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Short communication

OTES modified transparent dip coated silica coatings

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Abstract

The present paper describes the room temperature synthesis of dip coated water repellent silica coatings on glass substrates using octyltriethoxysilane (OTES) as a co-precursor with two-step sol–gel process. Silica sol was prepared by keeping the molar ratio of tetraethylortosilicate (TEOS) precursor, methanol (MeOH) solvent, acidic water (0.001 M oxalic acid) and basic water (12 M NH_4OH) constant at 1:11.03:0.17:0.58 respectively, throughout the experiments and the OTES weight percentage was varied from 0% to 15%. It was found that with an increase in wt% of OTES, the roughness and hydrophobicity of the films increased, however the optical transmission decreased from 93% to 88% in the visible range. The hydrophobic silica films retained their hydrophobicity up to a temperature of 259 °C and above this temperature, the films became hydrophilic. The hydrophobic silica thin films were characterized by taking into consideration the surface roughness studies, Fourier transform infrared (FT-IR) spectroscopy, percentage of optical transmission, scanning electron microscopy (SEM), Thermogravimetric-differential thermal analysis (TG-DTA) and contact angle measurements.

Keywords: Silica coatings; Transparent; Ultrahydrophobic; Dip coating

1. Introduction

Nature is an important source of new techniques and advanced materials. A typical example of this is the creation of superhydrophobic surfaces by bionic copying of the microstructure of lotus leaves [1]. The superhydrophobic behavior of lotus leaves is known as the lotus-leaf effect or self-cleaning effect. The surface of the lotus leaf is textured with 3–10 μm sized hills and valleys that are decorated with nanometer-sized particles of a hydrophobic wax-like material [2]. It has been well established that the wettability of a solid surface is governed by both the surface chemical composition and the surface geometrical microstructures. When rain falls on biological surfaces like lotus leaves, water drops promptly roll off the leaves collecting dirt along the way. Water on such a superhydrophobic surface forms a spherical droplet, and both the contact area and the adhesion to the surface are reduced. Various methods have been engineered employed to generate surfaces that can mimic the structure and chemistry of natural superhydrophobic surfaces [3]. Superhydrophobic surfaces hold considerable promise for various potential applications such as windshields of automobiles, dust-free and self-cleaning surfaces for solar cells, satellite dishes, building walls and roof glasses, photovoltaic, exterior architectural glass and green houses, and so on, have been studied [4,5].

The hydrophilicity of silica films is due to the presence of a large number of Si–OH groups on the surface of the films. Replacement of the Hs from the Si–OH groups by the hydrolytically stable Si–R (where, R = alkyl or aryl) groups through the oxygen bonds prevents the adsorption of water and hence results in the hydrophobic silica surfaces [6,7]. Several researchers have reported that it is possible to combine excellent optical transmission with high water contact angles [8–10]. There are many reports available on the synthesis of hydrophobic silica films by the sol–gel co-precursor method [11–14]. But till date, only a few reports are available on the preparation of water repellent surfaces using TEOS as a precursor [15–19]. In this paper, the preparation of the

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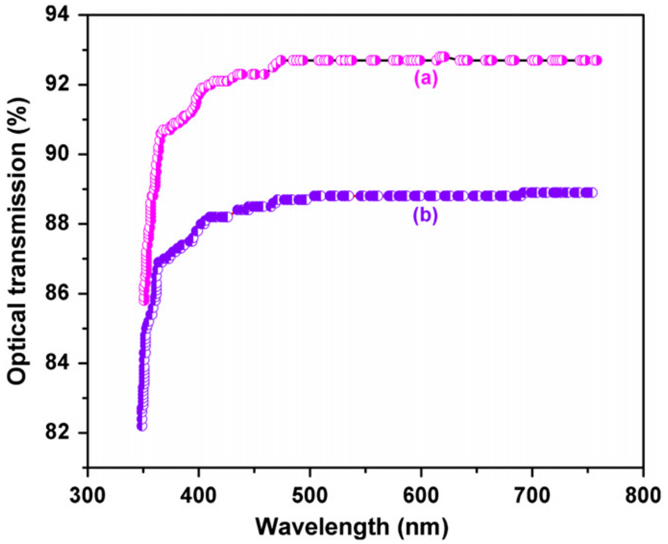


Fig. 1. Optical transmission of silica films (a) for unmodified silica coating and (b) modified with 15% OTES.

ultrahydrophobic surfaces (CA > 120°) by using OTES as co-precursor is reported. The sol–gel technique with simple dip coating method is used to prepare silica films on glass substrates. The aim of this study is to prepare water repellent silica films via the sol–gel process using non-fluorinated additives and to achieve quite similar water repellence like fluorine compounds enables.

