OPTIMIZATION OF THE PROCESS SYNTHESIS OF SILICA NANOPARTICLES FUNCTIONALIZED WITH SILANE AGENTS DESTINED FOR SUPERHYDROPHOBIC COATING

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Abstract. The aim of this study is to define the optimum process synthesis of silica (SiO₂) nanoparticles functionalized with silane agents destined for superhydrophobic coating thus to determine the minimum required silane agent needed to obtain proper superhydrophobic properties. Spherical SiO₂ nanoparticles were synthesized by using sol-gel method and functionalized to gain hydrophobic properties with two different silane agents: 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and 1H,1H,2H,2H-perfluoroctyltrichlorosilane (PFOTS).

The hydrophobic properties were evaluated by measuring the water drop contact angle and the inclination flowing angle.

Results show that, through manufacturing process optimization, the quantity of HMDS could be reduced by 142%, while the quantity of PFOTS could be reduced by 20% compared to the lab scale synthesis method developed by ICPE-CA, without having a negative effect on the hydrophobic properties of the functionalized SiO₂ nanoparticles.

Key words: silicon dioxide nanoparticles, sol-gel method, superhydrophobic surface, water drop contact angle, inclination flowing angle.

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1. INTRODUCTION

Hydrophobic and superhydrophobic surfaces have gained a lot of attention in the last decade due to their extreme water repellence which assures self-cleaning, anti-icing, anti-corrosive properties to the surface [1].

Superhydrophobic surfaces became attractive in various industrial sectors, such as in automotive industry for windshield glass, in solar energy industry for transparent coatings for photovoltaic panels and solar cells, in textile industry for stain and water resistant clothing; in telescope industry for lenses, for aerospace industry and wind turbine energy sector for anti-icing coatings; in metal and pipeline industry for corrosion protection coating, in marine industry for anti-
biofouling paints and in medicine for anti-bacterial coating of medical devices and equipment [2–4].

A hydrophobic surface is defined as the surface having a water droplet contact angle larger than or equal to 90° on itself (Fig. 1). In case of a superhydrophobic surface the contact angle that a water drop establishes on a solid surface is larger than 150° (Fig. 1), with an inclination angle of less than 10° at ambient conditions [1–5].

![Fig. 1 – Hydrophobe and superhydrophobe surface contact angle presentation.](image)

A good example of a superhydrophobic surface can be found in nature, such as the lotus leaf, that pushes back the dirt. Its water-repellent properties are due to a specific two size range roughness on the leaf’s surface. To obtain higher hydrophobicity the surface roughness is combined with low surface energy. Many good reviews appeared in the literature regarding the synthesis, applications and characterization of the superhydrophobic surfaces [2, 6–12] since 1990.

Functionalization of spherical SiO$_2$ nanoparticles (NPs) is a great option to create superhydrophobic surfaces [9–12]. Many chemical and physical methods are reported for modification the surface of the SiO$_2$ NPs in order to create proper roughness of it. Since the hydrophobic properties depend on the particle size, the Stöber method [13], a sol-gel technique, becomes an attractive method for the synthesis of SiO$_2$ NPs since it assures a high controllability of the obtained particle size [7, 9–10].

2. MATERIALS AND SAMPLE PREPARATION

2.1. SiO$_2$ NANO PARTICLES PREPARATION BY STÖBER TECHNIQUE

In order to obtain spherical shaped NPs with a narrow dimensional range of the diameter between 140–240 nm, the Stöber method was used. The method is described in detail [7, 10]. A mixture of 7.0 moles ethanol, 7.5 moles deionized water and 0.5 moles ammonia were homogenized by magnetic stirring at a temperature of 30°C. Later the tetraethyl orthosilicate (Si(OC$_2$H$_5$)$_4$ – TEOS) was added dropwise. The solution was mixed until particle suspensions were formed, then it was heat treated at high temperature to evaporate the volatiles.
Two type of SH NPs samples were synthesized: SiO$_2$ NPs functionalized with HMDS silane (SiO$_2$ fHMDS) and with PFOTS (SiO$_2$ fPFOTS). For this study, the processes of silica nanoparticles functionalization with silane, set-up at lab scale by ICPE-CA, were modified, through a substantial decreasing of silane amount, with benefits of raw material savings for the enterprise.

