

Comparative study of the hydrophobic properties of silicon dioxide particles functionalized with different agents

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Silica nanoparticles present special properties that give them extensive opportunities to be used in numerous applications, but one of the most spectacular application refers to the creation of surfaces with increased hydrophobicity and self-cleaning capabilities. The paper presents a comparative study of the hydrophobic properties of silicon dioxide (SiO₂) fine particles functionalized with different agents. Spherical SiO₂ particles with different sizes were synthesized by a sol-gel process and the modification of their surface was performed by a functionalization process with different silanes such as HMDS and PFOTS. The water contact angles for all analysed samples are higher than 138°, confirming the hydrophobic character of them. The functionalized SiO₂ particles obtained in this study could be used as additive in paints for applications that required self-cleaning properties.

(Received September 13, 2022; accepted February 14, 2023)

Keywords: Silicon dioxide fine particles, Sol-gel method, Hydrophobic surface, Water contact angle

1. Introduction

Various nanoparticles and nanostructures are used in different applications such as sensors [1, 2], biomedical [3, 4], protective coatings [5-8], and green energy. Depending on the domain, nanostructures must possess or be endowed with chemical and/or physical methods with application-specific properties.

Some researchers reported the synthesis of different titanium dioxide (TiO₂) nanoparticles or structures which presented hydrophobic properties [7,10]. Kim et al. prepared a photocatalytic paint using as additive modified TiO₂ nanoparticles [7]. Taib et al. grown micro-rods and flower structures of TiO₂ with hydrophobic properties on the FTO surface which could be used in self-cleaning applications [10].

Silicon dioxide nanoparticles (SiO₂ NPs) have applications in many domains such as chemical, biological and medical because of their chemical inertness, optical transparency, low toxicity, and biocompatibility [11-13]. Enache et al. developed functionalized mesoporous silicas, Fe₃O₄ and Fe₃O₄ nanoparticles coated with silica that could be used as adsorbents of Pb(II) from aqueous solutions [14,15].

SiO₂ NPs can also be used for hydrophobic coatings, but require functionalization to gain these special properties. Due to the high hydrophilicity of their surface, the SiO₂ NPs can be easily modified through chemical processes by addition of specific groups that give them hydrophobic properties.

Many methods have been reported regarding the obtaining of the surfaces with high hydrophobicity using

different chemical and physical methods in order to create roughness [16-18]. Different functional silane precursors were used in sol-gel synthesis in order to obtain superhydrophobic surfaces [19-21]. Purcar et al. reported the development of hydrophobic and antireflective coatings based on hybrid silica [22].

They obtained by sol-gel method and using different precursors homogenous and transparent hybrid films that could be used as hydrophobic and antireflective coatings [22].

One of the most facile techniques to prepare the SiO₂ nanospheres is the Stöber method [23], a sol-gel technique that involves two step processes: first, the alkyl silicates such as tetraethyl orthosilicate (TEOS) hydrolysis and second, the condensation of silicic acid in alcohol solutions. The particles' size can be controlled using this method, because the dimension has an important influence on the hydrophobic properties of the coatings.

In this paper we present the obtaining of silicon dioxide fine particles (SiO₂ FPs) by Stöber method and their surface functionalization with different silanes such as 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and 1H,1H,2H,2H-perfluorooctyltriethoxy-silane (PFOTS). Also, we present a comparative study of the hydrophobic properties of SiO₂ FPs functionalized with the two different silanes.

2. Experimental

2.1. Materials

For SiO₂ FPs synthesis the following materials were

used: tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$ - TEOS) purchased from Sigma-Aldrich, ethanol 96% ($\text{C}_2\text{H}_5\text{OH}$) and ammonia 25% (NH_3OH) purchased from Chemical Company.