2. Experimental

2.1. Materials

The chemicals used were Tetraethoxysilane, octyltriethoxysilane (Sigma-Aldrich Chemie, Germany), methanol (S. D. Fine Chem Ltd, Mumbai, India), oxalic acid (Qualigens Chemie, Mumbai, India) and ammonia (NH_3, Loba Chemie, India). All the reagents were used as received. Double distilled water was used for all experiments. The glass substrates (from BlueStar®, India) of 1.5 cm × 5 cm were used as substrates in all experiments. To get a uniform coating, the glass substrates were soaked in chromic acid overnight, cleaned with detergent and labolene, followed by deionized water and acetone rinses.

2.2. Preparation of silica coatings

The hydrophobic silica coatings are generally produced by two methods:

(i) co-precursor method and
(ii) surface derivatization method.

In the present study, the co-precursor method was used because it is simple and time consuming as compared to the second method. In order to study the effect of octyltriethoxysilane as a hydrophobic agent on the water repellent properties of silica coatings, the silica coatings were synthesized by the sol–gel co-precursor method.

The silica films are synthesized by keeping the molar ratio of TEOS, MeOH, oxalic acid and NH_4OH constant at 1:11.03:0.17:0.58 respectively and the percentage of OTES was varied from 0% to 15%. In the first step of the experiment, TEOS was diluted in the methanol along with the hydrophobic reagent OTES. The acidic water (oxalic acid, 0.001 M) was added to this solution, drop by drop, while stirring (~2 h). In the second step, basic water (ammonium hydroxide, 12 M) was added to the solution, drop-by-drop, while stirring (~10 min), after 12 h of hydrolysis reaction. The homogeneous alcosol thus obtained was transferred to airtight glass test tubes of 14 mm outer diameter and 85 mm height. No protective atmosphere was used for the deposition of silica films. Silica films were deposited at ambient conditions by dip coating (withdrawing speed 5 mm s^{-1}) from freshly made sol prior to gel formation. The films were dried at room temperature (27 °C) for 30 min to produce chemical bonds between the deposited sol and the substrate. The prepared silica films were annealed at 120 °C for 2 h with a ramping rate of 1 °C min^{-1}. The silica films so produced were taken out of the oven, after it was cooled to the ambient temperature.

2.3. Methods of characterization

The roughness of the film was determined by using a surface profilometer (Ambios XP-1 model, India). The contact angle (θ) measurements were carried out to quantify the degree of hydrophobicity using a contact angle meter equipped with a CCD camera (Ramehart Instrument Co., USA) at ambient temperature. A water droplet of 10 μl was placed at three different places on the surface of the film under investigation and the average value was taken as the contact angle (θ) to increase the accuracy in the measurement. The films were also characterized by Fourier transform infrared spectroscopy (FTIR) (Perkin–Elmer, model no. 783, USA), which gave information about various chemical bonds responsible for hydrophobicity, such as O–H, Si–C, C–H, and Si–O–Si. The optical transmittance of the films was measured in the visible wavelength range using a optical spectrophotometer (Systronic 119, USA). Thermogravimetric and differential thermal analyses (TGA and DTA) were used to investigate the stability of the water repellent coatings against temperature. The surface morphology of the silica coatings was studied by means of scanning electron microscopy (JEOL, JEM 6360).

