



Article

The Influence of New Hydrophobic Silica Nanoparticles on the Surface Properties of the Films Obtained from Bilayer Hybrids

Cristian Petcu, Violeta Purcar *, Cătălin-Ilie Spătaru, Elvira Alexandrescu, Raluca Șomoghi, Bogdan Trică, Sabina Georgiana Nițu, Denis Mihaela Panaitescu, Dan Donescu and Maria-Luiza Jecu

R & D National Institute for Chemistry and Petrochemistry—ICECHIM, Polymers Department, Spl. Independentei 202, 6th District, 060021 Bucharest, Romania; cpetcu@icf.ro (C.P.); spataru.catalin@gmail.com (C.-I.S.); elviraalexandrescu@yahoo.com (E.A.); r.somoghi@gmail.com (R.S.); trica.bogdan@gmail.com (B.T.); sabina.nitu@yahoo.com (S.G.N.); panaitescu@icf.ro (D.M.P.); ddonescu@chimfiz.icf.ro (D.D.); jecu.luiza@icechim.ro (M.-L.J.)

* Correspondence: violetapurcar@yahoo.com; Tel.: +40-21-316-3093

Academic Editors: Xianghui Hou and Fang Xu

Received: 3 November 2016; Accepted: 16 February 2017; Published: 20 February 2017

Abstract: Ultra-hydrophobic bilayer coatings on a glass surface were fabricated by sol–gel process using hexadecyltrimethoxysilane (C₁₆TMS) and tetramethoxysilane (TMOS) (1:4 molar ratio) as precursors. After coating, silica nanoparticles (SiO₂ NPs) functionalized with different mono-alkoxy derivatives (methoxytrimethylsilane, TMeMS; ethoxydimethylvinylsilane, DMeVES; ethoxydimethylphenylsilane, DMePhES; and methoxydimethyloctylsilane, DMeC₈MS) were added, assuring the microscale roughness on the glass surface. Influences of the functionalized SiO₂ NPs and surface morphology on the hydrophobicity of the hybrid films were discussed. The successful functionalization of SiO₂ NPs with hydrophobic alkyl groups were confirmed by Fourier transform infrared spectroscopy (FTIR). The thermal stability of hydrophobic SiO₂ NPs showed that the degradation of the alkyl groups takes place in the 200–400 °C range. Bilayer coating with C₁₆TMS/TMOS and SiO₂ NPs modified with alkoxy silane substituted with C₈ alkyl chain (SiO₂ NP-C₈) has micro/nano structure. Hydrophobicity of functionalized SiO₂ NPs-C₈ and its higher degree of nanometer-scale roughness gave rise to ultra-hydrophobicity performance for bilayer coating C₁₆TMS/TMOS + SiO₂ NPs-C₈ (145°), compared to other similar hybrid structures. Our synthesis method for the functionalization of SiO₂ NPs is useful for the modification of surface polarity and roughness.

Keywords: sol–gel process; silica nanoparticles; nanostructuring; organic–inorganic hybrids; trialkylmonoalkoxysilanes

1. Introduction

To obtain highly hydrophobic surfaces, a large number of review-type studies have been designed. The main properties of highly hydrophobic surfaces are weak water adhesion and self-cleaning behavior in the presence of wetting phenomenon. In most cases, these surfaces are used in construction, dyes, windshield and window manufacturing, headlights, automobiles, solar panels, good thermal transfer pipe-lines, sensors, etc. [1–4].

A large and diverse number of methods to obtain highly hydrophobic surfaces have been reported, such as multi-step chemical methods and physical methods that create roughness [1,5,6]. Various functional silane precursors—polymethylhydrosiloxane, poly(vinyl chloride), fluorinated

methacrylate, and mercapto functional monomers were used in most situations of sol–gel method in order to fabricate superhydrophobic surfaces [7].

From analysis of the published data, two approaches for obtaining hydrophobic surfaces from particles and binder were notable: mixing the two phases [8–11], or deposition of particles over films obtained from different film-forming procedures [12–22]. In this way, the possibility of obtaining superhydrophobic surfaces (contact angle $> 160^\circ$) by mixing silica nanoparticles (SiO_2 NPs) with a binder obtained from tetraethoxysilane (TEOS) and a fluorosilane (FAS) through acid-catalyzed sol–gel process were reported [8,9]. In the case of depositing SiO_2 NPs over different supports, ultrahydrophobic surfaces were obtained by functionalizing the fillers with hydrocarbon chains [12–15].

Thereby, functionalizing silica particles with trichlorosilanes led to the formation of surfaces whose hydrophobicity increase with increasing alkyl chain length. When n-octadecyltrichlorosilane (ODTS) was used for hydrophobic process, a contact angle (CA) of 162° was achieved [12]. Xiu et al. [13] report the effect of surface hydrophobicity on the measured contact angles on the rough surfaces. It was demonstrated that superhydrophobic surfaces can be obtained using silica nanoparticles functionalized with silanes containing different hydrocarbon or fluorocarbon chains.

