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Superhydrophobic surfaces obtained from bilayer hybrids and silica nanoparticles

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There have been studied hybrids obtained from hydrophobic modified silica nanoparticles with alkyltrialkoxysilanes and bilayered hybrids prepared by co-hydrolysis from hexadecyltrimethoxysilane and tetramethoxysilane (C_{16}TMS/TMOS=1/4). Two approaches were followed to achieve superhydrophobicity: (i) nanoparticles were deposited on smooth or microroughened substrates, under controlled conditions, to induce nanoscale surface roughness on substrates; (ii) particles were mixed with bilayered hybrids solutions and then deposited on smooth glass surfaces. The hydrophobization of silica nanoparticles prepared by sol-gel process was performed with alkyltrimethoxysilanes (C_1-C_{16}), aminopropyltrimethoxysilane (APTMS) or fluorooctyltriethoxysilane (OFTES). By mixing 80wt% filler (silica particles modified with octyltrimethoxysilane (OTMS)) with 20wt% binder-(C_{16}TMS/TMOS hybrid) there were obtained continuous heterogeneous thin films with a contact angle towards water of 158. The deposition of nanofillers modified with specific silanes (having alkyl chains between 3 and 16 carbon atoms) on C_{16}TMS/TMOS films leads also to superhydrophobic surfaces. The obtained hybrids were finally studied by infrared spectroscopy (FT-IR), thermal analyzes, refractometry, and scanning electron microscopy (SEM). The refractometric analyzes for alkyltrialkoxysilanes dispersed in ethanol has revealed the nanostructuration of the precursors used for the hydrophobic process of the silica particles.

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1. Introduction

In nature, lotus leaves, duck feathers, moth compound eyes, water strider feet, and cicada wings exhibit the unusual phenomenon of superhydrophobicity, i.e. water contact angles (CAs) above 150°. Those surfaces usually have binary structures on the micro/nanoscale, resulting in high CAs and low drop sliding angles (SAs) smaller than 10°. On the contrary, ultrahigh adhesion superhydrophobic surfaces like rose petals have recently been reported [1-4].

Though the CAs of water droplets are above 150° on such surfaces, the water droplets will not roll off even with the surfaces upside down. In recent years, a wide range of controllable adhesive superhydrophobic surfaces have attracted tremendous scientific interest due to their important applications in many fields, such as biochemical separation, transport of microdroplets, tissue engineering, and microfluidic chips.

Xu et al. prepared a superhydrophobic cauliflower-like morphology by introduction of organic groups in silica nanospheres, and the adhesion could be modulated by adjusting the phenyl group content [5]. However, many reported methods used for fabrication of superhydrophobic surfaces with controllable adhesion require high-cost, complex fabrication processes, and have tight restrictions on materials. More versatile and simple ways to fabricate superhydrophobic surfaces with controllable adhesion are still lacking.

In particular, the destruction of surfaces features by mechanical forces and the contamination of surfaces with compounds present in the atmosphere can lead to a rather fast loss of superhydrophobic properties. Lee et al. presented a mechanically durable superhydrophobic structure on a large-area substrate created by combining PMMA (Poly(methyl methacrylate)) microspheres and a silicon grease [6].

Detachment of a liquid droplet from the solid surface, as well as its corresponding dynamic behavior, is among the fundamental problems of wettability and its applications. The droplet will run away if the adhesive force (generated from contact surface) is overcome by the external drag forces (generated from gravity, vibration, air flow, etc.).

Song investigated the static and dynamic hydrophobicities of water droplets on a patterned surface prepared using fluoroalkylsilane with different molecular chain lengths [7]. These results suggested that it is feasible to control the sliding acceleration of water droplets over hydrophobic surfaces by changing the surface structure patterns and chemical composition [8].

