Silica-based superhydrophobic coating by a single-step process

Adhimoolam Bakthavachalam Kousaalya BTech
Department of Metallurgical and Materials Engineering, Materials Processing Section, Indian Institute of Technology Madras (IIT-Madras), Chennai, India

Nitish Garg MTech
Department of Metallurgical and Materials Engineering, Materials Processing Section, Indian Institute of Technology Madras (IIT-Madras), Chennai, India

Ravi Kumar PhD*
Associate professor, Department of Metallurgical and Materials Engineering, Materials Processing Section, Indian Institute of Technology Madras (IIT-Madras), Chennai, India

Silica-based superhydrophobic coatings were produced on glass substrate by dip-coating process. Colloidal solutions containing nanoparticles of silica synthesized via seed growth method (single- and dual-sized particles) and dispersed in three different solvents, ethanol, silica sol and acidic silica sol, were used. Coatings with dual-sized particles in ethanol showed superhydrophobicity with a water contact angle of 155°. The coating adhesion was improved with the use of acidic silica sol as solvent. Coatings prepared from colloidal solution containing 30 wt.% of dual-sized silica particles of 600 and 800 nm in acidic silica sol, showed hydrophilicity with water contact angle of 45° before heat treatment due to the presence of –OH groups from acidic sol. After heat treatment at 250°C for 2 h in atmospheric ambience, the –OH groups reacted to form cross-linked Si-O-Si resulting in superhydrophobicity of the coating with water contact angle of 147°. In this work, silica based superhydrophobic coating was fabricated by adjusting the ratios of the dual-sized silica particles without carrying out any secondary step such as chemical modification or fluorination process on the coating.

1. Introduction
Nature exhibits excellent superhydrophobic surfaces with a high contact angle (CA) of greater than 150° in certain plant leaves such as lotus leaves, rice leaves and butterfly wings, cicada wings, which are self-cleaning. This has attracted immense research interest to biomimic and fabricate artificial superhydrophobic surfaces, which are used for numerous applications such as window glasses, solar cell panels, energy conversion and conservation and navigation of ships to prevent marine fouling.

In the process of preparing superhydrophobic surfaces, a good control over chemistry coupled with geometry similar to hierarchical geometrical surface structures found in nature are used. For instance, (i) producing geometrically controlled rough surfaces of any material and reducing its surface energy by the addition of low surface energy materials or (ii) tailoring the low surface energy material, by creating roughness at micro/nano scales would achieve the objective.

Extensive research has focused on producing superhydrophobic coating by using the former (i) method. Table 1 provides details of coated material systems, and the method used for coating along with the achieved CA. In all the cases, superhydrophobicity was achieved only due to chemical modification of the coatings using low surface energy materials such as fluorine and silicone polymer. However, in the case of producing superhydrophobic coating via the later (ii) fluorine- and silicone-based polymers play an important role. The use of fluorine- and silicone-based materials for superhydrophobic coating...
is primarily due to the low surface-free energy exhibited by them. In general, the surface energy of polymers is typically lesser than water ($72 \cdot 2 \text{ mJ/m}^2$) due to the presence of organic groups, while the lowest is for fluorine-based polymers ($12 \cdot 4 \text{ mJ/m}^2$ for polyhexafluoropropane, $19 \cdot 1 \text{ mJ/m}^2$ for polytetrafluoroethylene) and silicone-based polymers ($22 \text{ mJ/m}^2$ for polydimethylsiloxane). Fluorination of silicone polymer will further reduce the surface energy of the material.

While nature exhibits superhydrophobicity due to the presence of waxes containing predominantly $-\text{CH}_2-$ groups (whose surface energy is lower than water), concomitant with surface roughness at nanoscale, it is reasonable to fabricate low surface energy material with hierarchical nanostructure to achieve superhydrophobicity.

Hence, to obtain superhydrophobic surfaces, materials with surface energy lesser than water are generally used, which contain toxic chemicals such as fluorine and involve multiple steps in producing the coatings. Development of superhydrophobic surfaces with eco-friendly chemicals is required and with a single-step process, that can be made more economical. The current work focuses on developing such a silica-based superhydrophobic coating using simple dip-coating process with good adhesion, in a single-step process without any additional processes like fluorination or any type of chemical modification, to reduce the surface energy of the coating. The ability to alter the particle size distribution helps in introducing nanoscale roughness on the coating resulting in superhydrophobicity.