2.2. SiO$_2$ NANO PARTICLES FUNCTIONALIZATION WITH HMDS SILANE

- Preparing the SiO$_2$ NPs for functionalization by hydrolising, thus by activating the hydroxyl groups on the NP: 1 g of SiO$_2$ nanoparticles were synthesized by using Stöber method. NPs then were dispersed in 20 ml of ultrasonically deionized water at room temperature for 1 hour. 0.1 N HCl was added dropwise to dispersion until pH reached the value of 1. The dispersion was stirred magnetically (500 rpm) at room temperature for 4 hours. The SiO$_2$ nanoparticles with reactive hydroxyl groups (SiO$_2$-OH) were separated under vacuum by using Büchner funnel filtration process. The obtained NPs were re-dispersed in deionized water and separated again under vacuum, using the Büchner funnel filtration process.

- Functionalization of SiO$_2$ NPs with HMDS silane agent: a volume of 5 ml of toluene was added to 0.1 g SiO$_2$-OH nanoparticles separated from the aqueous suspension and stirred magnetically (500 rpm) at room temperature for 1 hour. The HMDS was dispersed in 5.18 times more volume of toluene in another Berzelius glass by magnetic stirring at a speed of 500 rpm at room temperature for 1 hour. The two obtained suspensions were mixed together and placed in a round-bottomed flask with three necks and subjected to the reflux process at a temperature of 110°C, while it was stirring magnetically at a speed of 500 rpm for 16 hours. After the reaction was complete, the mixture was allowed to cool down to room temperature. The HMDS-functionalized SiO$_2$ NPs were separated under vacuum, by using the Büchner funnel filtration process. After the separation process the nanoparticles were washed three times with ethanol and finally dried in an oven at 110°C for 2 hours.

Two samples of SiO$_2$ nanoparticles functionalized with HMDS were tested, ROSEAL SiO$_2$ fHMDS-5 which was functionalized by the method described before, received from the ICPE-CA, and ROSEAL SiO$_2$ fHMDS-6, functionalized by the method modified by ROSEAL S.A. The difference was the significant reduction of the amount of HMDS by 142%, with the aim of making raw material consumption more efficient (see Table 1).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass ratio of HMDS to SiO$_2$-OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roseal SiO$_2$ fHMDS-5</td>
<td>42.6 : 1</td>
</tr>
<tr>
<td>Roseal SiO$_2$ fHMDS-6</td>
<td>0.3 : 1</td>
</tr>
</tbody>
</table>
2.3. SiO₂ NANOPARTICLES FUNCTIONALIZATION WITH PFOTS SILANE

An amount of 0.1 g SiO₂ nanoparticles obtained by the Stöber method was placed in a Berzelius glass and a mixture of 18 ml of ethanol and 2 ml of deionized water was added. The SiO₂ nanoparticles were then dispersed in the mixture of ethanol and deionized water by ultrasound at room temperature for 30 minutes. The resulting dispersion was pipetted over a 0.1 N HCl until the pH value reached 1. The dispersion thus obtained was magnetically stirred at a rate of 500 rpm at room temperature for 4 hours. Then 0.3 ml PFOTS were added dropwise to the SiO₂-OH nanoparticle dispersion. The mixture thus formed was placed in a round-bottomed flask with three necks and refluxed with magnetic stirring (500 rpm) at 80°C for 12 hours. After the reaction was complete, the mixture was allowed to cool down to the room temperature. After cooling, PFOTS-functionalized SiO₂ NPs were separated under vacuum by using the Büchner funnel filtration process. The separated functionalized SiO₂ NPs were washed 3 times with ethanol and finally dried under vacuum (50 mbar) at 40°C for 18 hours.

Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass ratio of PFOTS to SiO₂-OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roseal SiO₂ fPFOTS-1</td>
<td>4 : 1</td>
</tr>
<tr>
<td>Roseal SiO₂ fPFOTS-8</td>
<td>3.6 : 1</td>
</tr>
<tr>
<td>Roseal SiO₂ fPFOTS-9</td>
<td>3.2 : 1</td>
</tr>
</tbody>
</table>

Like in the case of functionalization of silica fine particles with silane type HMDS, also in the case of their functionalization with silane type PFOTS was reduced the amount of functionalizing agent added to hydrolysed silica (see Table 2), the sample ROSEAL SiO₂ PFOTS-9 being the specimen with the lowest content of silane.