Monofunctional ligands, which have only one point of attachment with the surface, can react with only a fraction of the available silanols due to steric hindrance, leaving a significant number of unreacted silanols exposed to the surface. The conventional remedy to this problem employs an end-capping method where a smaller, short-chained, monofunctional compound (e.g., chloro(trimethyl)silane) is allowed to react further with the silica surface that has already been modified [9].

These smaller monofunctional ligands have greater access to the surface than the corresponding long chains, so they consume some of the surface silanols that remain unreacted after the initial modification. Even when this remedy is exhaustively performed, previous studies showed that 50% or more of the surface silanols are still unreacted [10].

Due to this reason, there can be used alkyltrialkoxysilanes as agents for the hydrophobic process of the silica nanoparticles. Their concentration must be carefully chosen so that the ratio towards SiO_2 particles would not affect their morphology [11].

In previous studies, the sol-gel derived coating process was enhanced to obtain superhydrophobic surfaces composed of both dual scale roughness and hydrophobizing material. The hybrid coating materials were prepared from the mixture of a silica particle dispersion (SPD) in ethanol (EtOH) containing a small amount of fluoroalkylsilane (FAS) and a binder solution derived from a sol-gel reaction of tetraethoxysilane (TEOS), γ-glycidoxy propyltrimethoxysilane (GPTMS), and FAS in EtOH in the presence of nitric acid as a catalyst. In order to investigate the roughness induced by the aggregation of the silica particles on the hydrophobicity of the coating layer, the content of SPD was varied from 0 to 100wt% [12].

Two key approaches are suggested as strategies for producing superhydrophobic surfaces: the use of coating materials of low surface energy (chemical approach) and the creation of rough surfaces (physical approach), which, according to the Cassie-Baxter equation, enhances the hydrophobic character of a surface [13].

In some studies, fillers and nanoparticles were used to enhance surface roughening. Two approaches were followed to achieve superhydrophobicity: (i) nanoparticles were deposited on smooth or microroughened substrates, under controlled conditions, to induce nanoscale surface roughness on substrates; (ii) particles were mixed with polymer solutions and then deposited on smooth surfaces such as glass and silicon. In the latter approach (mixing particles with polymers prior to film deposition), either one of the two components of the polymer-particle mixture was an intrinsic hydrophobic material (polymer or particle/filler), or both polymer and particle were hydrophobic [14].

It is very important to preserve the monodispersity of particles after surface modification in applications such as photonic crystals, because the monodispersity of the particles is critical in the assembly of particles. Thus, it is very important to prepare modified silica particles with a good shape and a narrow size distribution for such applications [15].

It is well known that the wetting property of a solid surface is governed by both its chemical composition and geometric microstructure. In addition, a few methods have been reported to make the superhydrophobic coating on silica particles: by forming polyelectrolyte multilayer films by layer-by-layer deposition, or by forming the film of silica particles on a substrate by Langmuir–Blodgett (LB) technique, followed by the formation of an alkylsilane self-assembly monolayer (SAM) [16].

Spherical silica particles with different surface properties are important in many applications, including composite materials, adsorbents, pigments, detergents, cosmetics, and pharmaceuticals. Chemical treatment and functionalisation of the silica particles can be used to improve the hydrophilicity or hydrophobicity of the particle surface for specific applications.

In the present paper we have proposed to study the hydrophobic modification of the surface induced by the hydrophobicized silica nanoparticles. It was used as binder for these modified nanoparticles bilayered hybrids that have a hydrophobic and smooth surface [17].

2. Experimental

2.1. Materials

Tetramethylorthosilicate (TMOS) (Aldrich), methyltrimethoxysilane (MTMS) (Fluka), vinyltrimethoxysilane (VTMS), propyltrimethoxysilane (PTMS) (Fluka), fluorooctyltriethoxysilane (OFTES) (Aldrich), aminopropyltrimethoxysilane (APTMS) (Aldrich), octyltrimethoxysilane (OTMS), hexadecyltrimethoxysilane (C_{16}TMS), ethanol (EtOH, CHIMREACTIV SRL), Ammonia (25wt%, Scharlau), hydrochloric acid (37wt%, Riedel), toluene (CHIMREACTIV SRL) were used without supplementary purification.

