



Rapid Microwave-Assisted Synthesis of Organo-Modified Nanostructured Silica Coatings with Tunable Water-Repellence Properties

Catalina Ioana Gîfu¹, Bogdan Trică¹, Claudia Mihaela Ninciuleanu¹, Cătălin Ionuț Mihăescu¹, Cristian Petcu^{1,*}, Mihaela Cristina Lite², Alina Popescu², Mihai Anastasescu³, Sorina Nicoleta Voicu⁴, Maria Antonia Tanase⁵ and Ludmila Otilia Cinteza^{5,*}

- ¹ Polymers Department, National Institute for Research and Development in Chemistry and Petrochemistry—ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania; gifu_ioanacatalina@yahoo.com (C.I.G.); trica.bogdan@gmail.com (B.T.);
- claudia.ninciuleanu@yahoo.com (C.M.N.); mihaescu_catalin96@yahoo.com (C.I.M.)
 ² Textile Chemistry and Environment Protection Research Department, The National Research-Development
- Institute for Textiles and Leather Research, 16 Lucretiu Patrascanu Street, 030508 Bucharest, Romania; cristina.lite@certex.ro (M.C.L.); alina.popescu@certex.ro (A.P.)
- ³ 'Ilie Murgulescu' Institute of Physical Chemistry, Romanian Academy, 202 Spl. Independentei, 060021 Bucharest, Romania; manastasescu@icf.ro
- Department of Biochemistry and Molecular Biology, Faculty of Biology, ICUB-Research Institute of the University of Bucharest, University of Bucharest, 050095 Bucharest, Romania; sorina.voicu@bio.unibuc.ro
- ⁵ Physical Chemistry Department, University of Bucharest, 030018 Bucharest, Romania; maria.a.tanase@gmail.com
- * Correspondence: cpetcu@icf.ro (C.P.); ocinteza@gw-chimie.math.unibuc.ro (L.O.C.)

Abstract: A simple method to fabricate organo-modified silane coatings for water-repellent surface modification was proposed, by using a microwave sol-gel synthesis of hybrid materials. Low-cost fluorine-free tetraethoxysilane (TEOS) and dodecyltriethoxysilane (DDTES) were used as silane derivatives. The organo-modified silica coatings were prepared by the drop-casting method and were characterized by UV-VIS, FTIR spectroscopy, and AFM and SEM microscopy. The morphology of the film show the existence of submicrometer scale roughness due to the aggregation of modified silica nanoparticles. Contact angles of water and diiodomethane on surfaces modified with as prepared nanostructured film were determined in order to assess the hydrophobic and oleophobic properties. The TEOS/DDTES ratio was proved to be a crucial factor in tuning the wettability properties. The results suggest that significant increase of hydrophobicity could be achieved by using non-fluorinated cost-effective silica nanomaterials produced with a rapid ecofriendly method.

Keywords: organo-modified silica; highly hydrophobic coatings; contact angle; nanostructured silica films; non-fluorinated silica coatings

1. Introduction

Functional coatings which allow modification of wetting properties have received considerable attention due to the potential for various applications, such as self-cleaning, water repellent, super dry, antifouling, anti-icing, antireflection, corrosion-resistant coatings, and drag reduction [1–5]. Materials with hydrophobic surfaces are commonly used for resisting water and fog condensation, but also for many other applications, including prevention of biofilm formation [6,7]. Among special superwettability phenomena, superhydrophobicity is the most investigated [8]. It is a biomimetic effect that can be found in different plants, such as lotus and rice leaf, Chinese watermelon, taro plant leaf, purple setcreasea, ramee leaf, Indian cress, or in various insects and birds, such as water striders, *Diptera tabanus chrysurus*, and *Homoptera* [9]. Inspired by natural surfaces, scientists developed artificial superhydrophobic surfaces with water-contact angles larger than 150°, and hysteresis



Citation: Gîfu, C.I.; Trică, B.; Ninciuleanu, C.M.; Mihăescu, C.I.; Petcu, C.; Lite, M.C.; Popescu, A.; Anastasescu, M.; Voicu, S.N.; Tanase, M.A.; et al. Rapid Microwave-Assisted Synthesis of Organo-Modified Nanostructured Silica Coatings with Tunable Water-Repellence Properties. *Coatings* 2021, *11*, 1319. https://doi.org/10.3390/ coatings11111319

Academic Editor: Carlo Antonini

Received: 9 October 2021 Accepted: 27 October 2021 Published: 29 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). below 10°, on which water drops exhibit an almost spherical shape and easily roll off. The special wettability properties, i.e., superhydrophobicity, superoleophilicity, and superamphiphobicity, are related to chemical composition of the surface and, at the same time, to the morphology and textural features of the material. Combining both micro- and nanometer-scale roughness and chemical modification of the surface is considered the standard approach to obtain superhydrophobic surfaces [10]. Water-repellent materials have been prepared using a large variety of inorganic and organic substances, most of them highly nonpolar polymers with intrinsic hydrophobic properties. However, smooth surfaces of hydrophobic materials do not exhibit a water-contact angle beyond 120° (for fluorinated polymers). Nanostructured morphology of surfaces play a very important role in obtaining superhydrophobicity on a solid substrate, which increased water-contact angle higher than 150°. Thus, the fabrication of a superhydrophobic surface could be achieved by two approaches: (i) creating a suitable roughness on a hydrophobic material, and (ii) altering the chemical properties of a rough surface by chemical modification or deposition of a hydrophobic coating [11]. The second path usually uses solid substrate with fabric or mesh morphology that enable the suitable roughness of the surface. Thus, one of the applications of superhydrophobic and superoleophilic coatings which attracted increasing interest is for oil/water separating industry. Various techniques were proposed to fabricate such filters, for example, a stainless-steel mesh functionalized with a sprayed emulsion coating based on polytetrafluoroethylene (PTFE), adhesive, dispersant, surfactant, and thinner or with solutions of polystyrene sprayed under specific operating conditions [12].