3. SAMPLES CHARACTERISATION AND TESTING

3.1. MORPHOLOGICAL, DIMENSIONAL, AND ELEMENTAL MICRO-COMPOSITIONAL CHARACTERIZATION OF THE FUNCTIONALIZED SiO₂ NANOPARTICLES

The morphology and the sizes of the functionalized SiO₂ NPs were investigated using an Auriga Station Scanning Electron Microscope (SEM) from Carl Zeiss at an accelerating voltage of 5 kV at a 100k magnification by ICPE-CA. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using an energy dispersive spectrometer with X-MaxN Silicon Drift Detector and software AZtec for acquisition and interpretation, made by Oxford Instruments, UK. The Secondary Electrons
Secondary Ions (SES1) detector, available on the workstation, allows the dimensional analysis of the sample nanoparticles.

The silica nanoparticles prepared through the Stöber technique are amorphous, exhibiting a standard diffused peak at angle 20 ~ 22° [14]. The morphology of SiO₂ nanoparticles, as well as those of functionalized SiO₂, reveals a homogeneous structure of clearly outlined and highlighted nanospheres, the difference being in the average diameters of the nanoparticles, which are larger with 10–40 nm in the case of the functionalized ones, due to the silane layer deposited on the nanoparticle surface [15].

The sphere diameters of the NPs in the case of ROSEAL SiO₂ fHMDS-5 sample are situated in the range of 113–194 nm (Fig. 2a), and those corresponding to the ROSEAL SiO₂ fHMDS-6 sample are included in the range of 140–236 nm (Fig. 2b).

![Fig. 2 – SEM images of NPs ROSEAL SiO₂ fHMDS-5: a) and ROSEAL SiO₂ fHMDS-6 samples; b) (×100k).](image)

It can be observed that, with the reduction of the amount of functionalizing agent, the average size of the nanoparticles increases, with beneficial consequences on the hydrophobicity properties, as will be found later, after performing the specific tests (see 3.2.2 Contact angle measurement and 3.2.3 Inclination angle measurement).

The EDS spectrometry analysis identified on the investigated samples as major elements silicon (Si), oxygen (O) and carbon (C), carbon being an indicator of the presence of the coating polymer (silane) on the surface of the silica nanoparticles.

In the case of the ROSEAL SiO₂ fHMDS-5 sample, the EDS spectrometry analysis, according to the spectrum associated with the integrated area, identified silicon: 48%, oxygen – 46.3% and carbon – 5.7% (see Figs. 3 and 4). The spectral micro-compositional analysis, according to the spectrum associated with the integrated area of the investigated ROSEAL SiO₂ fHMDS-6 sample, reveals the following elemental concentrations: silicon – 38.6%; oxygen – 52.2%; carbon – 9.2% (see Figs. 5 and 6).
Figure 7a illustrates the SEM image of nanoparticles for ROSEAL SiO$_2$:fPFOTS-1 sample. From the morphological point of view of the investigated sample, its structure also consists of clearly highlighted spherical nanoparticles, with average sizes in the range of 115–180 nm.

For the investigated area of ROSEAL SiO$_2$:PFOTS-8 sample, the average sizes of the nanoparticles diameters are either in the range of 93–98 nm, or above 220 nm, the nanoparticles with sizes positioned at the extremes of the aforementioned range, i.e. 88–245 nm, being a minority (see Fig. 7b).

As in the case of functionalization with HMDS-type silane, and in the case of using PFOTS-type silane as a functionalizing agent for silica, reducing the silane amount leads to a change in the dimensions of the nanoparticles, in the sense of shifting their dimensional ranges to larger values. This fact favours the development of their hydrophobicity properties and determines the achievement of higher values for the functional characteristics measured in sections 3.2.2 and 3.2.3.
Optimization of the process synthesis of silica nanoparticles

Fig. 7 – SEM images of NPs ROSEAL SiO₂ fPFOTS-1: a) and ROSEAL SiO₂ fPFOTS-8 samples; b) (× 100k).

Fig. 8 – Secondary electrons SEM image for nanoparticles of ROSEAL SiO₂ fPFOTS-1 sample – integrated EDS analysis area (× 100k).

Fig. 9 – EDS spectrum 1, associated with the integrated area from Fig. 8, for nanoparticles of ROSEAL SiO₂ fPFOTS-1 sample.