2.2. Silica nanoparticles obtaining process

The obtaining of silica nanoparticles was adapted after an existing working procedure [11]. Firstly, 5 ml TMOS was diluted in 20ml EtOH. This solution was added over a mixture of 20ml aqueous ammonia solution diluted with 100ml EtOH. The mixture was stirred at 200rot/min for 2 hours at room temperature. After this period a mixture of alkyltrialkoxysilane/EtOH was slowly added in 1.5 hours, to keep an RTMS/TMOS ratio of 1/20 moles. The mixture was again stirred at 200 rot/min for another 2 hours.

In the case of methyltrimethoxysilane, the ratio between its concentration and of TMOS was 1.64 moles / 20 moles TMOS in order to ensure a higher concentration of hydrophobic chains.

The properties of the obtained silica particles are presented in Table 1

2.3. Mixing SiO_2 NP (SiO_2 nanoparticles) with bilayer hybrid

Separately, co-hydrolysis and polycondensation reactions were performed in a water-ethanol mixture according to a procedure from literature [18]. Briefly, 1.21g of C_{16}TMS and the required amount of tetramethoxysilane, in order to obtain a molar ratio of 1/4, were dissolved in 8.04ml EtOH under continuous stirring and heating at 40^{o}C. When the final temperature was achieved, 1.04 ml of a 0.1 N HCl solution was added, and then the solution was stirred for 90 min.

The molar ratio used for the reaction mixtures was as follows:

C_{16}TMS : TMOS : EtOH : H_2O : HCl = 1 : 4 : 50 : 19 : 0.03

A quantity of 0.01 g of freshly dried SiO_2 nanoparticles was dispersed in 10ml of EtOH for about 2 hours. The weight ratio between SiO_2 NP (filler) and the binder (C_{16}TMS/TMOS hybrid) was 80/20.

The two solutions were mixed and sonicated for another 2 hours.

The film was prepared via deposition onto a glass slide (mixture was horizontally deposited using a special knife) at 40ºC and was dried at room temperature.

2.4. Deposition of SIO_2 NP on bilayer hybrids

A hybrid solution was obtained by co-hydrolysis and polycondensation reactions performed in a water-ethanol mixture according to a procedure from the literature mentioned at 2.3. and further thin films were deposited over glass substrate; after were left to dry for 24h. A small quantity of freshly dried SiO_2 nanoparticles dispersed in a suitable quantity of EtOH was deposited over the thin films of hybrid solution as a secondary layer. These hybrids were analyzed after 24h.

2.5. Characterization methods

- **SEM** - The surfaces of the hybrid films were visualized by environmental scanning electron microscopy (ESEM) (FEI QUANTA 200). The ESEM images were obtained in the low-vacuum mode. The samples were deposited on a conductive stub and dried at room temperature.
- **DLS** (dynamic light scattering) - The initial solutions were examined by measuring the particle dimensions (Zetasizer, Malvern Nano ZS). The solutions were prepared in ethanol and methylene chloride by ultrasonication.
- **FT-IR** spectra of samples were obtained using a Fourier Transforms Infrared Spectrophotometer Tensor 37 from Bruker. The samples were ground with KBr and pressed to form a disc for FT-IR scanning. For all scans, the spectra were collected over the wavenumber range of 400-4000cm^{-1} with a resolution of 4cm^{-1}. The chemical modification of the samples gave the information about the various chemical bonds such as Si-O-Si (1000-1200cm^{-1} region) and C-H (2930-2800cm^{-1} region).
- **Thermal analyses** were performed in He (10ºC/min) using a TA TGA Q5000 IR instrument.
- **Contact angles** between the hybrid films and water were determined using a CAM 200 Contact Angle Tensiometer instrument from KSV Instruments equipped with a digital camera that was connected to a PC. Distillated water was used as the liquid for the contact angle measurements. The contact angles were calculated from drop images after the shape accentuation, radius and string reading were determined.
- **REFRACTIVE INDICES** were measured with an Abbe refractometer (Carl Zeiss Jena, Germany) at 25 ºC.