Yilgor et al. [14] synthesized SiO_2 NP depositions with controllable hydrophobicity using mixtures of hydrophilic silica with hydrophobic silica (modified with trimethylchlorosilanes) onto the polymer surface. Another research group obtained superhydrophobic films using SiO_2 nanoparticles (synthesized with TEOS in emulsions containing toluene and a mixture of neutral and anionic surfactants) deposited on glass substrates [15]. Superhydrophobic silica layers obtained by thermally treating a mixture that contained dual-sized polystyrene particles were reported [16]. The final process of hydrophobization was accomplished in dodecafluoroheptyl-methyldimethoxysilane vapors, showing excellent superhydrophobic property of silica film. Additionally, a covalent bond between the two phases can represent a special way of ensuring the deposition of silica particles over a polymer matrix [17–20]. “Layer-by-layer” (LBL) gradual deposition of dual-sized silica particles on glass functionalized with NH_3^+ groups and modified with dodecyltrichlorosilane was shown in [21]. Similar CA values were obtained for LBL depositions [22] of SiO_2 NP dispersions over polymer layers with polyalkylamine hydrochloride.

This paper will focus on the aspect of synthesis, size-dependent properties, and modification of silica nanoparticles (SiO_2 NPs) by sol–gel method using different alkoxy silanes (substituted with dimethyl and methyl, vinyl, phenyl, or octyl alkyl group) toward the preparation of bilayer coatings on a glass surface. The influence of the functionalized SiO_2 NPs with mono-alkoxy derivatives (methoxytrimethylsilane, TMeMS; ethoxydimethylvinylsilane, DMeVES; ethoxydimethylphenylsilane, DMePhES; methoxydimethyloctylsilane, DMeC₈MS) on the hydrophobicity is studied. The comparative analysis brings new information regarding the interactions between the alkyl group from the functionalized SiO_2 NPs layer and hexadecyltrimethoxysilane (C_{16}TMS)/tetramethoxysilane (TMOS) hybrid film. Our synthesis method is useful for the modification of surface polarity and wettability. The resultant coatings are characterized through various techniques, including dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), environmental scanning electron microscopy (ESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and water contact angles (CA).

2. Results and Discussion

For increasing hydrophobicity, it is well known that the only method which does not involve any additional oligomerization reactions is the use of monochloro- or monoalkoxy silanes [4,5,23]. In the case of functionalizing silica particles or dispersed layered silicates, silanes with two or three reactive groups can induce aggregation of the fillers due to the formation of multiple covalent bonds [24,25]. The only difficulty when the functionalization is performed with monofunctional silanes is weak reactivity [23,26]. In order to increase the reactivity, in this study, ultrasonication was used throughout the entire reaction and heating process [27].

The functionalization reaction was confirmed by measuring the average diameters of the silica particles dispersed in ethanol (Figure 1a) and methylene chloride (Figure 1b). The highest value was obtained for the silica functionalized with long alkyl chain (*sample 5*, Figure 1b). These results agree with previous results regarding mesoporous organized silica functionalization. When the auxiliary organic species are added to the reaction gel, they are solubilized inside the hydrophobic regions of material, causing an increase in the pore size of the final product [28]. Experiments have shown that the SiO₂ NPs functionalized with short alkyl groups in the reaction mixture lead to a smaller particle size compared to pristine SiO₂ NPs only as a source of silica. These findings indicate that the addition of organosilane with short alkyl group affect the nucleation process and lead to a larger number of formed nuclei. Thus, smaller particle size is obtained (*samples 2–4*). The average particle size increased for *sample 5* (see Figure 1b), and this effect can be caused by steric hindrance and is seen notably in branched chain (longer alkyl chain leads to lower hydrolysis rate). The stability of the particle dispersion can be achieved by steric stabilization, and is almost attained by proper particle surface functionalization.

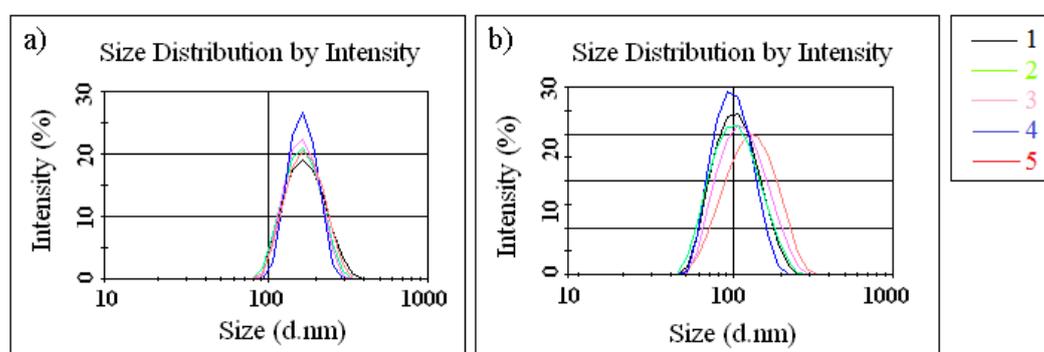


Figure 1. The average particle size of pristine silica nanoparticles (SiO₂ NPs) and functional SiO₂ NPs dispersed in: (a) ethanol and (b) methylene chloride.

The existence of alkyl groups on the silica surface is confirmed by FTIR spectra (Figure 2), in agreement with previously published data [12,27]. For all samples, the Si-O-Si symmetric and asymmetric bands located at $\sim 800\text{ cm}^{-1}$ and $\sim 1100\text{ cm}^{-1}$, respectively, and the band at 950 cm^{-1} corresponding to the Si-O group can be observed [29–31]. The intensity of the C-H stretching bands (peaks observed at 2923 cm^{-1} and 2863 cm^{-1} , respectively) is highest for the silica modified with longest alkyl chains (C₈) (*sample 5*). Substitution with a shorter alkyl chain is characterized by a change in the absorption maximum and a reduced intensity of the bands. This phenomenon can occur due to a different conformation of the alkyl chains [30] and a lower concentration [12] (*samples 2–4*). In the case of methyl group substitution (*sample 1*), no significant absorption can be observed in the mentioned wavelength domain.