Fig. 10 – Secondary electrons SEM image for nanoparticles of ROSEAL SiO₂ fPFOTS-8 sample – integrated EDS analysis area (× 100k).

Fig. 11 – EDS spectrum 1, associated with the integrated area from Fig. 10, for nanoparticles of ROSEAL SiO₂ fPFOTS-8 sample.
For ROSEAL SiO$_2$ fPFOTS-1 sample, the EDS spectrometry analysis identified silicon: 36–38.7%; oxygen: 52.3–53.9%, carbon: 7.6–9.3% and fluorine: 0.8–1.1%. Carbon and fluorine are indicators of the presence of the coating polymer (PFOTS-type silane) on the surface of the silica nanoparticles of the ROSEAL SiO$_2$ fPFOTS-1 sample (see Figs. 8 and 9).

In the case of the ROSEAL SiO$_2$ fPFOTS-8 sample, the EDS spectrometry analysis according to the spectrum associated with the integrated area identified the following major elements: silicon: 46.6%; oxygen: 44.9% and carbon: 8.4%. Fluorine could not be detected, perhaps because its concentration was too low (see Figs. 10 and 11).

### 3.2. TESTING OF HYDROPHOBIC PROPERTIES

#### 3.2.1. Surface coating

Several studies investigate the durability enhancement of superhydrophobic surfaces because of the limited abrasion resistance and small stability to corrosion and chemicals offered by various coating methods [13, 16].

This paper investigates the hydrophobicity of SiO$_2$-based composite hybrid structures functionalized with HMDS and PFOTS on different types of materials, such as metal, glass, ceramic, and wood.

The different surfaces were covered by using the same procedure, illustrated in Fig. 12. First, the surfaces were covered with transparent varnish by using an air brush with 0.5 mm nozzle at approximately 10 µm thickness.

Fig. 12 – Scheme of coating method.

Then 0.2 g of functionalized SiO$_2$ NPs were mixed for 1 minute in 10 ml acetone by using an ultrasonic processor Hielscher UP400St. The solution was
applied on the different surfaces, covered previously by varnish in an approximately thickness of 5 µm. The samples were dried at 40°C.

### 3.2.2. Contact angle measurement

The contact angle (CA) describes the capability of a fluid phase to spread on a solid surface. Many papers in surface science study the influence of the surface roughness and material heterogeneity on the droplet contact angle [17–18]. CA measurement is performed by establishing the tangent (angle) of a liquid drop with a solid surface at the base.

The water contact angle (CA) was determined on the covered surface using deionized ultrapure water as a wetting agent at standard temperature of 23 ± 2°C and relative humidity ≥ 50%. By using a microsyringe with a stainless-steel needle, 1 µl volume of water was dripped onto the surface of the covered layer. Picture was taken by using a camera of 108 MP, f/1.8, 0.8 µm, and the drop was visualized on the surface of the sample to be analyzed.

**Table 3**

Processed images for water CA measurement for functionalized silicon oxide NPs

<table>
<thead>
<tr>
<th>Metal</th>
<th>Glass</th>
<th>Ceramic</th>
<th>Wood</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

By using the Image J 1.53e software, Contact Angle Plugin, the image was processed in order to determine the contact angle of the water drop with the surface of the sample to be analyzed. Each measurement was repeated at least 3 times in order to assure the correctness of the results (see Table 4).

**Table 4**

CA measurements for SiO₂ NPs functionalized with silane coatings

<table>
<thead>
<tr>
<th></th>
<th>ROSEAL SiO₂ fHMDS-5</th>
<th>ROSEAL SiO₂ fHMDS-6</th>
<th>ROSEAL SiO₂ fPFOTS-1</th>
<th>ROSEAL SiO₂ fPFOTS-8</th>
<th>ROSEAL SiO₂ fPFOTS-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
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<td>143°</td>
<td>138°</td>
<td>144°</td>
<td>150°</td>
</tr>
<tr>
<td>Glass</td>
<td>136°</td>
<td>141°</td>
<td>151°</td>
<td>146°</td>
<td>150°</td>
</tr>
<tr>
<td>Ceramic</td>
<td>143°</td>
<td>150°</td>
<td>150°</td>
<td>154°</td>
<td>151°</td>
</tr>
<tr>
<td>Wood</td>
<td>143°</td>
<td>142°</td>
<td>149°</td>
<td>152°</td>
<td>151°</td>
</tr>
</tbody>
</table>
3.2.3. Inclination angle measurement

Self-cleaning capacity was determined by performing the tilt test for all samples. To perform the tests, a device was used, which allows both adjustment and measurement of the tilt angle and a microsyringe to ensure the uniformity of the distilled water drops (see Fig. 13).