3. Results and discussions

In Table 1 the TGA data were discussed regarding three temperature steps. From previously published papers [16, 19, 20] the weight loss in the 0-200ºC interval corresponds to the release of absorbed water content or some solvent traces. The thermo-oxidative degradation of the alkyl groups fixed by hydrophobic process takes place in the 200-400ºC interval. In the last degradation step, 400-700ºC respectively corresponds to the condensation reaction of the OH groups from the partially modified silica surfaces. The substitution degree was estimated from the weight loss in the interval 200-400ºC.

Tab. 1 Synthetic conditions and properties of the modified silica.

Sample no.	Synthesis RSi(OMe)$_3$	D (nm) (average diameter)	TGA (ΔG (wt %)/ T_{max} (ºC))				Substitution moles of R / 1 mole of SiO_2
			0-200ºC	200-400ºC	400-700ºC	Residue (%) (Residue - H_2O)	
243	TMOS	434.9	8.9/	1.9/ 320	2.1/ 527	87.1 (95.7)	-
244	C_{16}TMS/ 0.58	697.2	6.8/ 40	12.3/ 242; 320	4.8/ 558	76.1 (81.7)	0.0434
245	OTMS/ 0.39	469.7	6.8/ 44	8.0/ 213; 251	3.0/	82.2 (88.3)	0.0510
246	PTMS	431.5	8.5/ 49	4.6/ 212; 288	2.5/	84.4 (92.5)	0.0760
247	VTMS	336.3	7.9/ 48	3.3/ 203; 300; 360	2.9/	85.9 (93.2)	0.0645
248	MTMS	370.9	10.2/ 48; 138	2.7/ 201; 354	2.6/ 656	84.5 (93.7)	0.1280
249	OFTES	554.9	6.1/ 41	7.8/ 269	17.8/ 435; 509	68.3 (72.7)	0.0559
250	APTMS	441.3	9.8/ 47; 148	3.9/ 266; 384	4.1/	82.2 (91.2)	0.0780

ΔG, weight loss; T_{max}, highest temperature for the decomposition process; D (average diameter) was determined in EtOH

The sample containing 80% silica NP and 20% C_{16}TMS/TMOS binder solution (section 2.3) was investigated using thermogravimetric analysis to determine how the modification of organic-inorganic ratio depends on the filler and binder. The weight loss follows the same trend as the silica NP in the first two temperature intervals. The only difference between the presented systems can be observed in the 400-700ºC interval, and this more pronounced weight loss can be attributed to the loss of silane layers (the C_{16}-alkyl chain). As it can be seen, the presence of binder solution in the presented system offers in a certain way a higher stability, the degradation process starting after 200ºC.

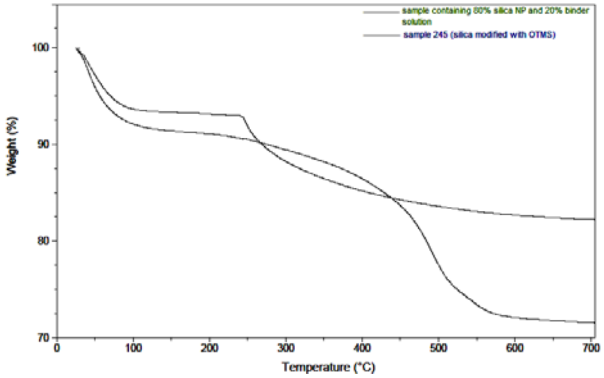
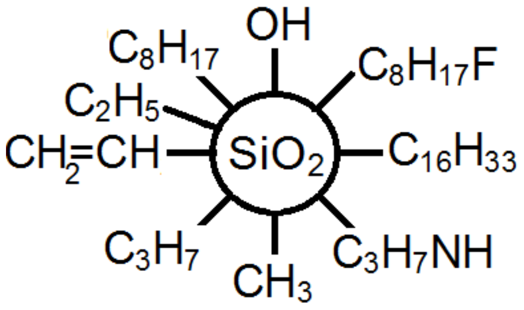