For SiO_2 FPs functionalization with HMDS the following materials were used: SiO_2 FPs previously synthesized by Stöber method, 1,1,1,3,3,3-hexamethyldisilazane (99%) purchased from Electronic Grade, toluene (98%) and 0.1 N hydrochloric acid purchased from Chimopar, ethanol (96%) purchased from Chimreactiv SRL and deionized water.

For SiO_2 FPs functionalization with PFOTS the following materials were used: SiO_2 FPs previously synthesized by Stöber method, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (97%) purchased from Alpha Aesar, 0.1 N hydrochloric acid purchased from Chimopar, ethanol (96%) purchased from Chimreactiv SRL and deionized water.

2.2. SiO_2 fine particles synthesis

Synthesis of SiO_2 FPs was performed by sol-gel technique using the Stöber method. For this, a mixture of 7.0 moles ethanol, 7.5 moles deionized water and 0.5 moles ammonia were homogenized by magnetic stirring and heated at 30°C , and finally, 0.13-0.18 moles tetraethyl orthosilicate (TEOS) were added dropwise. Then, the mixture was annealed at 80°C and the resulting powder was dried at 120°C for 24 hours. In this study SiO_2 FPs were prepared using TEOS in two different amounts for preparation of SiO_2 nanospheres with two different dimensions that will be further functionalized with silanes.

2.3. SiO_2 fine particles functionalization with HMDS

In a Berzelius beaker, 0.1 g of SiO_2 FPs obtained by the Stöber method were dispersed in 20 ml of ultrasonically deionized water at room temperature for 1 hour. To the dispersion thus obtained 0.1 N HCl was added dropwise to a pH value of about 1. The dispersion was then stirred magnetically (500 rpm) at room temperature for 4 hours. The SiO_2 FPs with reactive hydroxyl groups ($\text{SiO}_2\text{-OH}$) thus obtained were separated by centrifugation at a speed of 4000 rpm for 30 minutes. A volume of 5 ml of toluene was added to the $\text{SiO}_2\text{-OH}$ particles separated from the aqueous suspension and the mixture thus formed was stirred magnetically (500 rpm) at room temperature for 1 hour. A volume of 5.5 ml HMDS was dispersed in 28.5 ml of toluene in another Berzelius beaker by magnetic stirring at a speed of 500 rpm at room temperature for 1 hour. The two suspensions thus obtained were mixed and placed in a round-bottomed flask with three necks and subjected to the reflux process at a temperature of 110°C , under magnetic stirring at a speed of 500 rpm for 16 hours. After the reaction was complete, the mixture was allowed to cool to room temperature, and then the HMDS-functionalized SiO_2 FPs were separated by centrifugation at 4000 rpm for 15 minutes. After

separation, the particles were washed three times with ethanol and finally dried in an oven at 110°C for 2 hours.

2.4. SiO_2 fine particles functionalization with PFOTS

An amount of 0.1 g SiO_2 FPs obtained by the Stöber method was placed in a Berzelius beaker and a mixture of 18 ml of ethanol and 2 ml of deionized water was added. The SiO_2 FPs were then dispersed in the mixture of ethanol and deionized water by ultrasound at room temperature for 30 minutes. After ultrasound, the resulting dispersion was pipetted over a 0.1 N HCl pipette until a pH value of about 1 was reached. 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 $\text{SiO}_2\text{-OH}$ particles 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 to room temperature. After cooling, PFOTS-functionalized SiO_2 FPs were separated by centrifugation at 4000 rpm for 15 minutes. After separation the functionalized SiO_2 FPs were washed 3 times with ethanol and finally dried under vacuum (50 mbar) at 40°C for 18 hours.

2.5. SiO_2 fine particles characterization

The morphology and the size of the SiO_2 FPs were observed using an Auriga Station Scanning Electron Microscope (SEM) from Carl Zeiss at an accelerating voltage of 5 kV at a 100k magnification. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using an energy dispersive spectrometer with X-Max^N Silicon Drift Detector and software AZtec for acquisition and interpretation, made by Oxford Instruments UK.