3. Results and discussion

3.1. Reaction mechanism

In the sol–gel process, initially TEOS is hydrolyzed and condensed as per the following chemical reactions:

Hydrolysis:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad (1)$$

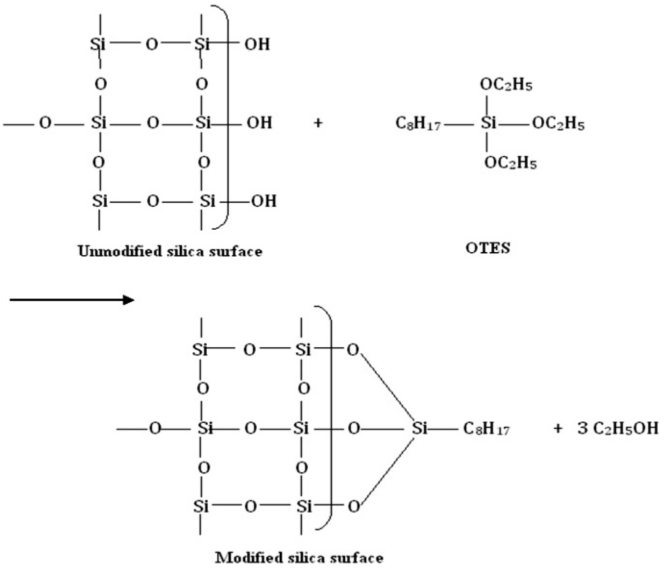
Condensation (water condensation):

$$n\mathrm{Si(OH)_4} \rightarrow n\mathrm{SiO_2} + 2n\mathrm{H_2O} \quad (2)$$

Alcohol condensation:

$$\mathrm{Si(OH)_4} + \mathrm{Si(OC_2H_5)_4} \rightarrow 2\mathrm{SiO_2} + 4\mathrm{C_2H_5OH}. \quad (3)$$

However, using OTES as co-precursor in the sol–gel processing stage, the Hs from the OH groups on the silica clusters are replaced by the hydrolytically stable ≡Si–octyl as per the following chemical reactions:



(4)

However, here we used octyltriethoxysilane co-precursor for the preparation of silica coatings. The hydrophobicity of silica surfaces is due to the attachment of –Si–octyl groups. Hence, as the percentage of OTES in TEOS increases then the hydrophobicity of silica coatings also increased.

3.2. Gelation time and optical transparency

Gelation time of the sol is determined by a simple laboratory method [20]. Table 1 shows the effect of the OTES percentage in TEOS on the gelation time of the silica alcosols. As the percentage of OTES have been increased from 0% to 15%, the gelation time considerably increased from 5 min to 3 h 15 min. It has been reported that the gelation time increases with the increase in the quantity of the hydrophobic reagents [21,22]. This is because, under the basic conditions, the co-precursor, OTES, hydrolyzes slowly than the TEOS precursor. Hence, with the increase in percentage of OTES, the hydrolysis and the subsequent condensation reactions takes place slowly, leading to longer gelation. Fig. 1 shows the percentage of optical transmission of the silica films for pure and OTES modified silica coatings. The silica films obtained with 0% were most transparent (93%) while the transparency gradually reduced to (88%) for 15% OTES modified silica coatings.

3.3. Roughness and contact angle measurement

According to Young's equation [23], the contact angle needs to increase accordingly to balance the enlarged surface energy between the solid substrate and the liquid droplet:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (5)$$

where, γ_{sl}, γ_{lv} and γ_{sv} are the interfacial tensions between the solid and the liquid, the liquid and the vapor, and the solid and the vapor, respectively.

Two different models were suggested to explain the increase in contact angle on the rough surface. Wenzel had modified the Young's equation as in the following [24]:

$$\cos\theta' = \frac{r(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} = r\cos\theta \quad (6)$$

where r is a roughness factor, which is defined as the ratio of the actual area of a rough surface to the geometric

