CHAPTER 7

Synthesis of TEOS based transparent and hydrophobic silica coatings by sol-gel process

7.1 Introduction

Hydrophobic surfaces with static water contact angle higher than 150° and a sliding angle close to 8° generated a lot of research interest both in academia and in industry because of the self-cleaning properties. In 1997, Barthlott and Neinhuis showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and hydrophobicity [1]. Hydrophobicity is a property that provides water repellency and non-wettability of a solid surface. The fabrication of hydrophobic coatings is an active area of research in recent years because of its wide range of applications, such as windshields of automobiles, dust-free and self-cleaning surfaces for solar cells, satellite dishes, building walls and roof glasses, photovoltaic’s, exterior architectural glass and green houses, heat transfer surfaces in air conditioning equipment and so on [2–4]. Various methods have been employed to generate engineering surfaces that can mimic the structure and chemistry of natural superhydrophobic surfaces [5]. Sol–gel derived coatings have been found to be useful for several applications mainly due to the ease of solution based processing and the synthesis flexibility, which can be used for forming a wide range of thin films and coatings [6, 7].

In general, the sol–gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a semi-solid “gel” phase. The dip coating method is a novel and facile route for the synthesis of transparent and uniform films by the sol–gel process. The sol–gel technique with simple dip coating method is used to prepare silica films on glass substrates [8–11] and the formation of nonfluorinated superhydrophobic surfaces at low temperatures is important for the fabrication of environment friendly coatings. Xiu et al. [12] prepared superhydrophobic durable self-cleaning silica films by the incorporation of isobutyl-trimethoxysilane into tetramethoxysilane causing hydrophobic isobutyl groups to be present on the film surface, thus generating surface hydrophobicity. Tadanaga et al. [13] reported the formation of transparent superhydrophobic films on glass plates through the sol–gel method by the combination
of microstructural and chemical approaches. 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 H 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 [14, 15].

In the last four chapters, we have been discussed about the synthesis, characterization and various properties of silica aerogels. The present chapter deals with synthesis of hydrophobic and transparent coatings using organosilane compounds. There are many reports available on the synthesis of hydrophobic silica films by sol–gel co-precursor method [16-19] but till date, only a few reports are available on the preparation of water repellent surfaces using TEOS as a precursor [20–23]. In this paper, the preparation of the hydrophobic surfaces (CA > 120°) by using PTMS and OTES as co-precursors are reported. 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.

7.2 Experimental

7.2.1 Chemicals

The chemicals used were Tetraethoxysilane, phenyltrimethoxysilane, octyltriethoxysilane (Sigma-Aldrich Chemie, Germany), methanol (s.d.fine –chem ltd, Mumbai) and ammonia (NH₃, 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.

7.2.2 Preparation of silica coatings

The hydrophobic silica coatings are generally produced by two methods:
(i) Co-precursor method
(ii) Surface derivatization method

In the present study, the co-precursor method was used because it is simple and time consuming as compared to second method. In order to study the effect of phenyltrimethoxysilane and 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.
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The silica films are synthesized by keeping the molar ratio of TEOS, MeOH, oxalic acid and NH₄OH constant at 1:11.03:0.17:0.58 respectively and the percentage of PTMS and OTES were varied from 0 wt% to 15 wt%. In the first step of the experiment, TEOS was diluted in the methanol along with the hydrophobic reagent, PTMS. The acidic water (oxalic acid, 0.001 M) was added to this solution, drop by drop, while stirring (~2 hour). 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 alcocol 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 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. The same procedure is carried out for OTES, only PTMS is replaced by OTES.

7.3 Results and Discussion

7.3.1 Reaction Mechanism

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

Hydrolysis:

\[ \text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH} \] (7.1)

Condensation:

Water condensation:

\[ n\text{Si(OH)}_4 \rightarrow n\text{SiO}_2 + 2n\text{H}_2\text{O} \] (7.2)

Alcohol condensation:

\[ \text{Si(OH)}_4 + \text{Si(OC}_2\text{H}_5)_4 \rightarrow 2\text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH.} \] (7.3)

However, using PTMS and OTES as co-precursors in the sol–gel processing stage, the Hs from the OH groups on the silica clusters are replaced by the hydrolytically stable ≡Si–phenyl and ≡Si–octyl as per the following chemical reactions:
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\[
\begin{align*}
\text{Unmodified silica surface} & \quad \text{PTMS} \\
\end{align*}
\]

\[
\begin{align*}
\text{Modified silica surface} \\
\end{align*}
\]

(7.4)

\[
\begin{align*}
\text{Unmodified silica surface} & \quad \text{OTES} \\
\end{align*}
\]

(7.5)
However, here we used phenyltrimethoxysilane and octyltriethoxysilane co-precursors for the preparation of silica coatings. The hydrophobicity of silica surfaces is due to the attachment of -Si-phenyl and -Si-octyl groups. Hence, as the percentage of each co-precursor in TEOS increases then the hydrophobicity of silica coatings also increased.