Chemical modifications with monoalkoxysilanes after the reaction were outlined by the thermal degradation of the new reaction products. In Table 1, the TGA data are given for the three temperature steps. From previously published studies [12,27], the weight loss in the 25–200 °C interval corresponds to the vaporization of the solvent adsorbed on the particles [32,33]. The thermo-oxidative degradation of the alkyl groups caused by a hydrophobic process takes place in the 200–400 °C range. The last degradation step—from 400 to 700 °C—corresponds to the condensation reaction of the OH groups from the partially modified silica surfaces [34].

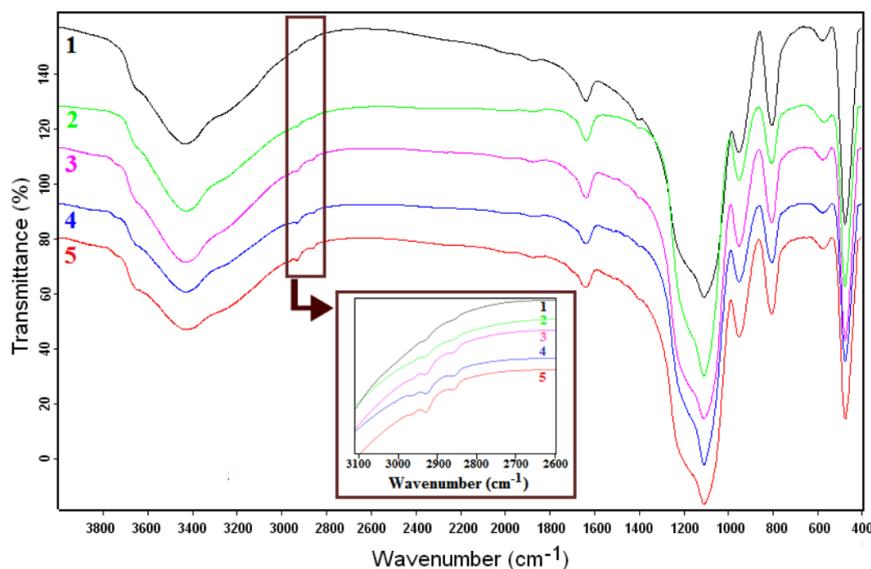


Figure 2. Fourier transform infrared (FTIR) spectra of dried SiO₂ NPs.

Table 1. Thermal degradation of dried SiO₂ NPs.

Sample No.	ΔG (% grav.)/ T_{max} (°C)			Residue (%)
	25–200 °C	200–400 °C	400–700 °C	
1	7.0/47.3	2.2/277.4	2.5/461.0	88.3
2	6.5/48.6	2.8/263.0	2.4/451.0	88.3
3	6.4/48.2	2.8/272.0	2.5/462.1	88.3
4	6.3/51.4	2.8/293.0	2.7/453.0	88.2
5	6.3/50.4	3.1/257.8	2.5/435.0	88.2

The morphology and size of the obtained particles have been examined by environmental scanning electron microscopy and transmission electron microscopy. ESEM and TEM analyses (Figures 3 and 4) were performed to confirm the DLS measurements. For this purpose, dried pristine SiO₂ NP (*sample 1*) and dried SiO₂ NP modified with C₈ (*sample 5*) dispersed in ethanol were analyzed. For *sample 1*, it can be observed that not all particles are spherical, and some of them are irregular. SiO₂ NPs with a size range of 140–170 nm were obtained. Synthesized silica nanoparticles functionalized with long alkyl chain are spherical in shape with diameter of ~150 nm (*sample 5*).

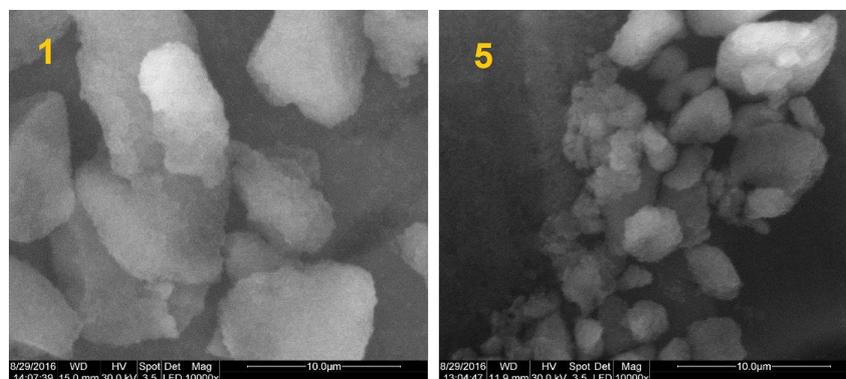


Figure 3. Environmental scanning electron microscopy (ESEM) images of dried pristine SiO₂ NPs (*sample 1*) and dried SiO₂ NPs modified with long alkyl chain (*sample 5*), dispersed in ethanol.