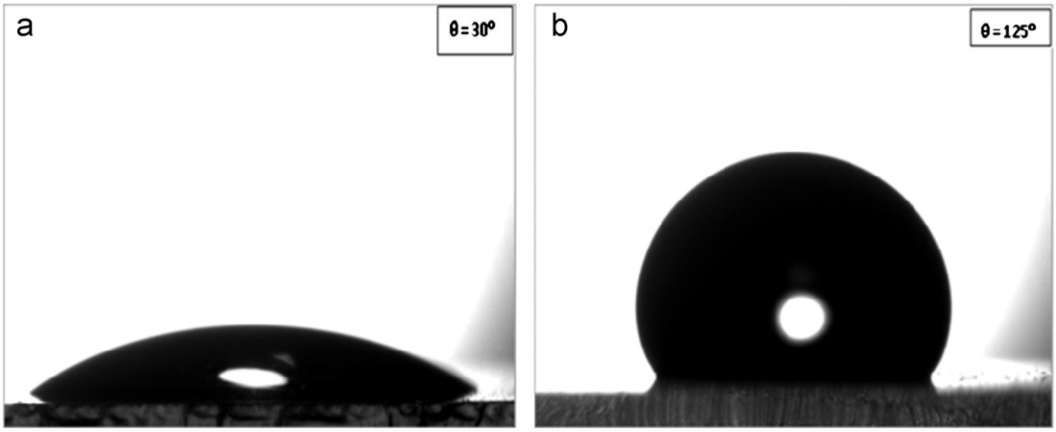


Fig. 2. Shape of water droplet on the silica films (a) unmodified and (b) modified with 15 wt% of OTES.

Table 1
Effect of wt% of OTES on the gelation time, roughness and contact angle of silica coatings.

Percentage of OTES (wt%)	Gelation time (min)	Roughness (nm)	Contact angle ($\theta \pm 2°$)
0	5	79.1	30
2.5	23	128.2	70
5	70	168.7	97
7.5	106	215.6	115
10	150	263.4	121
15	195	323.1	125

projected area. This law is applicable if there is no air entrapped in the pits of the rough surface below the liquid.

In contrast, Parrill [25] proposed an equation.

$$\cos\theta' = f\cos\theta + f - 1 \quad (7)$$

where f is the area fraction of the liquid–solid contact to the projected surface area. This law describes the contact angle θ^* for a surface trapping air below the water droplet in the hollows of a rough surface, so the droplet essentially rests on a layer of air.

Table 1 shows an increase in the roughness of the film surface with increase in percentage of co-precursor. The octyl groups present in the OTES contribute to the enhancement of surface roughness of the film. The water contact angle values are also increased with an increase in the surface roughness of the films.

To evaluate the hydrophobic properties of the silica films, the contact angle (θ) of the water droplet with surface of the films prepared with various percentage of co-precursors has been measured. It is found that θ increased with increase in percentage of co-precursor. As prepared silica films with 0 wt% of OTES contain a large number of hydroxyl and alkoxy groups which are responsible for the hydrophilic character ($\theta = 30°$) of the film surface. However, using OTES as co-precursor in the sol–gel processing stage, the OH groups are replaced by hydrolytically stable O–Si–octyl group as shown in the condensation reactions (3) and (4). The film surface becomes hydrophobic because of the hydrolytic stability of Si–C bonds. The water drop displayed a comparatively large contact angle (125°) on the OTES modified silica films compared with the contact angle (30°) on unmodified silica films as shown in Fig. 2. This result can be explained by the Wenzel's equation, which indicates that the water contact angle of the surface increases with increasing surface roughness when the surface is composed of hydrophobic materials. The effect of humidity on the wetting properties of OTES modified (15 wt%) films were carried out at a relative humidity of 85% at 30 °C over 40 days. After 30 days of storage in humidity, the values of the water contact angle remained essentially constant, indicating that the surface has long term durability.

3.4. FTIR studies and contact angle measurement

The chemical composition of the dip coated silica films on the glass substrates was investigated by the FT-IR spectroscopy using the KBr method in the transmission mode. Fig. 3 shows the FT-IR spectra of unmodified and OTES modified (15%) silica films, respectively. In Fig. 3(a) and (b), the peaks at 1084 cm^{-1} and 1091 cm^{-1} are associated with the transverse optical vibration mode corresponding to the asymmetric stretching of the inter-tetrahedral oxygen atoms in the Si–O–Si linkage [26]. The presence of this peak confirms the formation of a network structure inside the film. The relative intensity of this peak compared to densified glasses or sol–gels, suggests that the compressive stress in the sample is low, and that the silica network is comparatively stiff [27]. The OTES modified silica film confirmed the absorption band at 2930 cm^{-1} corresponding to asymmetric stretching vibrations of C–H bonds. The peaks at around 1600 cm^{-1} and the broad absorption band at around 3425 cm^{-1} are due to the –OH groups [28]. On the other hand, in Fig. 3(a) and (b), the development of sharp bands at 838 cm^{-1} corresponding to the rocking vibrations of Si–C bonds which are reported elsewhere [28]. For unmodified silica films, less intense C–H absorption peak at 2950 cm^{-1} is observed while at 1600 cm^{-1} and 3400 cm^{-1} more broad O–H peaks are observed indicating the hydrophilic nature of the silica film. It can be seen from the FTIR spectra that with an increase in percentage of co-precursors, the intensity of the