### 2. Experimental methods

#### 2.1 Synthesis of silica particles

Silica particles were synthesized by the hydrolysis of tetraethyl ester of orthosilicic acid (TEOS): $\text{Si(OC}_2\text{H}_5)_4$ (Alfa Aesar, USA) in ethanol, using ammonia as catalyst, by the following reaction, better known as seed growth method or “Stöber process.”

$$\text{Si(OCH}_2\text{H}_5)_4 + \text{H}_2\text{O} \rightarrow \text{Si(O)C}_2\text{H}_5 + 4\text{C}_2\text{H}_5\text{OH}$$

Silica seed sol was first synthesized by adding 1-g TEOS, 3-g water and 3-g ammonia in 4-g ethanol, followed by continuous stirring at room temperature (25 °C) for 1.5 h. Subsequently, a solution of 2-g TEOS in 8-g ethanol was added to the reaction mixture and stirred for 3 h as explained by Xu et al.”

#### Table 1. Silica-based coatings with various types of surface modification to achieve superhydrophobicity.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Material used for coating</th>
<th>Method</th>
<th>Maximum contact angle achieved</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silica prepared from Stöber process coated and modified with FAS</td>
<td>Colloid assembly method</td>
<td>160°</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Two different sizes of modified silica, coated and modified with polydimethylsiloxane layer</td>
<td>Drop coating</td>
<td>155°</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Polyelectrolyte/silica nanoparticle multilayers, followed by fluoroalkysilane treatment</td>
<td>Electrostatic layer-by-layer assembly</td>
<td>157°</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>Silica-polystyrene sol-gel coated and modified with FAS</td>
<td>Dip coating</td>
<td>160°</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Silane (METES and METES/DECYS) precursor with silica particles</td>
<td>Spin coating</td>
<td>158·3°</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>Colloidal silica particles and fluoroalkysilane in TEOS</td>
<td>Spin coating</td>
<td>150°</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>TEOS/MTMS in different ratios</td>
<td>Dip coating</td>
<td>135°</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>Silica nanoparticles coated and modified with tridecafluoro-1,1,2,2-tetrahydroxydimethylsilicone</td>
<td>Dip coating</td>
<td>165°</td>
<td>14</td>
</tr>
<tr>
<td>9</td>
<td>Silica obtained from tetramethyldisiloxane or tetramethoxyxilane, coated and modified with (heptadecafluoro-1,1,2,2-tetrahydro-decyl)-1-trimethoxysilane</td>
<td>Plasma-enhanced chemical vapor deposition</td>
<td>160°</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>Silica deposited and modified with trichloro(1H,1H,2H,2H-perfluorooctyl) silane</td>
<td>Layer-by-layer processing</td>
<td>160°</td>
<td>16</td>
</tr>
</tbody>
</table>

FAS, perfluoroalkysilane; TEOS, tetraethoxysilane; MTMS, methyltrimethoxysilane.

The precipitated silica particles (henceforth referred to P-SiO$_2$) were centrifuged using Eppendorf centrifuge 5810R, Germany, at three different speeds (1000, 2000 and 5000 rpm) for 5 min at 5°C, to separate P-SiO$_2$ of different sizes.

2.2 Preparation of colloidal solutions

The colloidal solutions were prepared using two differently sized P-SiO$_2$ mixed in different proportions as solutes: P-SiO$_2$ separated after centrifugation at 2000 rpm designated as P-SiO$_2$(A), and P-SiO$_2$ separated after centrifugation at 1000 rpm designated as P-SiO$_2$(B). The following three solvents, ethanol, a silica sol
– 20-nm silica in 50% H₂O colloidal solution (Alfa Aesar, USA), and an acidic silica sol were used. The acidic silica sol was prepared by adding 2-4-g hydrochloric acid (36.5%) and 2-g TEOS in 8-g ethanol followed by continuous stirring for 2 h at 60°C.

The colloidal solutions that were prepared are described in Table 2, in which the column on solute content gives the amount (wt.%) of P-SiO₂(A) and P-SiO₂(B) present in the solution. For example, the first solution given in Table 2 has 5 wt.% of P-SiO₂(A), no P-SiO₂(B) and the solvent used is ethanol, while the fifth solution in the table has 5 wt.% of P-SiO₂(A) and 10 wt.% of P-SiO₂(B) as solute and ethanol as the solvent. The solute, solvent mixtures mentioned in Table 2 were ultrasonicated for 30 min to obtain colloidal solutions for producing coatings on glass substrates.

2.3 Coating procedure
The glass substrates were etched with H₂SO₄/H₂O₂ (50/50%) solution for 6 h, ultrasonicated for 30 min, rinsed with acetone and distilled water. The glass substrates were then coated with the prepared colloidal solutions through a dip-coating process using single dip coater (SDC 2007C, Apex instruments Co., India) using the following parameters: dipping and withdrawal rate of 50 mm/min, holding time of 15 min and drying time of 5 min, and the cycle was repeated for 10 times. The coated glass substrates were heat treated at 250°C for 2 h in atmospheric ambience to ensure solidification and complete evaporation of the solvent.