### 7.3.2 Gelation time and optical transparency

Gelation time of the sol is determined by a simple laboratory method [24]. Table 7.1 shows the effect of the PTMS and OTES percentage in TEOS on the gelation time of the silica alcosols. As the percentage of both co-precursors have been increased from 0 to 15 wt%, the gelation time considerably increased from 5 min to 5 h 20 min for PTMS and 5 min to 3 h 15 min for OTES modified coatings. It has been reported that the gelation time increases with the increase in the quantity of the hydrophobic reagents [25, 26]. This is because, under the basic conditions, the co-precursors, PTMS and OTES, hydrolyses slowly than the TEOS precursor. Hence, with the increase in PTMS and OTES co-precursors the hydrolysis and the subsequent condensation reactions are takes place slowly, leading to longer gelation. Fig. 7.1 shows the percentage of optical transmission of the silica films for pure, PTMS and OTES modified silica coatings. The silica films obtained with 0% were most transparent (93%) while the transparency gradually reduced to 86% for 15 wt% OTES and 82 % for 15 wt% PTMS modified silica coatings.

<table>
<thead>
<tr>
<th>Percentage of PTMS (wt%)</th>
<th>Gelation time (min)</th>
<th>Percentage of OTES (wt%)</th>
<th>Gelation time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
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<td>5</td>
</tr>
<tr>
<td>2.5</td>
<td>30</td>
<td>2.5</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>7.5</td>
<td>160</td>
<td>7.5</td>
<td>106</td>
</tr>
<tr>
<td>10</td>
<td>205</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>15</td>
<td>320</td>
<td>15</td>
<td>195</td>
</tr>
</tbody>
</table>

**Table 7.1: Effect of wt % of PTMS and OTES on the gelation time**
Fig. 7.1 Optical Transmission of silica films (A) For unmodified silica coating, (B) modified with 15 wt% OTES and (C) modified with 15 wt% PTMS

<table>
<thead>
<tr>
<th>Percentage of PTMS (wt %)</th>
<th>Roughness (nm)</th>
<th>Contact Angle (θ±2°)</th>
<th>Percentage of OTES (wt %)</th>
<th>Roughness (nm)</th>
<th>Contact Angle (θ±2°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>79.1</td>
<td>30</td>
<td>0</td>
<td>79.1</td>
<td>30</td>
</tr>
<tr>
<td>2.5</td>
<td>131.0</td>
<td>84</td>
<td>2.5</td>
<td>128.2</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>200.4</td>
<td>112</td>
<td>5</td>
<td>168.7</td>
<td>97</td>
</tr>
<tr>
<td>7.5</td>
<td>288.7</td>
<td>128</td>
<td>7.5</td>
<td>215.6</td>
<td>115</td>
</tr>
<tr>
<td>10</td>
<td>390.4</td>
<td>132</td>
<td>10</td>
<td>263.4</td>
<td>121</td>
</tr>
<tr>
<td>15</td>
<td>456.3</td>
<td>133</td>
<td>15</td>
<td>323.1</td>
<td>125</td>
</tr>
</tbody>
</table>

Table 7.2: Effect of wt% of PTMS and OTES on Surface roughness and Contact angle

7.3.3 Roughness and Contact angle measurement

According to Young’s equation [27], the contact angle needs to increase accordingly to balance the enlarged surface energy between the solid substrate and the liquid droplet.

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  

(7.6)
where, $\gamma_{sl}$, $\gamma_{lv}$ and $\gamma_{sv}$ 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 [28]:

$$\cos \theta = \frac{r(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} = r \cos \theta$$  \hspace{1cm} (7.7)

Where, r is a roughness factor, which is defined as the ratio of the actual area of a rough surface to the geometric projected area. This law is applicable if there is no air entrapped in the pits of the rough surface below the liquid.

In contrast, Cassie and Baxter [29] proposed an equation:

$$\cos \theta' = f \cos \theta + f - 1$$  \hspace{1cm} (7.8)

Where, f is the area fraction of the liquid–solid contact to the projected surface area. This law describes the contact angle $\theta^*$ 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 7.2 shows an increase in the roughness of the film surface with increase in percentage of co-precursors. The phenyl and octyl groups present in the PTMS and OTES respectively 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.