The water contact angle was determined using an optical microscope DinoLite Pro, equipped with a camera for capturing images on the computer and through their processing with the help of Image J software, Drop Analysis-Drop Snake function.

3. Results and discussion

SiO_2 nanospheres with different average dimensions of the particles noted FPs were prepared using two different amounts of TEOS, and we will note them as SiO_2 FPs-1 and SiO_2 FPs-2. After SiO_2 FPs synthesis, both types of FPs were functionalized with HMDS and also with PFOTS, further noted SiO_2 FPs-1-HMDS, SiO_2 FPs-2-HMDS, SiO_2 FPs-1-PFOTS, and SiO_2 FPs-2-PFOTS.

3.1. SEM and EDS characterization

Fig. 1 (a-f) illustrates scanning electron microscopy (SEM) images to reveal the morphology of the SiO_2 FPs and the HMDS and PFOTS-functionalized SiO_2 FPs.

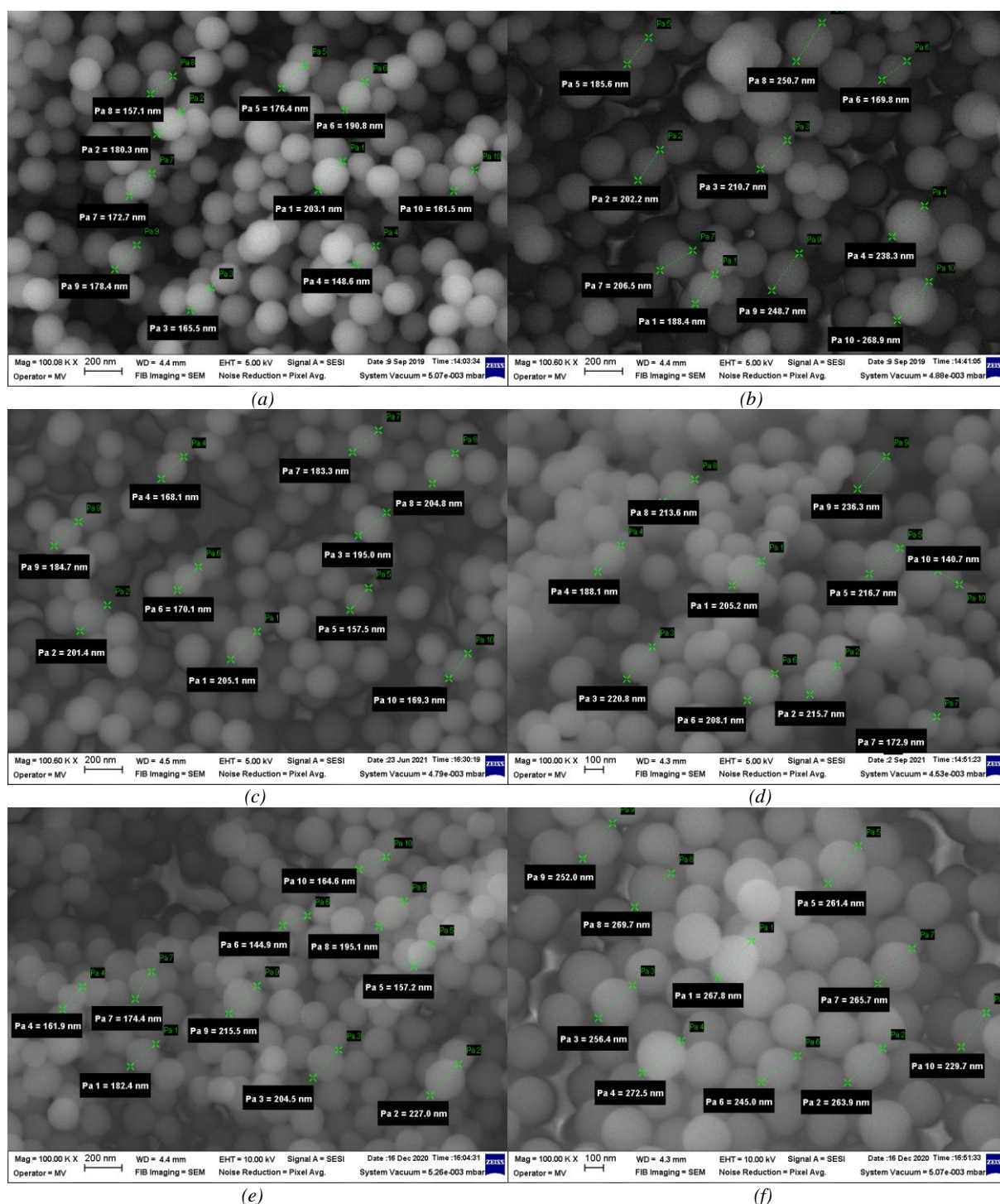


Fig. 1. SEM images of the samples SiO_2 FPs-1 (a), SiO_2 FPs-2 (b), SiO_2 FPs-1-HMDS (c), SiO_2 FPs-2-HMDS (d), SiO_2 FPs-1-PFOTS (e), and SiO_2 FPs-2-PFOTS (f) (color online)