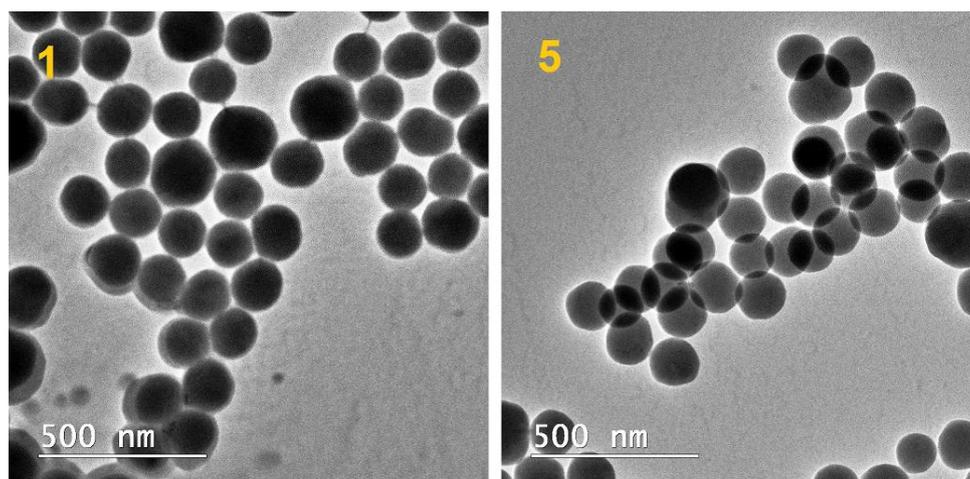


Figure 4. TEM images of dried pristine SiO₂ NPs (*sample 1*) and dried SiO₂ NPs modified with long alkyl chain (*sample 5*), dispersed in ethanol.

The wetting ability and surface roughness changes of the bilayer coatings were evaluated by contact angle (CA) measurement and AFM topography, respectively, and the results are as shown in Figures 5 and 6. Figure 5 shows the contact angle (CA) of a 5 μ L water droplet on the bilayer coatings. Comparing the CA values, a maximum value (145°) was obtained for bilayer coating with C₁₆TMS/TMOS and 0.01 g of SiO₂ NPs functionalized with DMeC₈MS dispersed in 1 mL EtOH (*coating C₅*). This observation means that the coated surface is rough on the micro/nanometer scale. For *coatings C₁–C₄*, the degree of roughness was not sufficient, and ultra-hydrophobicity was not achieved. This effect can be explained by considering the chemical reactivity of functionalized silica nanoparticles that were not strongly fixed to the first layer (C₁₆TMS/TMOS). The surface hydrophobicity is in fact due to the presence of functional hydrophobic groups that start to adhere to the base silicate matrix.

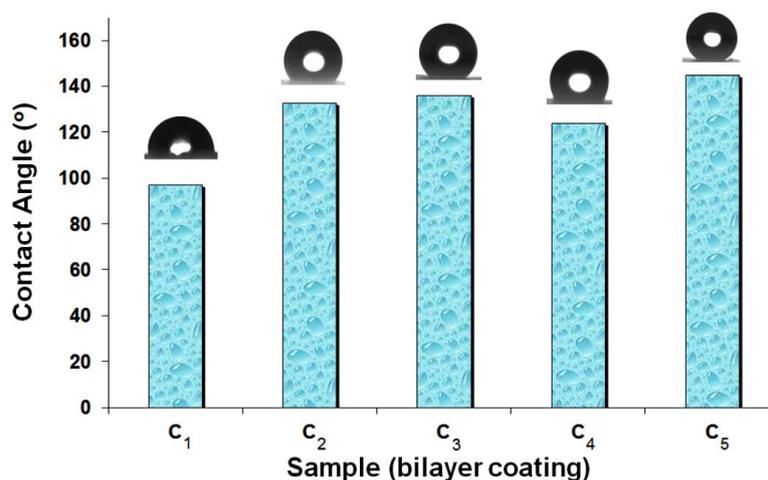


Figure 5. Contact angle of the bilayer coatings (see Table 3).

Figure 6 shows AFM topographic images of C₁₆TMS/TMOS monolayer hybrid film (*coating C₀*), and of bilayer coating (C₁₆TMS/TMOS + 0.01 g of SiO₂ NPs functionalized with DMeC₈MS dispersed in 1 mL EtOH, *coating C₅*). As can be observed, the starting C₁₆TMS/TMOS hybrid film surface is quite smooth. *Sample 5* presents a rough surface, which is attributed to the adhesion between functionalized SiO₂ NPs with long alkyl group and Si-O- groups from the C₁₆TMS/TMOS substrate. The higher degree of nanometer-scale roughness gave rise to ultra-hydrophobicity.