Fig. 13 – Tilt test (red continuous circle corresponds to water drop on surface covered by varnish and functionalized SiO$_2$ NPs; purple dashed line corresponds to water drop on surface covered only by varnish).

Three measurements were made on each sample (see Tables 5 and 6).

Table 5

<table>
<thead>
<tr>
<th>Surface type</th>
<th>Sample</th>
<th>Inclination angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>ROSEAL SiO$_2$ fHMDS – 5</td>
<td>10.8°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fHMDS – 6</td>
<td>11.1°</td>
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<tr>
<td>Ceramic</td>
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<td>2.7°</td>
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<tr>
<td></td>
<td>ROSEAL SiO$_2$ fHMDS – 6</td>
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<tr>
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<td>2.8°</td>
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<tr>
<td>Metal</td>
<td>ROSEAL SiO$_2$ fHMDS – 5</td>
<td>4.0°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fHMDS – 6</td>
<td>2.9°</td>
</tr>
</tbody>
</table>
Table 6  
Results of the inclination angle measurement for SiO$_2$ NPs functionalized with PFOTS coatings

<table>
<thead>
<tr>
<th>Surface type</th>
<th>Sample</th>
<th>Inclination angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>ROSEAL SiO$_2$ fPFOTS – 1</td>
<td>5.7°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fPFOTS – 8</td>
<td>1.9°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fPFOTS – 9</td>
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<td>Ceramic</td>
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<td>3.9°</td>
</tr>
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<td>ROSEAL SiO$_2$ fPFOTS – 8</td>
<td>0.5°</td>
</tr>
<tr>
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<td>ROSEAL SiO$_2$ fPFOTS – 9</td>
<td>1.4°</td>
</tr>
<tr>
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<td>2.8°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fPFOTS – 8</td>
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<tr>
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<td>Metal</td>
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<td>2.9°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fPFOTS – 8</td>
<td>1.5°</td>
</tr>
<tr>
<td></td>
<td>ROSEAL SiO$_2$ fPFOTS – 9</td>
<td>0.4°</td>
</tr>
</tbody>
</table>

3.2.4. Hydrophobic properties analysis

The average CA is increased by 4.1% in case of sample ROSEAL SiO$_2$ fHMDS-6 compared to ROSEAL SiO$_2$ fHMDS-5, due to the reduction of silane amount during the functionalization process.

The result for ROSEAL SiO$_2$ fPFOTS-9 shows an improvement of 1.4° compared to ROSEAL SiO$_2$ fPFOTS-1 and 2.4° increase in case of ROSEAL SiO$_2$ fPFOTS-8.

The average inclination angle is slightly decreased (by 1°) in case of silica nanoparticles functionalized with HMDS silane, when the quantity of HMDS was optimized.

When the percentage of PFOTS mass was reduced to 90% compared to the initial value, corresponding to ROSEAL SiO$_2$ fPFOTS-1 sample (Table 2), the average inclination angle is decreased by 2.5°. In case of ROSEAL SiO$_2$ fPFOTS-9 sample (with 80% PFOTS mass percentage compared to the initial value), the average inclination angle is decreased by 2.6°.

Further reduction of the mass ratio of PFOTS to SiO$_2$-OH to 2.8 does not produce satisfactory results.

4. CONCLUSIONS

The process synthesis of silica nanoparticles functionalized with silane agents, destined for superhydrophobic coating, was successfully optimized for both
types of silane agents. A substantial reduction of the HMDS silane amount, from 42.57 : 1 to 0.3 : 1 mass ratio to SiO$_2$ nanoparticles could be reached and proved to be adequate for obtaining proper hydrophobic properties. The HMDS silane agent quantity reduction even contributed for a slight improvement of the hydrophobic properties of the samples.

In the case of silica nanoparticles functionalized by PFOTS silane agent, the mass ratio of PFOTS to SiO$_2$-OH nanoparticles could be reduced from 4 : 1 to 3.2 : 1, which means a 20% reduction. The optimized process synthesis was demonstrated to be adequate to prepare superhydrophobic surfaces.

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