On the other hand, texturing the surface of non-polar materials with low surface energy is the common approach, and various chemical and physical methods have been proposed to obtain it. Most of the modern methods are physical, using various instruments to produce regular patterns with a specific design, in order to maximize the formation of air pockets under the liquid droplets deposited on the surface and reduce the contact between the water and the material. Nano- and micro-pattering of metallic or polymeric surfaces under laser treatment results in controlled modification of wettability, with the development of materials with superior superhydrophobic properties. Highly defined patterns or ripples with enhanced periodicity are obtained using ultra-short lasers that produce precise ablation without significant thermal impact [13]. Another promising way to modify the morphology of the surface is the etching/sputtering processes in atmospheric pressure plasma jet [14]. These methods do not protrude into the manufacturing industry since they involve the use of expensive, sophisticated instruments and operating infrastructure. Other methods to obtain suitable morphology of the surfaces, also considered limited by the high costs, are micro-machining of the injection mold or nanoimprint lithography combined with other conventional nanopattering techniques [15,16]. The most widely used method of forming rough surfaces due to its simplicity and cost-efficiency is the incorporation of nanoparticles in the coating, for example, nanoparticles of oxides or natural materials, such as cellulose [17].

Hydrophobic coatings that can be deposited on various supports to function are obtained from film-forming materials such as surfactants, polymers, or inorganic materials. One of the most used materials for coatings on various solid substrate is silica, which allows the preparation of robust, functionalizable films with tunable optical and mechanical properties. Silica films are most conveniently produced from tetraethyl orthosilane (TEOS) as a precursor and results in a highly hydrophilic coating, exhibiting very small values of water contact angle (close to 0°), due to the presence of hydroxyl groups on the surface of the obtained material. The hydrophobization of such materials is achieved by using organo-modified silane derivative into silica synthesis, thus some of the hydroxyl groups on the surface are replaced by hydrophobic ligands and the formation of an organic-inorganic hybrid.

Superhydrophobic coatings could be obtained from silane derivatives modified with alkyl chains with various length and chemical structure [18]. Hydrophobic silica coatings synthesized by the sol-gel method with different hydrophobic additives of alkoxysi-

lane with alkyl chains varied from 4 to 18 show various water-contact angles ranging from 30° to 120°. Xu et al. obtained transparent superhydrophobic coatings be using 3-aminopropyltriethoxysilane functionalized with 1H,1H,2H,2H-perfluorooctyltri methoxysilane [19]. The silica nanoparticles coated with polyimide precursor substrate followed by hydrophobization with fluoroalkyl silane conduct to superhydrophobic surfaces according to Zhao et al. [20]. The use of organo-fluoride alkoxysilanes as reagent to increase the hydrophobicity of the hybrid silica matrix results in a dramatic increase of the contact angle (CA), up to 170°, but in the last decades are seriously questioned due to their known carcinogenicity and negative environmental impact [21]. Thus, other silane reagent bearing organic moieties with relative low surface energy are added in the film synthesis, in order to develop a more environmental benign synthesis of superhydrophobic silica-based coatings.

To obtain silica with tailored textural properties the sol-gel process to produce nanostructured material is a commonly used method. Most of the conventional methods used for producing silica nanoparticles generate particles with a broad particle size distribution, variable morphology, and low purity. This conventional procedure involves several timeconsuming steps. Microwave heating proved to be a very efficient method for material synthesis. Besides being an economical and easily scalable technique, it has been used, for example, for sol-gel synthesis. The microwave heating method solves many of the drawbacks mentioned above, due to the fine control of the reaction parameters and it could significantly accelerate the synthesis process. For example, Zang et al. used microwave synthesis to obtain silica-DDR zeolite, and the synthesis time was reduced from 25 days to 2 days. This improvement can be attributed to the fast and homogeneous heating from microwave radiation [22].

Consequently, some studies have been focused on using conventional methods for optimizing the properties of the silica gel through aging treatments to promote the strength of the silica network and minimize the possible network collapsing during drying [23,24]. The crosslinks produced by aging reactions can be influenced by the acidic or basic character of a solution [25].

There are many papers available reporting the preparation of superhydrophobic silica films by sol-gel process. The introduction of organic silane derivative in the hybrid materials can be achieved by using two methods. In the first one, the co-condensation process of a hydrophilic silane precursor, such as TEOS with an organo-modified derivative, is conducted in various reaction conditions, resulting in the formation of homogeneous organic-inorganic hybrid silica matrix. In the second way, a two-step synthesis involves the obtaining of SiO₂ nanoparticles and their further functionalization with the organic layer onto the surface by the second-step hydrolysis of an organic modified silane reagent. The hydrophobization of pristine silica nanoparticles (NPs) was performed using various methods, through sol-gel reaction conducted in normal conditions, in supercritical fluids [26], in plasma [27], and in microwave irradiation.

Even with this background, there are few studies in the literature where this technology has been chosen to enhance the production process of silica materials. Most studies have used microwave heating after the gelation and curing process, where its role is restricted to merely evaporating residual water from the aged gels. Only a few studies have reported the sol-gel process being performed under microwave heating [28–30]. Other advantages include instantaneous and precise electronic control of the reaction, fewer side reactions, rapid volumetric heating, higher yields of products, selectivity and purity of the obtained compounds, energy-saving, and a green chemistry approach.

In this paper, we report our study obtaining an organically modified highly hydrophobic silica film by microwave process. Most of the coatings used in the fabrication of superhydrophobic surfaces are obtained from fluorinated silanes or polysiloxane oligomers, which are quite costly reagents. A less expensive alternative is considered the obtaining of silica materials with alkylsilanes with various hydrocarbon chains. Various surface roughnesses and morphology were achieved by carefully controlling the reaction condition and molar ratio of the selected precursors. The relationship between size particle, surface chemistry, contact angle, and surface roughness were compared and discussed. Furthermore, static contact angle and contact angle hysteresis were compared and discussed. Through this study, we intend to explore the possibility of designing and creating the desired surface roughness and, consequently, the increased hydrophobic behavior, by a simple drop casting procedure of an organo-modified silica coating material using environmentally friendly affordable silane precursor and microwave-assisted synthesis.

2. Materials and Methods

2.1. Materials

All the chemical reagents and solvents were commercially purchased and used without further purification: tetraethoxysilane (TEOS, 98%, Sigma-Aldrich, Philadelphia, PA, USA), dodecyltriethoxysilane (DDTES, 97%, Fluka, Philadelphia, PA, USA), ammonium hydroxide solution (NH₄OH, 35% aqueous solution, Sigma-Aldrich, Philadelphia, PA, USA), and ethanol (EtOH, 96%, ChimReactiv SRL, Bucharest, Romania). Bidistilled water was produced using a laboratory ultrapure water-purification system (Milli-Q[®] Advantage A10, Merck Millipore, Germany).