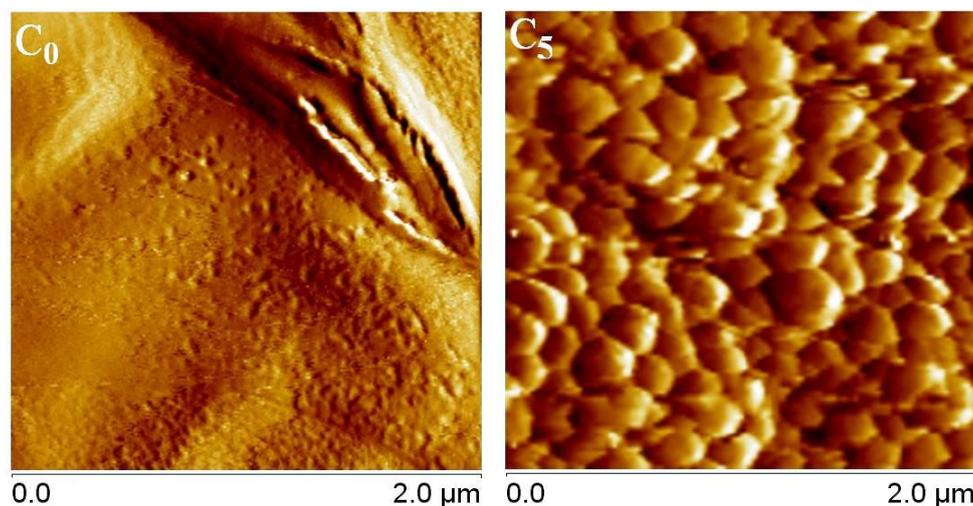


Figure 6. Atomic force microscopy (AFM) topographic images of structured coatings: monolayer hybrid hexadecyltrimethoxysilane/ tetramethoxysilane (C_{16} TMS/TMOS) film (*coating* C_0), and bilayer coating (C_{16} TMS/TMOS + 0.01 g of SiO_2 NPs functionalized with methoxydimethyloctylsilane (DMeC₈MS) dispersed in 1 mL EtOH, *coating* C_5).

3. Experimental Section

3.1. Materials

Tetraethylorthosilicate (TEOS, 98%, Aldrich, Steinheim, Germany), methoxytrimethylsilane (TMeMS, 97%, Fluka, Steinheim, Germany), ethoxydimethylvinylsilane (DMeVES, 97%, Alfa Aesar, Swedesboro, NJ, USA), ethoxydimethylphenylsilane (DMePhES, 97%, Fluka, Steinheim, Germany), methoxydimethyloctylsilane (DMeC₈MS, 98%, Aldrich, Steinheim, Germany), methoxydimethyloctadecylsilane (DMeC₁₈MS, 90%, Aldrich, Steinheim, Germany), hexadecyltrimethoxysilane (C_{16} TMS, 85%, Aldrich, Steinheim, Germany), ethanol (reagent grade, CHIMREACTIV SRL), ammonia (reagent grade, 32 wt. %, Scharlau, Sentmenat, Spain), hydrochloric acid (reagent grade, 37 wt. %, Riedel, Seelze, Germany), toluene (reagent grade, CHIMREACTIV SRL).

3.2. Preparation of Silica Nanoparticles (SiO_2 NPs)

The synthesis of hydrophobic modified SiO_2 nanoparticles (SiO_2 NPs) was realized in two steps by a method adapted from a study published by Kulkarni et al. [11].

3.2.1. Synthesis of the Pristine Silica Nanoparticles

TEOS (32.5 g) and 125 mL absolute ethanol (EtOH) were initially introduced in a three-neck round-bottom flask with a mechanical stirrer (400 rot/min) and a reflux condenser. Under stirring, a mixture of 75 mL NH_4OH (25%) and 570 mL absolute EtOH was added for 2 h. After addition of ~100 mL of ammonia solution, the mixture turned opalescent. At the end of the addition of the ammonia solution, the mixture was kept under stirring for another two hours. The mixture was put in Petri dishes, and the volatile compounds were allowed to evaporate at ambient temperature and in vacuum at 60 °C. After drying, 9.33 g SiO_2 NPs were obtained (*sample 1*) and used for their functionalization with various mono-alkoxy derivatives.

3.2.2. Functionalization of the Silica Nanoparticles with Various Mono-Alkoxy Derivatives

Different alkoxy silanes: methoxytrimethylsilane (TMeMS), ethoxydimethylvinyl silane (DMeVES), ethoxydimethylphenylsilane (DMePhES), and methoxydimethyloctylsilane (DMeC₈MS) were used to functionalize the SiO_2 NPs by sol-gel process. SiO_2 (1.5 g, synthesized in Section 3.2.1)

and 100 mL of toluene (dried on molecular sieves and deoxygenated with nitrogen) were added in a three-neck round-bottom flask provided with mechanical stirrer and reflux condenser. The entire mixture was heated at 50 °C under continuous stirring. Then, 7.5 mmoles of mono-alkoxy derivatives substituted with dimethyl and methyl, vinyl, phenyl, octyl, and octadecyl were added to the heated mixture. The mixture was kept at 50 °C under ultrasonication (in an ultrasonic bath) for 4 h. Subsequently, the mixture was dried in air at room temperature (*samples 2–5*) (see Table 2). The resulting functionalized silica particles and corresponding coatings are described in Table 3.

Table 2. Synthesis conditions for functionalization of silica.

Sample No.	Synthesis	
	Pristine SiO ₂ Particles (g)	R(CH ₃) ₂ SiOR' *
1	1.5	0
2	1.5	Me ₃ SiOMe
3	1.5	VMe ₂ SiOEt
4	1.5	PhMe ₂ SiOEt
5	1.5	C ₈ Me ₂ SiOMe

* R = -CH₃ (Me), -CH₂=CH₂- (V), C₆H₅- (Ph), CH₃-(CH₂)₇- (C₈); R' = -CH₃ (Me), -CH₂-CH₃ (Et).