Fig. 1 (a, b) reveals SiO_2 FPs with a uniform distribution of particles size for each sample, with medium diameter values of 173 ± 20 nm for the sample with low TEOS concentration (SiO_2 FPs-1) and 217 ± 20 nm, respectively, for the sample with higher TEOS concentration (SiO_2 FPs-2). Also, all the prepared samples have a well-defined spherical shape and are clearly individually separated.

Comparing the average diameter values of the SiO_2 fine particles, we find that larger particles are obtained in

the case of a higher TEOS concentration.

Fig. 1 (c, d) reveals HMDS-functionalized SiO_2 FPs with medium diameter values of 184 ± 20 nm for the sample with low TEOS concentration (SiO_2 FPs-1-HMDS) and 212 ± 20 nm, respectively, for the sample with higher TEOS concentration (SiO_2 FPs-2-HMDS).

Fig. 1 (e, f) reveals PFOTS-functionalized SiO_2 FPs with medium diameter values of 183 ± 20 nm for the sample with low TEOS concentration (SiO_2 FPs-1-

PFOTS) and 258 ± 20 nm, respectively, for the sample with higher TEOS concentration (SiO_2 FPs-2-PFOTS).

The average diameters of the SiO_2 FPs were increased as a result of the HMDS and PFOTS functionalizing agent layer present on the surface.