After centrifugation at 5000 rpm, the solution was clear with rather precipitated silica particles, obtained before and after centrifugation, were dispersed separately in ethanol and ultrasonicated for 30 min. A drop of both the solutions was deposited separately and dried over a carbon-coated copper grid and viewed through TEM. The surface roughness of the etched glass before coating was characterized using surface profilometer, Mitutoyo SJ-400, Japan. The surface morphology of the coatings was studied using field emission gun scanning electron microscope (FEG-SEM), FEI Quanta 400F, USA. The coatings were sputter coated with a gold layer of thickness 5 nm before imaging them using SEM in secondary electron mode. Optical imaging was carried out in bright field mode and differential interference contrast (Nomarski DIC) mode using Olympus IX71 inverted microscope, USA. The static CA measurements of the coated sample, before and after heat treatment, were carried out using CA goniometer, Digidrop GBX, France with 2.0–4.0 µl distilled water droplets at room temperature.

3. Results and discussion

3.1 Morphology of silica particles

The TEM micrograph of P-SiO₂ before centrifugation and P-SiO₂ separated after centrifugation at 1000 rpm is shown in Figure 1(a,b) and 1(c,d), respectively. Before centrifugation, the presence of debris on the P-SiO₂ is observed. However, after centrifugation, P-SiO₂ was found to be completely spherical of uniform diameter, free of debris and agglomerates. The silica particles with diameter of ~800 nm were separated out after centrifugation at 1000 rpm for 5 min, while particles with diameter of ~600 nm were separated out after centrifugation at 2000 rpm for 5 min. The selected area diffraction pattern shown as insert in Figure 1d exemplifies that the silica particles are amorphous. Since the particles separating out after centrifugation at 1000 rpm are completely spherical, free of agglomeration and debris, only a representative TEM image of P-SiO₂ is provided here in Figure 1(c,d). After centrifugation at 5000 rpm, the solution was clear with rather minimal presence of silica particles for any further consideration.

3.2 Coating and adhesion

The prepared colloidal solutions were coated on glass substrates with surface roughness (Rₛ) of ~0.05 µm. The coatings were found to be transparent, with presence of few silica particles on the glass substrate when coated with colloidal solution containing 5 wt.% (P-SiO₂(A) or P-SiO₂(B)) in ethanol/silica sol as solvents. Hence, the silica content was increased to 15 wt.% (P-SiO₂(A) or P-SiO₂(B)) to ensure additional silica particles were available in the colloidal solution for coating.

The coatings made using ethanol as solvent exhibited poor adhesion with the glass substrate, in both cases, before and after heat treatment,
Figure 1. TEM images of silica particles synthesized via Stöber process. (a,b) Before centrifugation and (c,d) after centrifugation at 1000 rpm P-SiO$_2$ (B) (size ~800 nm); diffraction pattern (shown as insert) exemplifying the amorphous nature of silica particles. TEM, transmission electron microscopy.

Figure 2. Crack patterns observed in the coating obtained from 15 wt. % P-SiO$_2$ (A) silica particles in silica sol (a) bright field optical micrograph: 50×; (b) image taken after 10 s; (c) image taken after 30 s; (d) bright field image: 20× and (e) differential interface contrast image.
which was clearly evident from the fact that the coating was easy to remove from the glass substrate while handling. In the case of silica sol as solvent, the obtained coatings were not stable even during the coating process. The coatings were found to crack during the drying time between the coating cycles. Hence, the development of crack patterns in the coating during drying was viewed through optical microscope in bright field mode and differential interface contrast mode. Figure 2 shows the development of cracks with time on glass substrate coated with colloidal solution of 15 wt.% P-SiO$_2$(A) in silica sol in bright field mode. Figure 2a shows the optical image obtained immediately after removal of the glass substrate from the colloidal solution after dipping the substrate for 15 min. Figure 2b and figure 2c were obtained after 10 and 30 s, respectively. From Figure 2a–2c, formation of cracks on the coating with increase in time is clearly evident. Figure 2d obtained after 90 s shows that the coating had completely cracked. Figure 2e shows the corresponding differential interference contrast image. The formation of cracks at a faster rate in the coating with silica sol as solvent could be due to the evaporation of water present in the silica sol resulting in spallation during 5 min of drying time between the cycles.