Table 3. Composition of functionalized silica particles and the corresponding coatings.

Sample No.	Composition	Corresponding Coatings
-	-	C ₀
1	Pristine SiO ₂ NP	C ₁
2	SiO ₂ NP functionalized with TMeMS	C ₂
3	SiO ₂ NP functionalized with DMeVES	C ₃
4	SiO ₂ NP functionalized with DMePhES	C ₄
5	SiO ₂ NP functionalized with DMeC ₈ MS	C ₅

3.3. Fabrication of the Bilayer Coatings on the Glass Substrate

3.3.1. Preparation of the First Coating Layer

The glass substrates were firstly covered with acidic solution (prepared in a similar way to that previously reported [6]) containing hexadecyltrimethoxysilane (C₁₆TMS) and tetramethoxysilane (TMOS). Then, 1.21 g of C₁₆TMS and the amount of TMOS required to obtain a molar ratio of 1/4 were dissolved under continuous stirring in 8.04 mL EtOH and then heated at 40 °C. When the final temperature was achieved, 1.04 mL of HCl (0.1 N solution) was added. The solution was stirred for another 90 min. The molar ratios used for the reaction mixture were as follows: C₁₆TMS:TMOS:EtOH:H₂O:HCl = 1:4:50:19:0.03. The obtained hybrid solution was deposited onto a glass slide by draw down sample coating with the manual applicator. The resultant first layer was left to dry at room temperature for 24 h (*coating C₀*).

3.3.2. Preparation of the Second Coating Layer

A second solution (0.01 g of dried functionalized SiO₂ nanoparticles dispersed in 10 mL EtOH and mixed for approximately 2 h) was deposited over the *first layer* in order to obtain *bilayer coatings* (*coatings C₁–C₅*).

The resultant functionalized silica particles and corresponding coatings are described in Table 3.

3.4. Characterization Methods

The initial solutions were examined by dynamic light scattering (DLS) to measure the particle diameters (Zetasizer, Malvern Nano ZS). The solutions were diluted in ethanol and methylene chloride (0.1 mL sample dissolved in 25 mL solvent and ultrasonicated 5 min.).

FTIR spectra of dried samples were obtained using a Fourier transform infrared spectrophotometer (Tensor 37 from Bruker). The samples were ground with KBr and pressed to form a disc for FTIR scanning. For all scans, the spectra were collected over the wavenumber range of 400–4000 cm^{-1} , with a resolution of 4 cm^{-1} .

TGA analyses of dried functionalized SiO_2 NPs were performed in N_2 (10 $^\circ\text{C}/\text{min}$), 25–700 $^\circ\text{C}$ range, using a TA TGA Q5000 IR instrument.

The morphology of silica particles was imaged using environmental scanning electron microscopy (ESEM) (FEI QUANTA 200) and by Transmission Electron Microscopy (TEM), employing a TecnaiTM G2 F20 TWIN Cryo-TEM instrument (FEI Company) at 200 kV acceleration voltages. The ESEM images were obtained in the low-vacuum mode. The samples were deposited on a conductive stub and dried at room temperature. For TEM analysis, the samples were observed directly without further staining to improve contrast. A droplet of diluted sample was poured on a carbon film-coated copper grid and allowed to dry in air at room temperature.

Contact angles of bilayer coatings were determined using a CAM 200 Contact Angle Tensiometer instrument from KSV Instruments equipped with a digital camera that was connected to a PC. Water was used as the liquid for the contact angle measurements. The contact angles were calculated from the drop images after the shape accentuation, radius, and string reading were determined.

The roughness of bilayer coatings were studied using an atomic force microscope (AFM) from Bruker, Santa Barbara, equipped with a Nanoscope V controller and a MultiMode head. The equipment was operated in tapping mode using an etched silicon tip (nominal radius 8 nm), a cantilever length of 225 μm , and a resonant frequency of approximately 75 kHz. AFM measurements were performed at room temperature with a scan rate of 1 Hz and a scan angle of 0 $^\circ$.

4. Conclusions

Bilayer coatings on glass surfaces were fabricated using functionalized silica nanoparticles obtained by sol-gel process (ultrasonication at 50 $^\circ\text{C}$). FTIR spectra confirmed the existence of the alkyl groups over the silica surface, in agreement with previously published data. The intensity of the C-H stretching bands was the highest in the case of silica modified with long alkyl chain (C_8). Substitution with a shorter alkyl chain was characterized by a modified absorption maximum and a reduced intensity of the bands; methyl group substitution proved to have no significant absorption that could be observed in the mentioned wavelength domain. The thermal stability of the dried silica nanoparticles showed that the weight loss occurred stepwise, and indicated that silica nanoparticles began to lose hydrophobicity when heated in the 200–400 $^\circ\text{C}$ range. ESEM and TEM analyses of samples dried and dispersed in ethanol showed that the silica nanoparticles are mostly spherical in shape, with diameter of ~ 150 nm. The AFM measurements showed that the starting $\text{C}_{16}\text{TMS}/\text{TMOS}$ hybrid film surface has smooth surface. Bilayer coating with SiO_2 NPs modified with C_8 chain present a higher degree of nanometer-scale roughness ($\text{CA} = 145^\circ$). The obtained bilayer coatings can be useful and helpful to construct artificial anti-wetting surfaces for numerous practical applications.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/7/2/47/s1>, Table S1: DLS results for functionalized silica nanoparticles.