2.2. Organo-Modified Silica Coatings Synthesis

Coating materials were prepared as hybrid organic-inorganic silica films containing silica nanoparticles further functionalized with organo-modified silane derivatives. The synthesis was based on modified Strober method conducted in a microwave reactor. Modified silica nanoparticles were prepared with microwave heating, using a microwave reactor Monowave 200 (Anton Paar GmbH, Graz, Austria). The synthesis of modified silica nanoparticles was conducted in two steps. In the first step, the silica nanoparticle was prepared from TEOS precursor and then functionalized with organo-modified silane precursors. The solvent mixture composed of ethanol and distilled water in an appropriate molar ratio was prepared, followed by the addition of the ammonium hydroxide solution to obtain an alkaline medium. The mixture is then heated at ~40 °C, under vigorous magnetic stirring. In a typical synthesis, the required volume of TEOS in 500 μ L ethanol is added to the reaction solvent, to ensure the designated ethanol/water/TEOS molar ratio. In order to obtain silica nanoparticles with different sizes, the TEOS and ammonia concentrations in the reaction mixture was varied. After 5–10 min the system became slightly opalescent which indicates the formation of the silica nuclei. The mixture was poured into a vial and transferred to the microwave reactor. During this step, the temperature was raised at 70 °C under fast microwave irradiation and kept for 30 min for silica nanoparticles growth and aging. After that, appropriate amounts of the organo-modified silane precursor were added, dropwise, to the previous silica sol to obtain the organic functionalized silica nanoparticles. The reaction took place at a constant temperature of 70 °C for 30 min, under magnetic stirring.

After synthesis and cooling at room temperature, the obtained materials were characterized and used to prepare the protective coatings. The dispersions containing functionalized silica particles were deposited onto microscope glass slides as model solid substrate, by dropping method. The glass slides were previously washed with commercial detergents, then cleaned with hot concentrated NaOH solution to remove organic and detergent traces and, finally, rinsed with distilled water. The films were dried at room temperature for 48 h and then used for further characterization.

2.3. Characterization

The particle size of silica and modified silica particles were measured after their preparation using a ZetasizerNanoZS instrument (Malvern Instruments Ltd., Malvern, UK), without dilution of samples.

Fourier Transform Infrared (FT-IR) spectra were recorded in the 400–4000 cm⁻¹ range on a Tensor 37 Bruker spectrophotometer (Woodstock, NY, USA), equipped with a Golden Gate ATR unit.

A contact angle instrument OCA 15 (DataPhysics, Filderstadt, Germany) was used for the evaluation of wettability properties, with water, di-iodomethane, and 1-bromonaphta lene as reference liquids. The static contact angles of selected liquids on deposited films were obtained by analyzing the captured images using sessile drop method at room temperature. The reported contact-angle values were obtained as the average of five measurements (liquid droplets placed in various regions of the film surface).

The morphology of the resulting modified silica films was studied via environmental scanning electron microscopy (ESEM) using an FEI-Quanta 200 microscope (FEI, Eindhoven, The Netherlands), without coating on silica films.

Transmission electron microscopy was used to investigate the shape and size of the obtained silica nanoparticles. The measurements were performed on a Tecnai[™] G2 F20 TWIN Cryo-TEM instrument (FEI Company, Eindhoven, The Netherlands) in Bright Field Mode, at an acceleration voltage of 120 kV. For sample measurements, 10 µL from each of the ethanolic samples was placed on copper grids coated with a formvar/carbon film (FCF-300-Cu-TC, Electron Microscopy Sciences, USA). The excess volume was removed using filter paper and the thin liquid film was left to dry at room temperature.

Atomic force microscopy (AFM) measurements were performed with XE-100 (Park Systems, Suwon, Korea) working in a true non-contactTM mode, in order to minimize the tip-sample interaction. The XE-100 AFM was equipped with flexure-guided, cross-talk eliminated scanners thus obtaining accurate, free-artifact images. All AFM images were recorded with sharp tips (PPP-NCLR from NanosensorsTM) with less than 10 nm radius of curvature, 225 μ m mean length, 38 μ m mean width, ~48 N/m force constant, and 190 kHz resonance frequency. The recorded AFM images were processed with the XEI program (v 1.8.0—Park Systems) for display purpose and roughness evaluation.

3. Results and Discussion

The silica dispersions were prepared by the modified Stober synthesis, in the presence of ammonia as the basic catalyst. The mechanism of nanoparticle formation is based on the hydrolysis and condensation of silane derivatives (R denote the alkyl radicals), according the main following reactions [31]:

$$\equiv SiOR + H_2O \xrightarrow[Alcohol]{NH_4OH} \equiv SiOH + ROH$$
(1)

$$\equiv SiOR + HOSi \equiv \xrightarrow{NH_4OH}_{Alcohol} \equiv SiOSi \equiv +ROH$$
(2)

$$\equiv SiOH + HOSi \equiv \xrightarrow{NH_4OH}_{Alcohol} \equiv SiOSi \equiv +H_2O$$
(3)

On the surface of prepared silica nanoparticles, organic groups can be introduced by further addition of alkyl-modified silane derivatives. Those reactants can be converted in hydrolysates under basic catalysis and condense with the silanol groups of the pristine silica nanoparticles.

The molar ratio between the TEOS and the organically modified precursor is described in Table 1.

The sol-gel synthesis of silica nanomaterials is performed in various conditions of reaction (reagent concentration, solvents, and temperatures), thus the growth and maturation of nanoparticles require a long period of time—up to 24 h [32]. In the present study a rapid and facile synthesis of such material is proposed, by using microwave irradiation to boost the processes involved in SiO₂ formation.

Silica nanoparticles with various sizes and size distribution were obtained, as is determined from DLS measurement, summarized in Table 2.

Sample	Molar Ratio TEOS:NH4OH:H2O	Molar Ratio TEOS:DDTES
SiO ₂ -1	1:3.4:15.2	_
SiO ₂ -1-Org1	1:3.4:15.2	1:20
SiO ₂ -1-Org2	1:3.4:15.2	1:10
SiO ₂ -1-Org3	1:3.4:15.2	1:5
SiO ₂ -2	1:12.7:57.3	_
SiO ₂ -2-Org1	1:12.7:57.3	1:20
SiO ₂ -2-Org2	1:12.7:57.3	1:10
SiO ₂ -2-Org3	1:12.7:57.3	1:5

Table 1. Composition of silica-based nanocoatings.