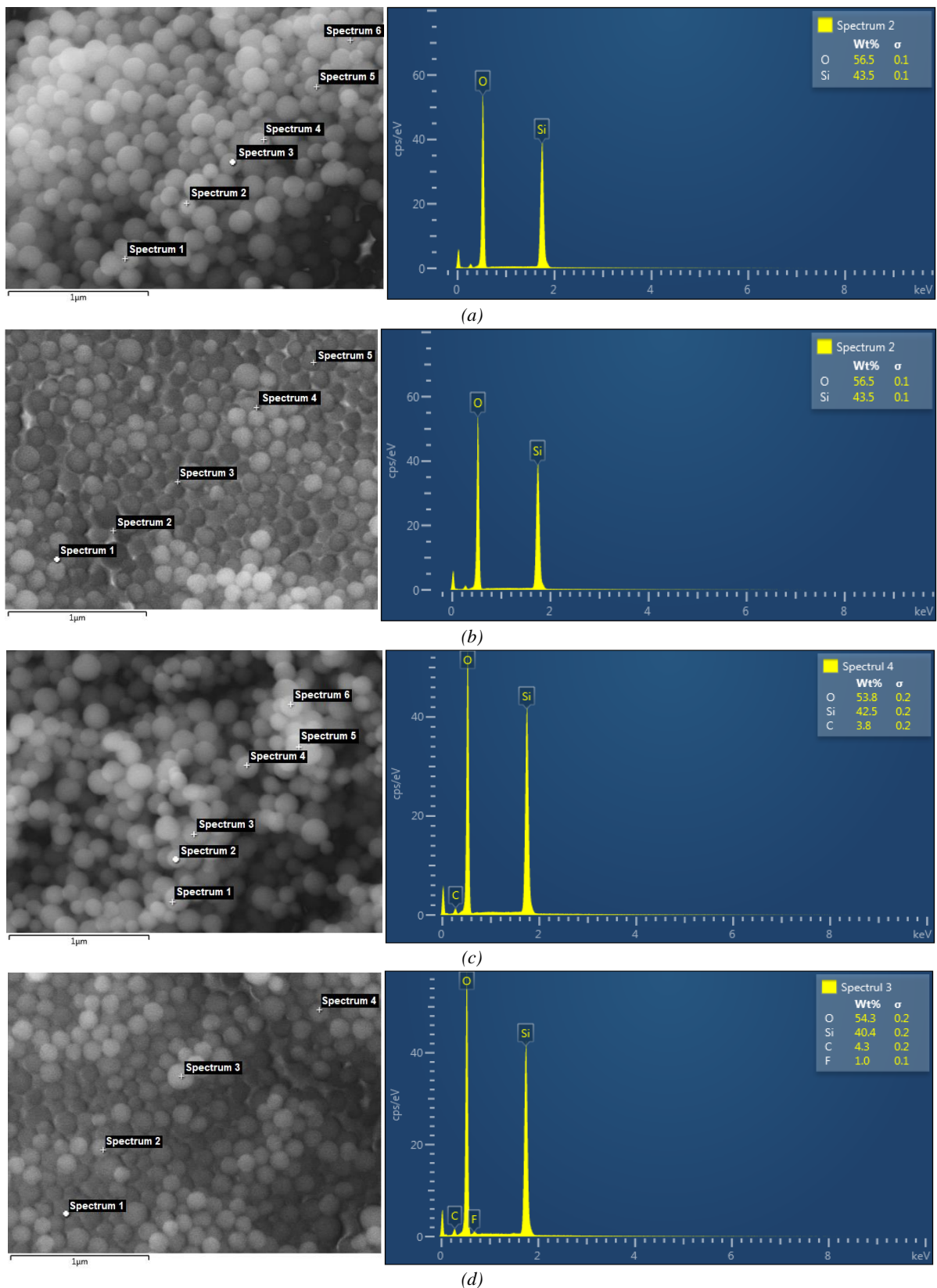


Fig. 2. EDS spectra of the samples SiO_2 FPs-1 (a), SiO_2 FPs-2 (b), SiO_2 FPs-1-HMDS (c), and SiO_2 FPs-1-PFOTS (d) (color online)

Fig. 2 (a, b) shows the multipoint EDS analysis that was performed to provide data about the composition and the purity of the prepared SiO_2 FPs. Analyzing the EDS spectra of the two samples of SiO_2 FPs we can observe the characteristic peaks of Si and O in different proportions, which indicates that the main component of the particles is SiO_2 .

Fig. 2 (c, d) shows the multipoint EDS analysis of the functionalized SiO_2 FPs with HMDS and PFOTS. The appearance in the EDS spectra of the chemical elements carbon, respectively fluorine, confirms the presence of the functionalizing agents on the surface of the SiO_2 FPs.

3.2. Water contact angle determination

The water contact angle (CA) was determined on powder samples using deionized water as a wetting agent

at standard temperature of $23 \pm 2^\circ\text{C}$ and relative humidity $\geq 50\%$. To ensure the flatness of the powder samples, they will be placed and pressed on the glass slides. A drop of deionized water was dripped onto the surface of the powder layer from a microsyringe with a stainless steel needle. With an optical microscope, the drop was visualized on the surface of the sample to be analysed, and with a camera, the image was acquired and stored in a computer. Using the Image J software, Drop Analysis-Drop Snake function, the image was processed in order to determine the contact angle of the water drop with the surface of the sample to be analysed. In order to highlight the stability of the powder properties and the correctness of the measurements, several determinations (minimum 5) were performed on the same sample.