Hence, subsequently coatings were carried out with acidic silica sol as solvent using colloidal solutions containing varying amount of solutes as mentioned in Table 2. Sakka et al.\textsuperscript{20} has shown that the use of acidic

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Solvent used</th>
<th>Amount of solute present (wt.%)</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P-SiO$_2$(A)</td>
<td>P-SiO$_2$(B)</td>
</tr>
<tr>
<td>1</td>
<td>Ethanol (after heat treatment)</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol (after heat treatment)</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol (after heat treatment)</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol (after heat treatment)</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Ethanol (after heat treatment)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol (after heat treatment)</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>Ethanol (after heat treatment)</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>Ethanol (after heat treatment)</td>
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<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Silica sol (before heat treatment)</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>Silica sol (before heat treatment)</td>
<td>15</td>
<td>0</td>
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<td>11</td>
<td>Silica sol (before heat treatment)</td>
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<td>5</td>
</tr>
<tr>
<td>12</td>
<td>Silica sol (before heat treatment)</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>Acidic sol</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>Acidic sol</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>Acidic sol</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 3. Wettability of various compositions of colloidal solutions for coating: P-SiO$_2$ separated after centrifugation at 2000 rpm designated as P-SiO$_2$(A) and P-SiO$_2$ separated after centrifugation at 1000 rpm designated as P-SiO$_2$(B).
catalyst will result in the formation of a linear silica-based polymer as opposed to formation of silica particles with the use of base catalyst. Hence, the use of hydrochloric acid as catalyst with absence of sufficient amount of water was used in the preparation of acidic silica sol. This acidic silica sol contains abundant active hydroxyl groups (-OH) in silica-based linear oligomer/polymer formed from TEOS. During the coating process, P-SiO$_2$ and linear silica-based polymer present in acidic sol get assembled onto the surface, which on subsequent drying at 250°C for 2 h, results in gradual volatilization of hydrochloric acid and ethanol present in the solvent. The surface morphology of the coated surface characterized by FEG-SEM reveals the presence of cross-linked adhesive type layer (Figure 3) in the coating. Xu et al. has shown that active hydroxyl (-OH) groups present in the linear silica-based polymer react with silica present in the solute and the hydroxyl groups present on the surface of glass substrate during heat treatment resulting in cross-linked Si-O-Si bonds, thereby ensuring better adhesion of the coated particles. The obtained coating exhibited substantial improvement in adhesion to the glass substrates.

3.3 Surface wettability

Table 3 lists the CAs achieved on all the coatings provided on the glass substrates as explained in Table 2. Figure 4 shows the CA measurement carried out on the coating with 15 wt.% of P-SiO$_2$(A) in ethanol and silica sol as solvents. Silica coatings with 15 wt.% of (P-SiO$_2$(A) or P-SiO$_2$(B)) in ethanol exhibits a CA of ~36°. The coatings made using 15 wt.% of (P-SiO$_2$(A) or P-SiO$_2$(B)) in silica sol as solvent are hydrophobic with maximum CA of ~110°, in spite of its poor adhesion as shown in Figure 2 and explained in Section 3.2. In case of coatings with silica sol as solvent, it is important to note that silica particles of two different sizes, 600-nm silica particles from solute and 20-nm silica particles from solvent are present. The enhanced CA achieved on the coating is attributed to the nanoscale roughness created by the presence of two differently sized particles, which is in agreement with earlier literature.

Hence, coatings on glass substrates were made using dual-sized particle distribution (10 wt.% of P-SiO$_2$(A) and 5 wt.% of P-SiO$_2$(B)) in ethanol. Figure 5 shows the CA measurement carried out on the fabricated coatings with 10 wt.% of P-SiO$_2$(A) and 5 wt.% of P-SiO$_2$(B) in ethanol. In case of coating uni-particle size, uniformity of the silica particle spheres as seen from the SEM images (Figure 6a), makes the surface smooth enough and thus making it hydrophilic. On the contrary, coating with dual-sized distribution of P-SiO$_2$, the microstructure provides nanoscale roughness as is seen from the SEM image (Figure 6b). Due to this roughness, nano-air pockets that are created on the surface of the coating could decrease the wettability of the surfaces and therefore could be responsible for the superhydrophobic nature of the coating.

The CA measurements were carried out before and after heat treatment on the samples coated with acidic sol as solvent as shown in Table 3. It was found that the coating has a hydrophilic nature with CA of ~45° (image not shown) before heat treatment and was found to increase significantly after heat treatment. Saman et al. has shown that acidic silica sol has a monolithic morphology. However, this monolithic morphology results in smoothing of the
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4. Conclusions
Superhydrophobic coatings with CAs of ~150° with good adhesion on the glass substrates were produced by a simple and inexpensive layer-by-layer colloidal assembly method without any requirement of secondary process such as fluorination. Nanosized, highly uniform spherical silica particles were produced using seed growth “Stöber Method.” The particles were separated to various sizes by centrifugation and used in appropriate ratio to obtain superhydrophobicity. The acidic silica binder helped increasing the adhesive strength by forming cross-links with the glass substrate and silica particles.

Acknowledgements
The authors would like to acknowledge Department of Biotechnology, IIT-M for performing centrifugation experiments.
and also Medical Materials Laboratory, Department of Metallurgical and Materials Engineering, IIT-M and Polymer Engineering Laboratory, Department of Chemical Engineering, IIT-M for carrying out contact angle measurement.

REFERENCES

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