Table 2. Size and size distribution of silica dispersion obtained in the microwave-assisted method.

Sample	Average Size (nm)	PdI	Observation
SiO ₂ -1	189.5	0.005	Monomodal distribution
SiO ₂ -1-Org1	189	0.095	Monomodal distribution
SiO ₂ -1-Org2	194.1	0.045	Monomodal distribution
SiO ₂ -1-Org3	201	0.032	Monomodal distribution
SiO ₂ -2	393.9	0.056	Monomodal distribution
SiO ₂ -2-Org1	395	0.211	Bimodal distribution Additional peak at ~5000 nm
SiO ₂ -2-Org2	406.3	0.145	Monomodal distribution
SiO ₂ -2-Org3	427.4	0.057	Monomodal distribution

By altering the molar concentration of TEOS, NH₄OH, and solvent EtOH/water, NPs with average size approximately 200 nm and 400 nm, respectively, were obtained. The average diameter of SiO₂ NPs increase when organic coating is formed during the second step of reaction involving hydrolysis of dodecyltriethoxy silane derivative (Table 2). As is expected, the particles' size increase with increasing concentration of NH₄OH and water in the reaction mixture.

The sol-gel synthesis performed under microwave irradiation results in remarkable monodispersed particles for all samples, according to the polydispersity index (PdI) values, which range from 0.005 to 0.211. A representative DLS diagram is shown in Figure 1, for samples prepared at molar ratio TEOS/NH₄OH/H₂O = 1/12.7/57.3.



Figure 1. Size distribution of unmodified SiO₂ dispersion (SiO₂-2 black) and for organo-modified SiO₂ dispersions: SiO₂-2-Org1 (green), SiO₂-2-Org2 (blue), and SiO₂-2-Org3 (purple).

The DLS diagrams show monomodal distribution, with no additional signals present, with the exception of sample SiO₂-2-Org2, which shows a second population with average diameter of 5000 nm, probably some aggregates, as a negligible per cent of 1.8%.

The dimension of NPs and the monodispersity of samples are confirmed by the analysis of the TEM images (Figure 2).

The obtained SiO₂ NPs are spherical in shape, with smooth surface and exhibit uniform size that confirm the DLS data. In the case of samples prepared with adding organo-silane DDTES, a distinct organic shell is observed, with increasing thickness when TEOS:DDTES ratio increase (approximately 10–15 nm for the sample SiO₂-1-Org3 prepared with highest TEOS:DDTES ratio of 5:1).

The presence of the organic layer from the alkyl modified silane reagent was evidence from the FTIR analysis. The FTIR spectra of silica samples are presented in Figure 3.

Similar peaks are evidenced in both series of silica dispersion prepared in various molar ratio of silane and organo-modified silane reagents. From the FTIR spectrum strong Si–O–Si asymmetric stretching and C–O stretching vibration were observed between 1000 and 1300 cm⁻¹, which is the structural backbone of the organic-inorganic hybrid silica material. The band at intermediate frequencies at 791 cm⁻¹ can be attributed to symmetric stretching motions of the oxygen atoms, and also from the SiOCH₂CH₃ group due to incomplete hydrolysis of TEOS. The absorption infrared spectrum of the dodecyltriethoxysilane shows strong peaks at 2923 and 2857 cm⁻¹, which were assigned to the C–H asymmetric and symmetric stretching of aliphatic CH₂ groups, respectively, in the aliphatic chain of the organosilane [33].

The spectrum exhibits an O–H stretching region around $3200-3500 \text{ cm}^{-1}$, which is represented by a broad band, due to the free vibration of OH groups and hydrogen bonded OH groups. The SiO-H stretching of surface silanols hydrogen-bonded to molecular water were indicates in the FT-IR spectra around 3740 cm^{-1} [33]. Also, in Figure 3 it could be observed that by increasing the dodecyltriethoxysilane concentration the specific C–H asymmetric and symmetric stretching bands are more intensive.

Then translucent organic-inorganic hybrid silica sol was dropped onto the glass slide as a model solid substrate, to produce the nanostructured deposited films. It is presumable that silica nanoparticles interacted with the substrate by forming hydrogen bonds with hydroxyl groups on the glass surface.



Figure 2. TEM image of silica and organically modified silica SiO₂-1 (**a**), SiO₂-1-Org1 (**b**), SiO₂-1-Org2 (**c**), and SiO₂-1-Org3 (**d**).

The special wettability properties of surfaces, i.e., superhydrophobicity and superoleophobicity, results from the combination of three factors: (i) intrinsic hydrophobicity of the surface material, which need to possess low surface tension, (ii) surface roughness, and (iii) the biomimetic topography of the surface with hierarchically nano/micro architecture. The superoleophobic and superamphiphobic properties could be achieved only when the third factor is present, while superhydrophobic behavior is shown often when low surface tension materials are combined with suitable roughness of the substrate.

Thus, the morphology of the deposited hybrid nanocoatings was investigated by scanning electron microscopy. Representative images are shown in Figures 4 and 5 for samples prepared at low and high concentration of ammonia and water, respectively, with different TEOS-organosilane ratio.



Figure 3. FTIR spectra for pure silica and organically modified silica obtained at various EtOH:water:NH₄OH molar ratio: Series TEOS:NH₄OH:H₂O = 1:3.4:15.2 (**a**); Series TEOS:NH₄OH:H₂O = 1:12.7:57.3 (**b**).



Figure 4. SEM image of silica and organically modified silica prepared at TEOS:NH₄OH:H₂O ratio of 1:3.4:15.2. SiO₂-1 (**a**), SiO₂-1-Org1 (**b**), SiO₂-1-Org2 (**c**), and SiO₂-1-Org3 (**d**).



Figure 5. SEM image of silica and organically modified silica prepared at TEOS:NH₄OH:H₂O ratio of 1:12.7:57.3. SiO₂-2 (**a**), SiO₂-2-Org1 (**b**), SiO₂-2-Org2 (**c**), and SiO₂-2-Org3 (**d**).