Fig. 3 (a-d) reveals the processed images for water CA measurement for functionalized SiO_2 FPs.

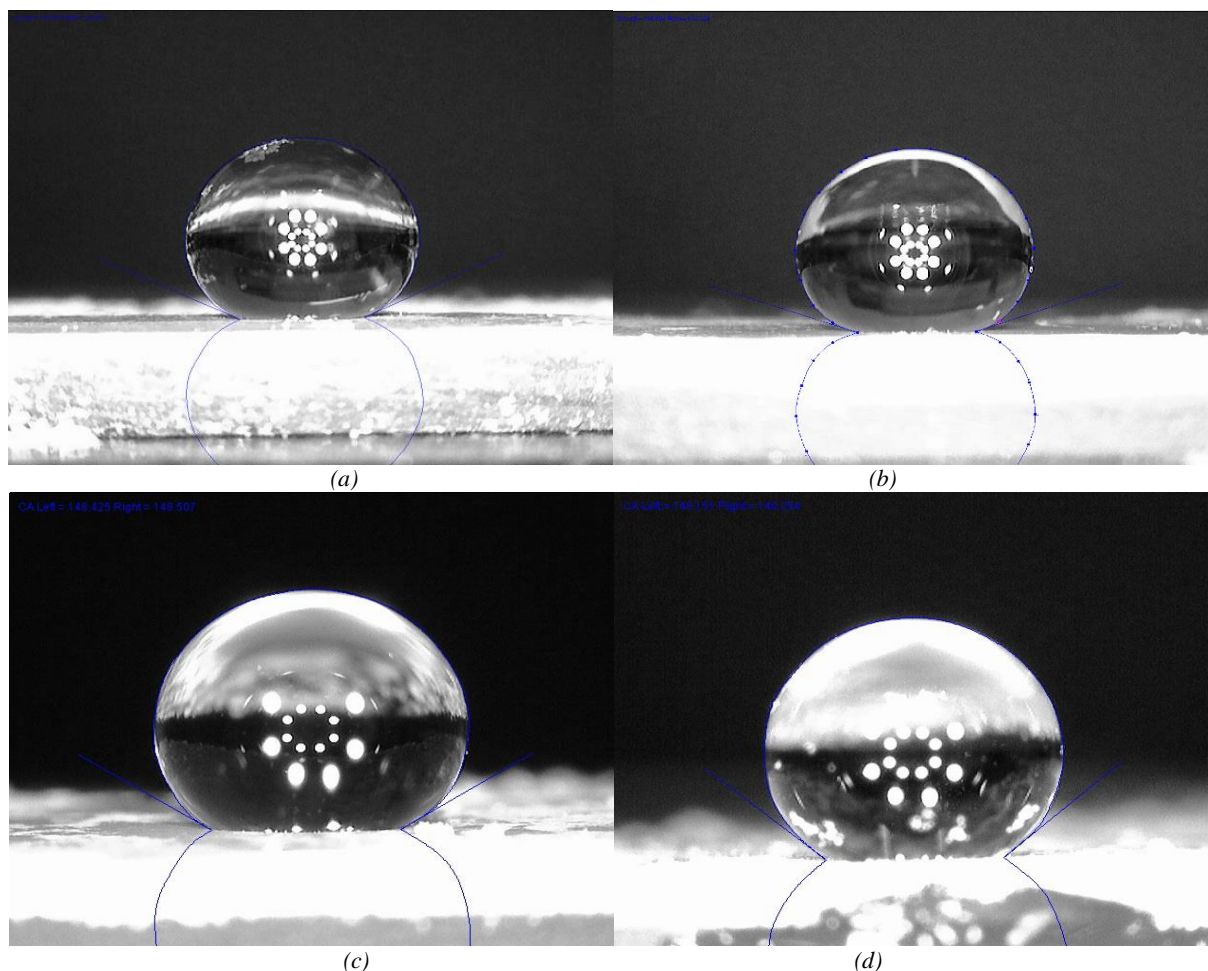


Fig. 3. The processed images for water CA measurement of the samples SiO_2 FPs-1-HMDS (a), SiO_2 FPs-2-HMDS (b), SiO_2 FPs-1-PFOTS (c), SiO_2 FPs-2-PFOTS (d) (color online)

The results obtained by measuring the water CA are presented in Table 1. Here is presented an average value of

the CA calculated for each measured sample.

Table 1. Values of CA measured on SiO₂ FPs functionalized with HMDS and PFOTS

Sample	Water contact angle, °		
	Left	Right	Average
SiO ₂ FPs-1-HMDS	155.422	155.279	155.350
SiO ₂ FPs-2-HMDS	160.347	160.277	160.312
SiO ₂ FPs-1-PFOTS	144.386	144.579	144.482
SiO ₂ FPs-2-PFOTS	138.422	138.450	138.436

From the table above we noticed that HMDS-functionalized SiO₂ FPs have a higher water contact angle than PFOTS-functionalized SiO₂ FPs. Surfaces with a contact angle greater than 150° have a superhydrophobic character [24]. Thus, we can conclude that HMDS-functionalized SiO₂ FPs have a superhydrophobic character, while those functionalized with PFOTS have a high hydrophobic character.

In addition to the fact that the contact angle is influenced by the type of silane used for functionalization, we find that the size of the SiO₂ FPs also influences the contact angle.

In the case of HMDS-functionalized SiO₂ FPs, we find a higher contact angle for SiO₂ FPs with a higher particle size. Instead, in the case of particles functionalized with PFOTS, we obtained a higher contact angle for the SiO₂ sample with a smaller particle size.

The result obtained for the water contact angle confirmed the change in the surface character of SiO₂ FPs from hydrophilic to hydrophobic. The good hydrophobic properties developed by functionalization of SiO₂ FPs recommend them to be used in hydrophobic and superhydrophobic surface coatings.