Acknowledgments: The work has been funded by the Program ERANET “Towards an ERA in Industrial Biotechnology” (ERA-IB), project number 62/2016 and by the grant funded by the Romanian National Authority for Scientific Research, project number PN16.31.03.04.

Author Contributions: Violeta Purcar, Cristian Petcu, Dan Donescu, were involved in designing the aim of this manuscript, did the experiments and prepared the manuscript. Cătălin-Ilie Spătaru, Elvira Alexandrescu, Raluca Șomoghi, Bogdan Trică, Sabina Georgiana Nițu and Denis Mihaela Panaitescu performed the analyses. Maria-Luiza Jecu contributed as manuscript advisor. Each contributor was essential to the production of this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Roach, P.; Shirtcliffe, N.J.; Newton, M.I. Progress in Superhydrophobic Surface Development. *Soft Matter* **2008**, *4*, 224–240. [[CrossRef](#)]
2. Ma, M.; Hill, R.M. Superhydrophobic surfaces. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193–202. [[CrossRef](#)]
3. Feng, X.J.; Jiang, L. Design and creation of superwetting/antiwetting surfaces. *Adv. Mater.* **2006**, *18*, 3063–3078. [[CrossRef](#)]
4. Gao, L.; McCarthy, T.J. How Wenzel and Cassie Were Wrong. *Langmuir* **2007**, *23*, 3762–3765. [[CrossRef](#)] [[PubMed](#)]
5. Shimojima, A.; Kuroda, K. Designed synthesis of nanostructured siloxane-organic hybrids from amphiphilic silicon-based precursors. *Chem. Rec.* **2006**, *6*, 53–63. [[CrossRef](#)] [[PubMed](#)]
6. Spataru, C.I.; Purcar, V.; Ghiurea, M.; Radovici, C.; Stanga, G.; Donescu, D. Effects of the nanoassociation of hexadecyltrimethoxysilane precursors on the sol–gel process. *J. Sol-Gel Sci. Technol.* **2013**, *65*, 344–352. [[CrossRef](#)]
7. Nagappan, S.; Park, S.S.; Ha, C.S. Recent advances in superhydrophobic nanomaterials and nanoscale systems. *J. Nanosci. Nanotechnol.* **2014**, *14*, 1441–1462. [[CrossRef](#)] [[PubMed](#)]
8. Li, L.; Li, B.; Dong, J.; Zhang, J. Roles of silanes and silicones in forming superhydrophobic and superoleophobic materials. *J. Mater. Chem. A* **2016**, *4*, 13677–13725. [[CrossRef](#)]
9. Han, J.T.; Kim, S.Y.; Woo, J.S.; Lee, G.W. Transparent, conductive, and superhydrophobic films from stabilized carbon nanotube/silane sol mixture solution. *Adv. Mater.* **2008**, *20*, 3724–3727. [[CrossRef](#)]
10. Wu, Z.; Han, H.; Han, W.; Kim, B.; Ahn, K.H.; Lee, K. Controlling the hydrophobicity of submicrometer silica spheres via surface modification for nanocomposite applications. *Langmuir* **2007**, *23*, 7799–7803. [[CrossRef](#)] [[PubMed](#)]
11. Manoudis, P.; Karapanagiotis, I.; Tsakalof, A.; Zuburtikudis, I.; Panayiotou, C. Superhydrophobic composite films produced on various substrates. *Langmuir* **2008**, *24*, 11225–11232. [[CrossRef](#)] [[PubMed](#)]
12. Kulkarni, S.A.; Ogale, S.B.; Vijayamohanan, K.P. Tuning the hydrophobic properties of silica particles by surface silanization using mixed self-assembled monolayers. *J. Colloid Interface Sci.* **2008**, *318*, 372–379. [[CrossRef](#)] [[PubMed](#)]
13. Xiu, Y.; Zhu, L.; Hess, D.W.; Wong, C.P. Biomimetic Creation of Hierarchical Surface Structures by Combining Colloidal Self-Assembly and Au Sputter Deposition. *Langmuir* **2006**, *22*, 9676–9681. [[CrossRef](#)] [[PubMed](#)]
14. Yilgor, I.; Bilgin, S.; Isik, M.; Yilgor, E. Tunable Wetting of Polymer Surfaces. *Langmuir* **2012**, *28*, 14808–14814. [[CrossRef](#)] [[PubMed](#)]
15. Yang, T.; Tian, H.; Chen, Y. Preparation of Superhydrophobic Silica Films with Honeycomb-Like Structure by Emulsion Method. *J. Sol-Gel Sci. Technol.* **2009**, *49*, 243–246. [[CrossRef](#)]
16. Shang, Q.Q.; Gao, L.J.; Liu, H.; Xiao, G.M. Fabrication of Superhydrophobic Silica Film by Removing Polystyrene Spheres. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 334–337. [[CrossRef](#)]
17. Xu, D.; Wang, M.; Ge, X.; Lam, M.H.W.; Ge, X. Fabrication of raspberry SiO₂/polystyrene particles and superhydrophobic particulate film with high adhesive force. *J. Mater. Chem.* **2012**, *22*, 5784–5791. [[CrossRef](#)]
18. Petcu, C.; Nistor, C.L.; Purcar, V.; Cinteza, L.O.; Spataru, C.I.; Ghiurea, M.; Ianchis, R.; Anastasescu, M.; Stoica, M. Facile preparation in two steps of highly hydrophobic coatings on polypropylene surface. *Appl. Surf. Sci.* **2015**, *347*, 359–367. [[CrossRef](#)]
19. Purcar, V.; Cinteza, O.; Ghiurea, M.; Balan, A.; Caprarescu, S.; Donescu, D. Influence of the hydrophobic characteristic of organo-modified precursor on the wettability of silica film. *Bull. Mater. Sci.* **2014**, *37*, 107–115. [[CrossRef](#)]
20. Purcar, V.; Cinteza, O.; Donescu, D.; Bala, D.; Ghiurea, M.; Petcu, C.; Caprarescu, S. Surface modification of silica particles assisted by CO₂. *J. Supercrit. Fluids* **2014**, *87*, 34–39. [[CrossRef](#)]
21. Tsai, H.J.; Lee, Y.L. Facile method to fabricate raspberry-like particulate films for superhydrophobic surfaces. *Langmuir* **2007**, *23*, 12687–12692. [[CrossRef](#)] [[PubMed](#)]