The hydrolysis of pure TEOS results in obtaining spherical silica. Small SiO₂ NPs obtained in samples synthesized with the TEOS:NH₄OH:H₂O ratio of 1:3.4:15.2 form a rather coherent film, with a dense packing of particles (Figure 4a), while in the case of larger particles a certain tendency of aggregation in the deposited films is shown. Agglomerates of these particles could be observed in SEM images (Figure 5a). In Figure 4b–d for all samples with organo-silane derivative formation of large island of agglomerated nanoparticles are present. No silica entities with shape other than spherical are present, even in sample SiO₂-1-Org3, which contains the largest amount of dodecyl triethoxysilane precursor.

The synthesis used in the present study, in two steps, involving the formation of silica NPs from TEOS in the first step, followed by the growth of the organosilane shell in the second one, results in a matrix of spherical particles closely packed, as is evidenced in all SEM images. The co-condensation of mixtures of TEOS with organo-modified silane derivatives leads to a variety of morphologies, from large aggregates with irregular shapes to

quasi-uniform smooth surfaces [34,35]. Thus, in this case it become very difficult to control the roughness of the deposited film and consequently, to control the wettability changes.

In SEM images recorded for the series with larger particles, a more regular deposition of particles is observed. In general, with the increase of the organo silane derivative content, the coating surface tends to became smooth [36], but in our study even at the highest DDTES ratio the nanostructured morphology is still clear.

The topography and roughness of the deposited organo-modified silica films were also investigated by AFM and the results are shown in Figures 6 and 7.



Figure 6. AFM images of silica and organically modified silica. SiO₂-1 (**a**), SiO₂-1-Org1 (**b**), SiO₂-1-Org2 (**c**), and SiO₂-1-Org3 (**d**).



Figure 7. AFM images of silica and organically modified silica. SiO₂-2 (**a**), SiO₂-2-Org1 (**b**), SiO₂-2-Org2 (**c**), and SiO₂-2-Org3 (**d**).

Figure 6 presents three-dimensional topographic AFM images recorded at the scale of $(2 \times 2) \ \mu m^2$ of the glass substrate coated with silica and organically modified silica (SiO₂-1 series of samples with small particles). In Figure 6a, where the glass is covered with unmodified silica, it could be observed uniform and compact quasi-spherical SiO₂ particles. The uniform aspect of the surface particles suggests the self-assembling character of the silica particles dispersed in an aqueous solution of ethanol. The SiO₂ particles

from Figure 6a appears to be flat due to the presence of a deep hole (~300 nm depth), visible as a dark spot in the middle, upper part. The morphological features for the organically modified silica films (Figure 6b–d) reveal a corrugated topography wherein air bubbles could be embedded. Figure 6b exhibit the topography of the SiO₂-1-Org1 silica coated particles, which completely differs from the topography of uncoated silica particles in Figure 6a. Figure 6b shows bigger organic-coated silica particles with a wavy-like, expanded aspect. This is well reflected by the surface profile (line-scans) plotted in the graphs below the 3D AFM images. Thus, most of the surface features of unmodified silica particles are located in a vertical domain (Δz) of 20 nm (from -10 to 10 nm), while for the SiO₂-1-Org1 silica organo-modified particles, the Δz interval equals ~250 nm, which is one order of magnitude higher (from -150 to 100 nm) than the profile of silica particles. The associated root mean square (RMS) roughness along the depicted line scans are 6.3 nm for the unmodified silica and 70.9 for SiO_2 -1-Org1 sample. By increasing the organic content in the silane derivative ratio, in comparison with SiO_2 -1-Org1, the expanded aspect of the surface is decreased, the SiO₂-1-Org2 sample increasing its uniformity (Figure 6c), as suggested also by the line-scan (surface profile) depicted below the corresponding 3D AFM image. The RMS roughness along the selected line-scan is 20.5 nm (app. 3.5 lower than the roughness along the line selected for SiO_2 -1-Org1 sample). Further increasing the organic content in the sample in comparison with SiO₂-1-Org1, the functionalized silica particles tend to increase their lateral adhesion locally, leaving some depressions between the packed parcels. In agreement with the line-scan from Figure 6d, the particles appear smaller, but waved, thus leading to a roughness value of 33.8 nm along the plotted line.

Figure 7 shows the AFM images of the second series (SiO_2 -2) of silica and organically modified silica particles with higher particles. As a distinct feature, it can be observed from Figure 7a that much bigger silica particles resulted from this preparation route, the quasi-spherical unmodified silica particles having two to three times higher diameters than SiO_2 -1 series. The corresponding roughness along the plotted line scan is 23.6 nm, almost four times bigger than the one noted for unmodified SiO₂-1 particles. Most probably that the shape and dimension (in other words peculiar roughness) will strongly influences the organics adherence to the silica particles. Thus, for sample SiO₂-2-Org1 with little organic content (Figure 7b) it is suggested (by both AFM image and corresponding line scan) that the silica particles are coated with a thin layer of organic, probably the rest of the organics being segregated in other areas on the surface (see, for example, the bottom part of the AFM figure). The RMS roughness along the line-scan depicted in Figure 7b is 23.9 nm. By increasing the organic content by half, most probably that equilibrium between the organics' viscosity and hydrophilicity of the SiO₂-2 particles is reached, as the silica particles appear to be embedded in the surrounding organics (Figure 7c). The shapes of the silica particles are still discernible, protruding from the organic coat, but the roughness is decreased to 11.7 nm. Finally, by further increasing the organic content (sample SiO_2 -2-Org3), the organic coat again becomes discontinuous, a part covering the individual silica particles, and another located mainly between the silica particles, and some rests being visible on the surface of individual silica particles (Figure 7d). The corresponding roughness along the line from Figure 7d is 58.9 nm, the largest in this series.

In Table 3 the roughness measurements of silica films are summarized.

Usually when alkyl silane derivatives are added to produce silica hybrid films, the roughness of the surfaces decreases with the increase of organic content. In our study no trend could be established between the DDTES content and roughness index, since the amount of added organic silane reagent is very low and the final morphology of the film is the results of interplay of many factors, such as aggregation behavior of SiO₂ NPs according to their size and degree of organic coverage.

Sampla	Roughness		
Sample	Rq (nm)	Ra (nm)	
SiO ₂ -1	24.340 ± 1.46	8.930 ± 0.53	
SiO ₂ -1-Org1	64.142 ± 7.05	48.927 ± 4.72	
SiO ₂ -1-Org2	32.949 ± 1.87	25.240 ± 1.06	
SiO ₂ -1-Org3	114.982 ± 10.92	82.601 ± 7.02	
SiO ₂ -2	27.644 ± 1.67	20.767 ± 0.73	
SiO ₂ -2-Org1	41.737 ± 3.71	31.771 ± 1.17	
SiO ₂ -2-Org2	10.181 ± 0.63	7.657 ± 0.18	
SiO ₂ -2-Org3	55.416 ± 4.38	40.285 ± 1.61	

Table 3. Roughness values of hybrid silica coatings at various TEOS/DDTES ratios.

