Mahadik SA, Mahadik DB, Kavale MS, Parale VG, Wagh PB, Barshilia HC, Gupta SC, Hegde ND and Rao AV 2012 *Journal of Sol-Gel Science and Technology* **63** 580.
[16] Reemann P, Kangur T, Pook M, Paalo M, Nurmis L, Kink I, Porosaar O, Kingo K, Vasar E, Koks S, Jaks V and Jarvekulg M 2013 *Journal of materials science. Materials in medicine* **24** 783.