Fig. 7.2(a) Shape of water droplet on the unmodified silica films
Fig. 7.2(b) Shape of water droplet on the silica films modified with 15 wt% of OTES

Fig. 7.2(c) Shape of water droplet on the silica films modified with 15 wt% of PTMS

To evaluate the hydrophobic properties of the silica films, the contact angle (θ) of the 5µl water droplet with surface of the films prepared with various percentage of co-precursors have been measured. It is found that θ increased with increase in percentage of co-precursor. Fig. 7.2(a-c) shows water drop contact angle images on unmodified, OTES modified and PTMS modified silica coatings. The as prepared silica films with 0 wt% of PTMS and OTES contain a large number of hydroxyl and alkoxy groups which are responsible for the hydrophilic character (θ = 30°) of the film surface. However,
using PTMS and OTES as co-precursors in the sol–gel processing stage, the OH groups are replaced by hydrolytically stable O–Si–phenyl and O–Si–octyl groups as shown in the condensation reactions (7.4) and (7.5). The film surface becomes hydrophobic because of the hydrolytic stability of Si–C bonds. The water drop displayed a comparatively large contact angle (135°) and (125°) on the PTMS and OTES modified silica films compared with the contact angle (30°) on unmodified silica films with increase in surface roughness. This result can be explained by the Wenzel 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 PTMS modified (15 wt%) and 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.

7.3.4 FTIR spectroscopy studies

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. 7.3 shows the FT-IR spectra of unmodified, PTMS modified (15 wt%) and OTES modified (15 wt%) silica films, respectively. In Fig. 7.3(b) and (c), 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 intertetrahedral oxygen atoms in the Si-O-Si linkage [30]. 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 [30]. The PTMS modified silica film confirmed the absorption band at 2983 cm\(^{-1}\) corresponding to asymmetric stretching vibrations of C-H bonds. Also in case of OTES modified silica film asymmetric stretching vibrations of C-H bonds are at 2930 cm\(^{-1}\). The development of sharp and intense band at 1430 cm\(^{-1}\), corresponding to symmetric deformation or vibration of Si-phenyl bonds, represents phenyl groups get attached to silicon atoms as shown in Fig. 7.3 (b) [31]. The peaks at around 1600 cm\(^{-1}\) and the broad absorption band at around 3425 cm\(^{-1}\) are due to the -OH groups [32]. On the other hand, in Fig 7.3 (b) and (c), the development of sharp bands at 837 and 838 cm\(^{-1}\) corresponding to the rocking vibrations of Si-C bonds which are reported elsewhere [32].
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 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 \(\equiv\text{Si–phenyl}\) and \(\equiv\text{Si–octyl}\) groups and hence an increase in the hydrophobicity of the films.

### 7.3.5 Surface morphological studies

The morphological study of unmodified, PTMS modified (15 wt %) and OTES modified (15 wt %) silica coatings has been carried out by using SEM micrographs. Fig. 7.4(a), (b) and (c) shows the SEM images of unmodified, PTMS and OTES modified silica coatings respectively. The microstructure of the unmodified silica coating shows the uniform, less dense and porous surface morphology as shown in Fig. 7.4(a). The silica coatings modified with PTMS shows highly dense morphology and pore sizes ranging from 100 to 150 nm, whereas for OTES modified silica coatings shows porous morphology having pore diameter 200 to 270 nm distributed on substrate. 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 PTMS and OTES modified silica films due to the Cassie–Baxter’s model.

Fig. 7.4(a) SEM image for unmodified silica coating

Fig. 7.4(b) SEM image for 15 wt% PTMS modified silica coating
7.3.6 Thermal stability analysis

The Fig. 7.5(a) and (b) shows the TG-DTA curve for coatings material. In such case, TG-DTA analysis carried out at rate 10 °C/min under an oxygen atmosphere up to 1000 °C. In Fig. 7.5(a) the exothermic peak is observed at temperature 259 °C causes sudden weight loss corresponding to the oxidation of surface organic -CH₃ groups present in material with oxidation [33]. In case of PTMS modified silica coatings the thermal stability of the coating is more as shown in Fig.7.5(b) in which the exothermic peak is observed at 386 °C corresponding to the oxidation of surface –CH₃ groups. The PTMS modified coating is hydrophobic up to 386 °C whereas in case of OTES modified sample it is 259 °C and after this temperature the coatings becomes hydrophilic in nature.
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Fig. 7.5(a) TG-DTA of 15 wt% PTMS modified silica coatings

Fig. 7.5(b) TG-DTA of 15 wt% OTES modified silica coatings
References:

[27] T. Young, Phil. Trans. R. Soc., 95 (1805) 65.


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