The homogeneity of unmodified and modified silica assemblies consisting of different sizes of silica nanoparticles was verified using scanning (SEM), transmission (TEM), and AFM microscopies. SEM imaging revealed undulated surfaces due to the nanoparticles' assemblies. The surface morphology and roughness information was obtained by AFM which demonstrated that by simply varying the silica nanoparticles' size and amount of organic compound, the surface topography on the nanometer length scale can be altered. Furthermore, increasing the amount of organic compound, results in a corresponding variation of the roughness values, depending both on peculiar roughness (shape and dimensions) and chemical interactions between silica particles and surrounding organics. All modified silica films reveal an irregular morphology consisting of hills and valleys.

The wettability properties of the deposited films were evaluated from the values of contact angles (CA) using water as polar reference liquid (surface tension 72.8 mN/m) and diiodomethane and bromonaphtalene as two nonpolar liquids (surface tension 50.8 and 44.4 mN/m, respectively). The Wenzel model describe the wettability of the rough surface in terms of "real" or "Wenzel" contact angle θ_w related to the ideal CA ("equilibrium" or "Young"), denoted θ_Y , measured on smooth surface by the following equation:

$$\cos \theta_{\rm W} = \mathbf{r} \cdot \cos \theta_{\rm Y} \tag{4}$$

where r is the dimensionless roughness factor computed as the ratio of real surface area to the geometrical projection (area of the ideal flat surface).

According to the Wenzel model, for the hydrophobic materials that possess CA larger than 90° on smooth surfaces an increase of contact angle occurs when the real surface area increases, thus the roughness factor r is larger than 1. However, recent researches reveal the limitations of Wenzel and other current models, which are not actually able to predict the suitable variation of roughness to obtain a desired contact-angle value [37].

In spite of many efforts to adjust the theory by analyzing the free energy of the wetting process in various conditions of droplet size and geometric description of the surface, few results are acquired that fit the experimental data on non-uniformly rough surfaces.

The contact angle measured on various silica coatings deposited on glass are summarized in Figure 8.

As is expected, samples SiO₂-1 and SiO₂-2, prepared only from TEOS as silane precursor show very low water-contact angles (22.5° and 12.8°, respectively) with similar values regardless of the size of the silica nanoparticles that form the nanocoatings. The hydrolysis of TEOS leads to the formation of many hydroxyl groups on the surface of the material, thus exhibiting a highly hydrophilic behavior. The further condensation of organo-modified derivative DDTES onto the pristine silica nanoparticles results in the replacement of hydroxyl groups with alkyl ones, and the transformation of the surface in a hydrophobic one. A significant increase in the water CA values is obtained in samples with dodecyl triethoxysilane, ranging from 131.6° to 146.8° (close to the superhydrophobic regime >150°). It is noted that CA values are higher for the series SiO₂-2-Org with larger particles compared to the ones for series SiO₂-1-Org, with smaller particles. The packing pattern of the small particles is less ordered, generating more random spread aggregated on the surface during the film deposition. Again, no direct correlation could be found between the content of organo-modified silane, roughness, and water-contact angle values. However, the highest hydrophobicity (contact angle of 146.8°) is obtained for the sample with the highest roughness index and highest value of TEOS/DDTES ratio (5/1). The crucial factor in fabrication of highly hydrophobic materials remains the topography of the surface. Contact-angle values for water ranging from 140° to 150° are reported on materials obtained from hybrid TEOS-alkylsilane sols when the co-condensation method was used only for high content of organo-modified derivative (from 40% to 75%) [34]. Simultaneous addition of methyl triethoxysilane or octadecyl triethoxysilane derivatives in TEOS reaction mixtures leads to the formation of hybrid materials with large non-spherical entities that produce a rather flat film when deposited on solid substrate.



Figure 8. Variation of contact angle values for water, diiodomethane, and bromonaphtalene on silica samples prepared with different TEOS/DDETS ratio: Series TEOS: $NH_4OH:H_2O = 1:3.4:15.2$ (a); and Series TEOS: $NH_4OH:H_2O = 1:12.7:57.3$ (b).

Thus, in this work a simple method to fabricate cost-effective highly hydrophobic coatings, with CA value ranging from 133° to 146° was proposed, using reduced amount or organic modified silica derivative.

The contact angle values for liquids with low surface energy (non-polar liquids) decrease drastically on flat hydrophobic surfaces, compared to water. The amphiphobic property, i.e., the ability to repel both hydrophilic and hydrophobic liquids, is one of the most desired behaviors of material with special wettability. The medium polar and non-polar tested liquids (diiodomethane and bromonaphtalene) exhibit low values of contact angles, thus the obtained silica materials do not exhibit amphiphobic properties. The contact-angle values of diiodomethane on coatings prepared from series SiO₂-1 are found to be in the range 49–58° and in the range 42–53° for series SiO₂-2, respectively. For the most non-polar liquid bromonaphtalene the CA obtained are even smaller, between 14–39° on the coatings from samples with smaller particles (series SiO₂-1) and between 16–26° for coatings prepared from silica sols for series SiO₂-2.

The topography of surfaces, with quasi ordered packing of SiO₂ NPs and rare submicronic aggregates is not enough structured hierarchy to produce a suitable degree of roughness, able to generate amphiphobicity.

The organo-modified SiO_2 nanohybrid produced by a simple, rapid synthesis, without a sophisticated method to texturize the surface seems to be a promising coating with highly hydrophobic properties, suitable for usual industrial applications.