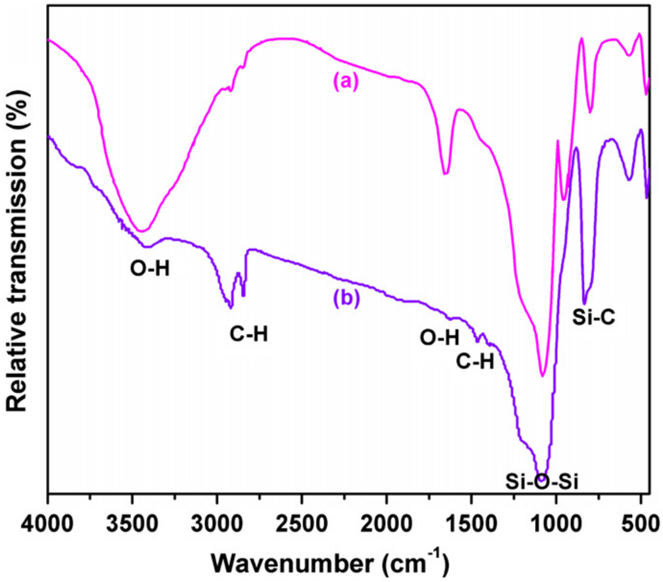


Fig. 3. FTIR spectra of (a) unmodified silica film (b) modified with 15% OTES.

C–H absorption peaks and the Si–C absorption peak increased, clearly indicating the replacement of surface H from the Si–OH groups by the nonhydrolyzable ≡Si–octyl groups and hence an increase in the hydrophobicity of the films.

3.5. Surface morphological studies

The morphological study of OTES modified (15 wt%) silica coating is carried out by using SEM micrographs. Fig. 4(a) and (b) shows the SEM images of unmodified and OTES modified silica coatings respectively. The microstructure of the modified silica film shows the uniform porous surface morphology for unmodified and OTES modified silica coatings respectively. This porous morphology tends to trap the air in the pores of the film contributing to the easy rolling of water drop off the surface. This strongly implies that the contact model of a water droplet on the OTES modified silica films is due to the Cassie–Baxter's model.

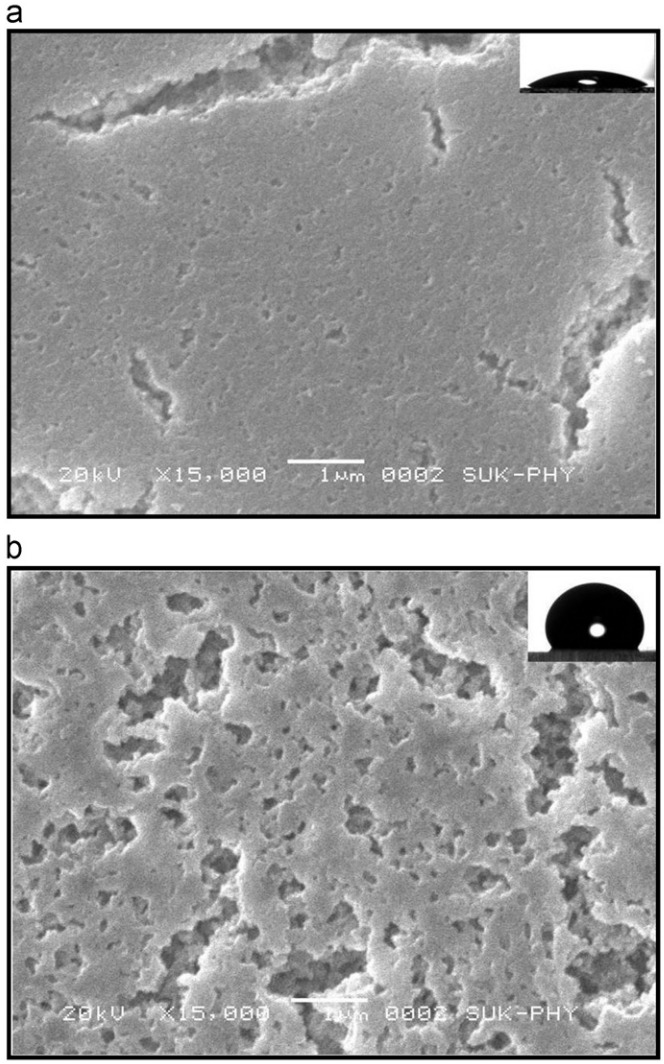


Fig. 4. (a) SEM micrograph of unmodified (0% modified) silica films (b) SEM micrograph of 15% OTES modified silica films.