Fig. 1 Thermal decomposition of the obtained samples

The substitution reaction was also confirmed by measuring the average diameters of the particles dispersed in ethanol. The highest value was obtained for the silica substituted with 16 carbon atoms alkyl chain (sample Table1).



Scheme 1. Schematic representation of modified SiO_2 NP

In section 2.2. the hydrophobization of SiO_2 NP was performed by adding RTMS (R = alkyl chains from alkyltrialkoxysilanes) – EtOH mixtures to the pristine nanoparticles dispersions. As in previous published paper it was considered very important the study of nanoassociation of RTMS in the presence of EtOH [20]. For this kind of study, a mixture of RTMS-EtOH was prepared in the range of molar fraction 100/0 up to 0/100. For this homogeneous mixture, the refractive indexes were measured. As reported in a previous study [21], the dependence of the refractive index on the mole fraction of RTMS (where R = methyl, vinyl, propyl, octyl, hexadecyl, octadecyl, etc.) was determined to be nonlinear. This phenomenon was attributed to the self-assembly of the alkyl groups.

To evaluate the tendency for each system to self-assemble, the derivates of the mole fraction/refractive index curves (e.g., Fig. 2) are very important. The maximum rate of the d_n/d_x value [$(d_n/d_x)_{max}$—for d_n/d_x estimation, the curve from Fig. 2a was associated with a polynomial; using a dedicated program, d_n/d_x was calculated] decreases, can be used to determine the behavior of the alcoholic precursor mixtures.

The results are presented in Fig. 2a. (d_n/d_x) for PTMS – EtOH. The $(d_n/d_x)_{max}$ increase with the number of carbon atoms from the alkyl group. This modification has two reasons: the differences between refractive indices of the precursor and ethanol, and the nanostructuration tendency.

These results put in evidence that the modification of silica nanoparticles takes place in the presence of associated RTMS in EtOH.

The efficiency of this analytical method was confirmed also by fluorescence method [22].

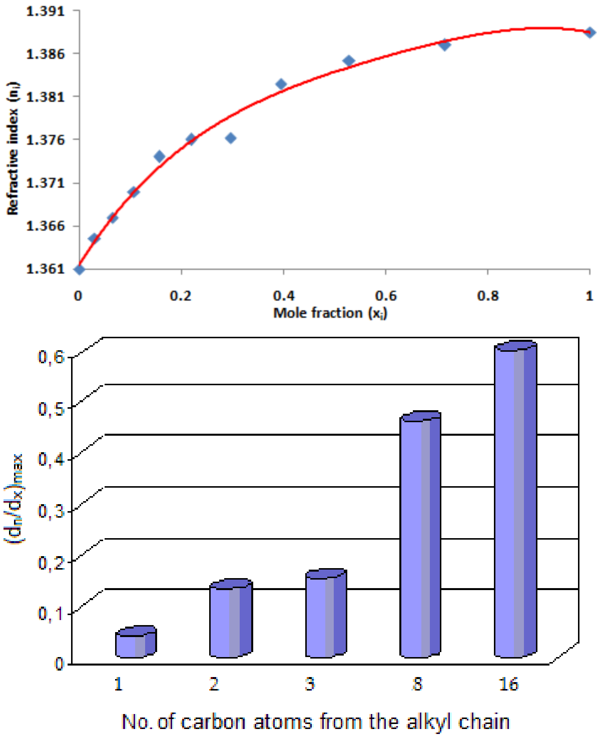


Fig. 2. a) The dependence of the refractive index on the mole fraction of PTMS; b) The maximum value of d_n/d_x as function of the hydrocarbon chain

The FTIR spectra of modified silica samples using different silane molecules are shown in Fig. 3, which gives a clear evidence for surface modification.