4. Conclusions

The complicated fabrication processes, expensive instruments for production of textured surfaces, the requirement for high-cost fluorosilane modification, time-consuming deposition procedures are some of the major drawbacks in the practical application of superhydrophobic materials. In this paper a simple and effective method to fabricate highly hydrophobic coatings via microwave process of TEOS-organically modified on glass model substrates was presented. To the best of our knowledge, this is the first study on the use of dodecyl triethoxysilane (DDTES) as a hydrophobization reagent in obtaining of organicinorganic hybrid in sol-gel synthesis conducted in a microwave reactor. Tuning the size of the silica NPs and the ratio between TEOS and organo-modified silane precursor highly hydrophobic coatings could be obtained with a reduced amount of affordable non-fluorinated silane derivative. Two series of samples were investigated, with different average size of NPs, approximately 200 nm and 350 nm, respectively. Various surface roughnesses and morphologies were achieved by carefully controlling the reaction condition and molar ratio of the selected precursors. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) reveal that SiO₂ NPs spherical in shape and monodispersed were obtained in all cases. The deposited films contain closely packed particles and, in some cases, aggregates that produce rough surfaces, responsible for the high values of contact angles (up to 146°) obtained even at a low degree of organic content in the hybrid materials.

Compared with other hydrophobic surfaces reported in the literature, this feasible and simple method makes it easy to prepare highly hydrophobic coatings on a large scale and will lay a foundation for the development of many high-performance surfaces for industrial use in self-cleaning glasses.

Author Contributions: Conceptualization, L.O.C. and C.P.; methodology, L.O.C.; validation, C.P. and L.O.C.; investigation, C.I.G., B.T., C.M.N., C.I.M., M.C.L., A.P., M.A., S.N.V. and M.A.T.; writing—original draft preparation, L.O.C. and C.I.G.; writing—review and editing L.O.C. and C.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by grants from the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0743 (PC5), within PNCDI III.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not Applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

- Guo, F.; Guo, Z. Inspired Smart Materials with External Stimuli Responsive Wettability: A Review. RSC Adv. 2016, 6, 36623–36641. [CrossRef]
- Wang, S.; Liu, K.; Yao, X.; Jiang, L. Bioinspired Surfaces with Superwettability: New Insight on Theory, Design, and Applications. Chem. Rev. 2015, 115, 8230–8293. [CrossRef] [PubMed]
- Chen, Y.; Quan, Z.; Sun, Y.; Chi, D.; Liu, D.; Zhou, L.; Zhang, J.; Mu, Z.; Wang, Z.; Li, B.; et al. Durable and Superhydrophobic Aluminium Alloy with Microscale Hierarchical Structures and Anti-Drag Function Inspired by Diving Bell Spider. *Coatings* 2021, 11, 1146. [CrossRef]
- 4. Wang, J.; Zhang, C.; Yang, C.; Zhang, C.; Wang, M.; Zhang, J.; Xu, Y. Superhydrophilic Antireflective Periodic Mesoporous Organosilica Coating on Flexible Polyimide Substrate with Strong Abrasion-Resistance. *ACS Appl. Mater. Interfaces* **2017**, *9*, 5468–5476. [CrossRef] [PubMed]
- Wahby, M.H.; Atta, A.M.; Moustafa, Y.M.; Ezzat, A.O.; Hashem, A.I. Hydrophobic and Superhydrophobic Bio-Based Nano-Magnetic Epoxy Composites as Organic Coating of Steel. *Coatings* 2020, 10, 1201. [CrossRef]
- 6. Emelyanenko, A.M.; Domantovsky, A.G.; Kaminsky, V.V.; Pytskii, I.S.; Emelyanenko, K.A.; Boinovich, L.B. The Mechanisms of Antibacterial Activity of Magnesium Alloys with Extreme Wettability. *Materials* **2021**, *14*, 5454. [CrossRef]
- Al-Amshawee, S.; Yunus, M.Y.B.M.; Lynam, J.G.; Lee, W.H.; Dai, F.; Dakhil, I.H. Roughness and Wettability of Biofilm Carriers: A Systematic Review. *Environ. Technol. Innov.* 2021, 21, 101233. [CrossRef]