22. Han, J.T.; Kim, S.; Karim, A. UVO-Tunable Superhydrophobic to Superhydrophilic Wetting Transition on Biomimetic Nanostructured Surfaces. *Langmuir* **2007**, *23*, 2608–2614. [[CrossRef](#)] [[PubMed](#)]
23. Fadeev, A.Y.; McCarthy, T.J. Self-assembly is not the only reaction possible between alkyltrichlorosilanes and surfaces: Monomolecular and oligomeric covalently attached layers of dichloro- and trichloroalkylsilanes on silicon. *Langmuir* **2000**, *16*, 7268–7274. [[CrossRef](#)]
24. Pham, K.N.; Fullston, D.; Sagoe-Crentsil, K. Surface modification for stability of nano-sized silica colloids. *J. Colloid Interface Sci.* **2007**, *315*, 123–127. [[CrossRef](#)] [[PubMed](#)]
25. Herrera, N.N.; Letoffe, J.M.; Putaux, J.L.; David, L.; Bourgeat-Lami, E. Aqueous dispersions of silane-functionalized laponite clay platelets. A first step toward the elaboration of water-based polymer/clay nanocomposites. *Langmuir* **2004**, *20*, 1564–1571.
26. Durdureanu-Angheluta, A.; Ardeleanu, R.; Pinteala, M.; Harabagiu, V.; Chiriac, H.; Simionescu, B.C. Silane covered magnetite particles, preparation and characterization. *Dig. J. Nanomater. Biostruct.* **2008**, *3*, 33–40.
27. Daniel, L.M.; Frost, R.L.; Zhu, H.Y. Edge-Modification of Laponite with Dimethyl-octylmethoxysilane. *J. Colloid. Interface Sci.* **2008**, *321*, 302–309. [[CrossRef](#)] [[PubMed](#)]
28. Zeid, A.A. A Review: Fundamental Aspects of Silicate Mesoporous Materials. *Materials* **2012**, *5*, 2874–2902.
29. Ianchis, R.; Donescu, D.; Petcu, C.; Ghiurea, M.; Anghel, D.F.; Stanga, S.; Marcu, A. Surfactant-free emulsion polymerization of styrene in the presence of silylated montmorillonite. *Appl. Clay Sci.* **2009**, *45*, 164–170. [[CrossRef](#)]
30. Brambilla, R.; Pires, G.P.; Joãa dos Santos, H.Z.; Lacerda Miranda, M.S.; Chornik, B. Octadecylsilane-modified silicas prepared by grafting and sol–gel methods. *J. Electron. Spectrosc.* **2007**, *156–158*, 413–420. [[CrossRef](#)]
31. Petcu, C.; Purcar, V.; Ianchis, R.; Spataru, C.I.; Ghiurea, M.; Nicolae, C.A.; Stroescu, H.; Atanase, L.I.; Frone, A.N.; Trica, B.; et al. Synthesis and characterization of polymer-silica hybrid latexes and sol-gel-derived films. *Appl. Surf. Sci.* **2016**, *389*, 666–672. [[CrossRef](#)]
32. Jeon, B.J.; Hah, H.J.; Koo, S.M.; Byung, J.J.; Hoe, J.H.; Sang, M.K. Surface modification of silica particles with organoalkoxysilanes through two-step (acid-base) process in aqueous solution. *J. Ceram. Process. Res.* **2002**, *3*, 216–221.
33. Ianchis, R.; Rosca, I.D.; Ghiurea, M.; Spataru, C.I.; Nicolae, C.A.; Gabor, R.; Raditoiu, V.; Preda, S.; Fierascu, R.C.; Donescu, D. Synthesis and properties of new epoxy-organolayered silicate nanocomposites. *Appl. Clay Sci.* **2015**, *103*, 28–33. [[CrossRef](#)]
34. Raditoiu, V.; Raditoiu, A.; Wagner, L.E.; Raduly, M.F.; Amăriutei, V.; Nicolae, C.A.; Fierascu, R.C. Synthesis, characterization and photoisomerization behavior of some organic modified silica—Azo dye hybrid films. *Optoelectron. Adv. Mater. Rapid Commun.* **2011**, *5*, 363–369.