In the low frequency region, 700–1400cm^{-1}, fundamental Si–O bands (bending vibrations at ~800cm^{-1}

and stretching vibrations at ~1000cm^{-1}, respectively) are invariant with surface modification, but confirm the formation of silica network.

The bands at ~2850 and ~2900cm^{-1} of –CH2 corresponding to C–H symmetric and antisymmetric stretching, respectively could be attributed to the entanglements of hydrocarbon chains. The intensity of the C-H stretching bands is higher for the silica modified with longest alkyl chains (C_{16} and C_8). This fact confirms the existence of alkyl groups on the silica surface, which is in agreement with previously published data [16, 23].

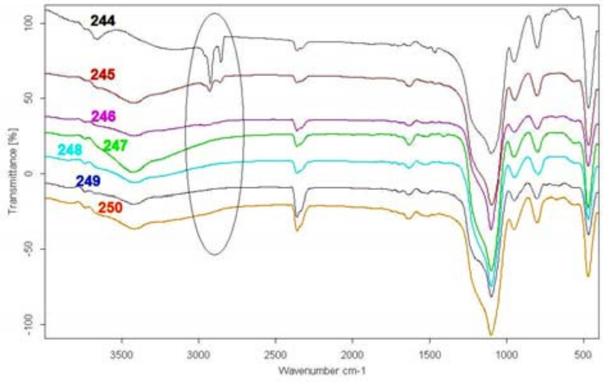


Fig. 3. FT-IR spectra of the hydrophobic modified silica particles

3.1 Mixing SiO_2 NP with bilayer hybrid

This method consists in mixing SiO_2 NP with bilayer hybrids C_{16}TMS/TMOS. The samples were obtained as follows: a known quantity of freshly dried SiO_2 nanoparticles was dispersed in a suitable quantity of EtOH (section 2.3). Separately, a hybrid solution was obtained by co-hydrolysis and polycondensation reactions performed in a water-ethanol mixture according to a procedure from the literature [18]; after the two solutions were mixed and sonicated, thin films were deposited over glass substrate and further contact angle measurements were made and the results are presented in Table 2.

The CA value of last sample (158.7°) was due to the fact that the roughness of the final sample was enough to ensure a high contact angle towards H_2O. This means that the SiO_2 NP concentration was so high that it could induce a high topological modification of the surface. This high value of CA allows to estimate that the sample prepared by this method is superhydrophobic. In the future will be studied also other types of SiO_2 NP from Table 1.

3.2 Deposition of SiO_2 NP on bilayer hybrids

This method consists in layer-by-layer deposition of bilayer hybrids and dispersion of SiO_2 NP. The samples were prepared as follows (section 2.4): hybrid solution was obtained by co-hydrolysis and polycondensation reactions performed in a water-ethanol mixture according to a procedure from the literature and further thin films were deposited over glass substrate; after were left to dry for 24 h. A small quantity of freshly dried SiO_2 nanoparticles dispersed in a suitable quantity of EtOH was deposited over the thin films of hybrid as a secondary layer; contact angle measurements were made and the results are presented in Table 2.

Table 2. Contact angles towards water determined for samples containing different silica type.