4. Conclusions

In this work SiO₂ FPs were synthesized by sol-gel technique using Stöber method. SiO₂ FPs with different average dimensions were prepared using two different amounts of TEOS, and after that both types of FPs were functionalized with 1,1,1,3,3,3-hexamethyldisilazane and also with 1H,1H,2H,2H-perfluorooctyltrichlorosilane.

With a homogeneous distribution of particle size for each sample, the SEM analysis revealed FPs with well-defined spherical shapes and clearly distinct individual separations, as well as medium diameter values of 173 and 217 nm for the samples of SiO₂ FPs-1 and SiO₂ FPs-2, respectively.

Also, in the case of SiO₂ FPs functionalized with HMDS and PFOTS, larger particle diameters were obtained due to the presence of a functionalizing agent layer on the particles surface.

The hydrophobic properties of SiO₂ FPs were evaluated by measuring the water CA. The resulting values of the water CA for all the analysed samples are higher than 138°, showing the change in the surface character of SiO₂ FPs from hydrophilic to hydrophobic. SiO₂ FPs functionalized with HMDS exhibit a

superhydrophobic character because the measured water CA is greater than 150°.

Taking into account that the cost of functionalization of SiO₂ FPs with PFOTS is higher than that of functionalization with HMDS and the functionalization with HMDS has proved a higher efficiency, we can consider that the latter is more suitable to be used for industrial applications.

The functionalized SiO₂ particles obtained in this study could be introduced as additive into paints used as surface coatings in applications that required self-cleaning properties.

Acknowledgements

This work was supported by the Competitiveness Operational Programme, project no. P_40_403, code My SMIS 105568, subsidiary ctr. no. 133 D4 ROSEAL/2018.

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