- 8. Parvate, S.; Dixit, P.; Chattopadhyay, S. Superhydrophobic Surfaces: Insights from Theory and Experiment. J. Phys. Chem. B 2020, 124, 1323–1360. [CrossRef] [PubMed]
- 9. Jeevahan, J.; Chandrasekaran, M.; Britto Joseph, G.; Durairaj, R.B.; Mageshwaran, G. Superhydrophobic Surfaces: A Review on Fundamentals, Applications, and Challenges. J. Coat. Technol. Res. 2018, 15, 231–250. [CrossRef]
- Nguyen-Tri, P.; Tran, H.N.; Plamondon, C.O.; Tuduri, L.; Vo, D.-V.N.; Nanda, S.; Mishra, A.; Chao, H.-P.; Bajpai, A.K. Recent Progress in the Preparation, Properties and Applications of Superhydrophobic Nano-Based Coatings and Surfaces: A Review. *Prog. Org. Coat.* 2019, *132*, 235–256. [CrossRef]
- 11. Vidal, K.; Gómez, E.; Goitandia, A.M.; Angulo-Ibáñez, A.; Aranzabe, E. The Synthesis of a Superhydrophobic and Thermal Stable Silica Coating via Sol-Gel Process. *Coatings* **2019**, *9*, 627. [CrossRef]
- 12. Tu, C.-W.; Tsai, C.-H.; Wang, C.-F.; Kuo, S.-W.; Chang, F.-C. Fabrication of Superhydrophobic and Superoleophilic Polystyrene Surfaces by a Facile One-Step Method. *Macromol. Rapid Commun.* **2007**, *28*, 2262–2266. [CrossRef]
- 13. Rebollar, E.; Castillejo, M.; Ezquerra, T.A. Laser Induced Periodic Surface Structures on Polymer Films: From Fundamentals to Applications. *Eur. Polym. J.* 2015, *73*, 162–174. [CrossRef]
- 14. Asadollahi, S.; Profili, J.; Farzaneh, M.; Stafford, L. Development of Organosilicon-Based Superhydrophobic Coatings through Atmospheric Pressure Plasma Polymerization of HMDSO in Nitrogen Plasma. *Materials* **2019**, *12*, 219. [CrossRef]
- 15. Maghsoudi, K.; Vazirinasab, E.; Momen, G.; Jafari, R. Advances in the Fabrication of Superhydrophobic Polymeric Surfaces by Polymer Molding Processes. *Ind. Eng. Chem. Res.* **2020**, *59*, 9343–9363. [CrossRef]
- Atthi, N.; Dielen, M.; Sripumkhai, W.; Pattamang, P.; Meananeatra, R.; Saengdee, P.; Thongsook, O.; Ranron, N.; Pankong, K.; Uahchinkul, W.; et al. Fabrication of High Aspect Ratio Micro-Structures with Superhydrophobic and Oleophobic Properties by Using Large-Area Roll-to-Plate Nanoimprint Lithography. *Nanomaterials* 2021, 11, 339. [CrossRef]
- Zheng, X.; Fu, S. Reconstructing Micro/Nano Hierarchical Structures Particle with Nanocellulose for Superhydrophobic Coatings. Colloids Surf. A Physicochem. Eng. Asp. 2019, 560, 171–179. [CrossRef]
- 18. Hoppe, C.E.; Williams, R.J.J. Tailoring the Self-Assembly of Linear Alkyl Chains for the Design of Advanced Materials with Technological Applications. *J. Colloid Interface Sci.* **2018**, *513*, 911–922. [CrossRef] [PubMed]
- 19. Xu, L.; He, J. Fabrication of Highly Transparent Superhydrophobic Coatings from Hollow Silica Nanoparticles. *Langmuir* **2012**, *28*, 7512–7518. [CrossRef]
- Zhao, Y.; Li, M.; Lu, Q.; Shi, Z. Superhydrophobic Polyimide Films with a Hierarchical Topography: Combined Replica Molding and Layer-by-Layer Assembly. *Langmuir* 2008, 24, 12651–12657. [CrossRef] [PubMed]
- Zahid, M.; Mazzon, G.; Athanassiou, A.; Bayer, I.S. Environmentally Benign Non-Wettable Textile Treatments: A Review of Recent State-of-the-Art. Adv. Colloid Interface Sci. 2019, 270, 216–250. [CrossRef] [PubMed]
- Wang, M.; Bai, L.; Li, M.; Gao, L.; Wang, M.; Rao, P.; Zhang, Y. Ultrafast Synthesis of Thin All-Silica DDR Zeolite Membranes by Microwave Heating. J. Membr. Sci. 2019, 572, 567–579. [CrossRef]
- 23. Bisson, A.; Rigacci, A.; Lecomte, D.; Rodier, E.; Achard, P. Drying of Silica Gels to Obtain Aerogels:Phenomenology and Basic Techniques. *Dry. Technol.* 2003, *21*, 593–628. [CrossRef]
- 24. He, F.; Zhao, H.; Qu, X.; Zhang, C.; Qiu, W. Modified Aging Process for Silica Aerogel. J. Mater. Process. Technol. 2009, 209, 1621–1626. [CrossRef]
- 25. Estella, J.; Echeverría, J.C.; Laguna, M.; Garrido, J.J. Effects of Aging and Drying Conditions on the Structural and Textural Properties of Silica Gels. *Microporous Mater.* **2007**, *102*, 274–282. [CrossRef]
- 26. 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]
- Vijayan, V.M.; Tucker, B.S.; Dimble, P.S.; Vohra, Y.K.; Thomas, V. Dusty-Plasma-Assisted Synthesis of Silica Nanoparticles for in Situ Surface Modification of 3D-Printed Polymer Scaffolds. ACS Appl. Nano Mater. 2020, 3, 7392–7396. [CrossRef]
- Santiago, A.; González, A.; Iruin, J.J.; Fernández-Berridi, M.J.; Irusta, L. Preparation of Superhydrophobic Silica Nanoparticles by Microwave Assisted Sol–Gel Process. J. Sol-Gel Sci. Technol. 2012, 61, 8–13. [CrossRef]
- Inada, M.; Nishinosono, A.; Kamada, K.; Enomoto, N.; Hojo, J. Microwave-Assisted Sol–Gel Process for Production of Spherical Mesoporous Silica Materials. J. Mater. Sci. 2008, 43, 2362–2366. [CrossRef]
- 30. Kumar, N.S.; Suvarna, R.P.; Babu Naidu, K.C.; Kumar, G.R.; Ramesh, S. Structural and Functional Properties of Sol-Gel Synthesized and Microwave Heated Pb0.8 Co0.2-ZLazTiO3 (z = 0.05–0.2) Nanoparticles. *Ceram. Int.* **2018**, 44, 19408–19420. [CrossRef]
- 31. Boukari, H.; Long, G.G.; Harris, M.T. Polydispersity during the Formation and Growth of the Stöber Silica Particles from Small-Angle X-ray Scattering Measurements. *J. Colloid Interface Sci.* **2000**, 229, 129–139. [CrossRef] [PubMed]
- 32. Shen, M.-W.; Chen, S.-T. Fabrication of an Organo-Fluoride–Free Hydrophobic Film Using the Sol-Gel Method by Factors Screening and Poly-Acrylic Acid Addition. *Coatings* **2020**, *10*, 1011. [CrossRef]
- 33. Rahimi, H.; Mozaffarinia, R.; Najafabadi, A.H. Corrosion and Wear Resistance Characterization of Environmentally Friendly Sol–Gel Hybrid Nanocomposite Coating on AA5083. *J. Mater. Sci. Technol.* **2013**, *29*, 603–608. [CrossRef]
- Len, A.; Paladini, G.; Románszki, L.; Putz, A.-M.; Almásy, L.; László, K.; Bálint, S.; Krajnc, A.; Kriechbaum, M.; Kuncser, A.; et al. Physicochemical Characterization and Drug Release Properties of Methyl-Substituted Silica Xerogels Made Using Sol–Gel Process. *IJMS* 2021, 22, 9197. [CrossRef]
- 35. Purcar, V.; Cinteza, O.; Ghiurea, M.; Balan, A.; Caprarescu, S.; Donescu, D. Influence of hydrophobic characteristic of organomodified precursor on wettability of silica film. *Bull. Mater. Sci.* 2014, *37*, 107–115. [CrossRef]

- Sheen, Y.-C.; Chang, W.-H.; Chen, W.-C.; Chang, Y.-H.; Huang, Y.-C.; Chang, F.-C. Non-Fluorinated Superamphiphobic Surfaces through Sol–Gel Processing of Methyltriethoxysilane and Tetraethoxysilane. *Mater. Chem. Phys.* 2009, 114, 63–68. [CrossRef]
 Kim, D., Puene, N.M., Pare, G. Wetting, Theory for Cruell Development of Solid Surfaces. *Cir. Ben.* 2016, 6 (27812) [CrossRef]
- 37. Kim, D.; Pugno, N.M.; Ryu, S. Wetting Theory for Small Droplets on Textured Solid Surfaces. Sci. Rep. 2016, 6, 37813. [CrossRef]