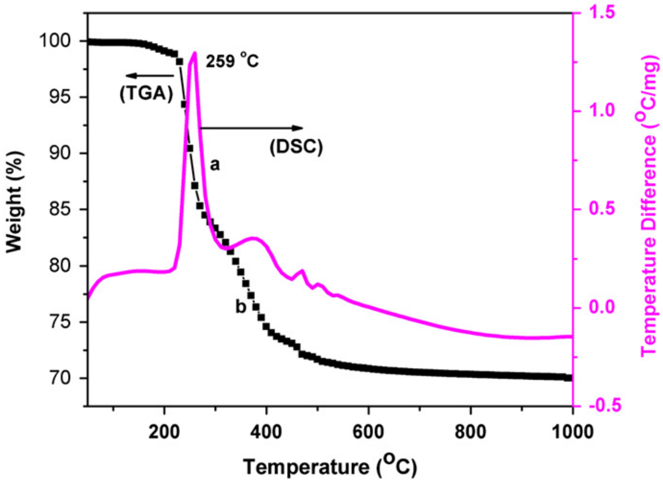


Fig. 5. TG-DSC measurement of 15% OTES modified silica film.

3.6. Thermal stability analysis

Fig. 5 shows the TGA–DSC curve for coatings material. In such case, TGA–DSC analysis is carried out at a rate of 10 °C/min under an oxygen atmosphere up to 1000 °C. In Fig. 5 the exothermic peak is observed at temperature 259 °C that causes sudden weight loss corresponding to the oxidation of surface organic $-CH_3$ groups present in material with oxidation [29]. In case of OTES modified silica coatings the thermal stability of the coating is more as shown in Fig. 5 in which the exothermic peak is observed at 259 °C corresponding to the oxidation of surface $-CH_3$ groups. The OTES modified coating is hydrophobic up to 259 °C and after this temperature the coatings becomes hydrophilic in nature.

4. Conclusions

The TEOS based uniform porous, ultrahydrophobic silica films were obtained using OTES as the co-precursor by the two-step sol–gel process on a glass substrate. These films are optically transparent, thermally stable, and highly durable against humidity. The highest water contact angle of 125° is obtained for OTES modified coatings (15 wt%). The hydrophobicity of the as-prepared silica films was enhanced by increasing the roughness of the surface with increasing OTES weight percentage in silica sol. The FTIR spectra showed an increase in the intensity of Si–C and C–H peaks and decrease in the intensity of O–H peaks with increase in percentage of OTES, which clearly indicate the increased chemical modification of the silica surface by the organic groups. By modification of silica sols OTES, sol–gel coatings could be prepared on glass substrates at room temperature owning to excellent water repellent properties without any addition of fluorine containing compounds. Therefore, the films could find application as self-cleaning windshields of automobiles, in which a high transmission of visible light is desirable.

Acknowledgments

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References

[1] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination inbiological surfaces, Planta 202 (1997) 1.

[2] A. Nakajima, K. Hashimoto, T. Watanabe, Recent studies on superhydrophobic films, Monatshefte Fur Chemie 132 (2001) 31.

[3] H. Tada, H. Nagayama, Chemical vapor surface modification of porous glass, Langmuir: The ACS Journal of Surfaces and Colloids 11 (1) (1995)136 11 (1) .

[4] X.J. Feng, L. Jiang, Design and creation of superwetting/antiwetting surfaces, Advanced Materials 18 (2006) 3063.

[5] J.D. Mackenzie, E.P. Bescher, Physical properties of sol–gel coatings, Journal of Sol–Gel Science and Technology 19 (2000) 23.

[6] M. Guglielmi, Sol–gel coatings on metals, Journal of Sol–Gel Science and Technology 8 (1997) 443.

[7] A.V. Rao, D. Haranath, Effect of methytrimethoxysilane as a synthesis component on the hydrophobicity and some physical properties of silica aerogels, Microporous and Mesoporous Materials 30 (1999) 267.

[8] H. Yokogawa, M. Yokoyama, Hydrophobic silica aerogels, Journal of Non-Crystalline Solids 186 (1995) 23.

[9] H. Yabu, M. Shimomura, Single-step fabrication of transparent superhydrophobic porous polymer, Films and Chemical Materials 17 (21) (2005) 5231.

[10] G. Gu, H. Dang, Z. Zhang, Z. Wu, Fabrication and characterization of transparent superhydrophobic thin films based on silica nanoparticles, Applied Physics A 83 (2006) 131.

[11] A. Hozumi, O. Takai, Preparation of silicon oxide films having a water-repellent layer by multi-step microwave, Thin Solid Films 334 (1998) 54.

[12] S.S. Latthe, H. Hirashima, A.V. Rao, TEOS based water repellent silica films obtained by a co-precursor sol–gel method, Smart Materials and Structure 18 (2009) 095017.

[13] W.A. Daoud, J.H. Xin, X. Tao, Superhydrophobic silica nanocomposite cooling by a low temperature process, Journal of the American Ceramic Society 87 (9) (2004) 1782.

[14] S.S. Latthe, D.Y. Nadargi, A.V. Rao, TMOS based water repellent silica thin films by co-precursor method using TMES as a hydrophobic agent, Journal of Applied Surface Science 255 (2009) 3600.

[15] H.M. Shang, Y. Wang, K. Takahashi, G.Z. Cao, D. Li, Y.N. Xia, Nanostructured superhydrophobic surfaces, Journal of Materials Science 40 (2005) 3587.

[16] N. Khummalai, V. Boonamnuayvitaya, Suppression of arsenopyrite surface oxidation by sol–gel coatings, Journal of Bioscience and Bioengineering 99 (2005) 277.

[17] Y. Liu, X. Chen, J.H. Xin, Super-hydrophobic surfaces from a simple coating method: a bionic nanoengineering approach, Nanotechnology 17 (2006) 3259.

[18] S. Smitha, P. Shajesh, P. Mukundan, T.D.R. Nair, K.G.K. Warrier, Colloids and Surfaces B: Biointerfaces 55 (2007) 38.

[19] B.R. Kim, J.W. Kang, K.Y. Lee, J.M. Son, M.J. Ko, Physical properties of low-k films based on the co-condensation of methyltrimethoxysilane with a bridged silsesquioxane, Journal of Materials Science 42 (2007) 4591.

[20] D. Boschel, H. Roggendorf, Synthesis of biocompatible hydrophobic silica–gelatin nano-hybrid by sol–gel process, Journal of Sol–Gel Science and Technology 25 (2002) 191.

[21] A.V. Rao, G.M. Pajonk, Effect of methyltrimethoxysilane as a co-precursor on the optical properties of silica aerogels, Journal of Non-Crystalline Solids 285 (2001) 202.

[22] T. Young, An essay on the cohesion of fluids, Philosophical Transactions of the Royal Society 95 (1805) 65.

[23] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Industrial and Engineering Chemistry 28 (1936) 988.

[24] A.B.D. Cassie, S. Baxter, Wettability of solid surfaces, Transactions of the Faraday Society 40 (1944) 546.

[25] T.M. Parrill, Transmission infrared study of acid-catalyzed sol–gel silica coatings during room ambient drying, Journal of Materials Research 7 (1992) 2230.

[26] A.V. Rao, R.R. Kalesh, G.M. Pajonk, Hydrophobicity and physical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component, Journal of Materials Science 38 (2003) 4407.

[27] J.K. Hong, H.R. Kim, H.H. Park, Thin Solid Films 332 (1998) 449.

[28] B.E. Yoldas, Modification of polymer–gel structures, Journal of Non-Crystalline Solids 63 (1984) 145.

[29] M.S. Kavale, D.B. Mahadik, V.G. Parale, P.B. Wagh, S.C. Gupta, H.C. Barshilia, Optically transparent, superhydrophobic methyltrimethoxysilane based silica coatings without silylating reagent, Applied Surface Science 258 (2011) 1548.