Sample Nr.	Silica type* (g)	CA** (°)
1	C_{16}TMS (0.01 g of sample 244)	157.1
2	OTMS (0.01 g of sample 245)	148.9
3	PTMS (0.01 g of sample 246)	156.0
4	VTMS (0.01 g of sample 247)	132.6
5	MTMS (0.01 g of sample 248)	132.9
6	OFTES (0.01 g of sample 249)	150.8
7	APTMS (0.01 g of sample 250)	116.2
Silica 80%	80 % C_8TMS SiO_2 + 20% C_{16}TMS/TMOS hybrid solution	158.7

* dispersed in 1 ml EtOH
** CA towards water

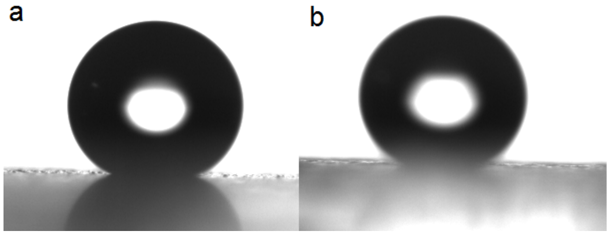


Fig.4. Images that show measurements of static contact angle (θ_s) on samples containing 80% silica particles and 20% binder solution (Fig. 4a) and silica particles deposited as layer-by-layer deposition (sample 2) (Fig. 4b).

The superhydrophobic surfaces were obtained for samples using SiO_2 NP substituted with long alkyl chain (C_3, C_8, C_8FTES, C_{16}). The small CA values modified with methyl, vinyl, and aminopropyl are a good proof that small alkyl chain and amino group are not hydrophobically enough.

4. Surface morphology of the hybrids

The SEM micrographs of the silica particles deposited as layer-by-layer deposition are shown in Figure 5a (sample 2), while in Figure 5b is presented the surface of the mixture containing 80% silica particles and 20% C_{16}TMS/TMOS binder solution indicating a sharp contrast in the morphology (80 % C_8TMS SiO_2 + 20% C_{16}TMS/TMOS hybrid solution).

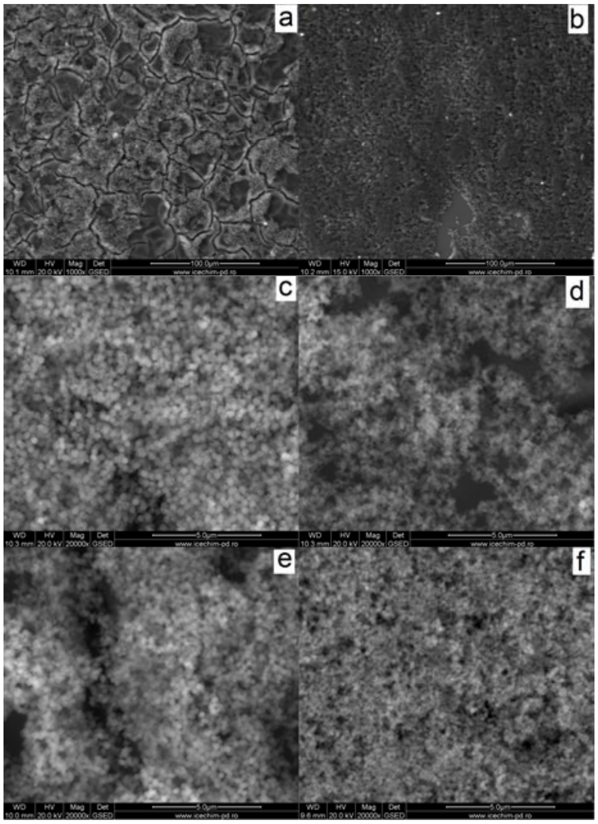


Fig. 5 SEM analyses for obtained samples: a - sample 2; b - the surface of the mixture containing 80% silica particles and 20% C_{16}TMS/TMOS binder solution; c, d, e, f - samples 1, 2, 4, 7.

In the case of "filler-binder" film, it can be observed a fairly ordered arrangement of silica hybrid but also an almost continuous rough surface, while bare silica particles deposited over the C_{16}TMS/TMOS layer exhibits considerable non-uniformity. These results may be used to obtain the film-forming hydrophobic surface by a very versatile method.

The morphology of the deposited film is developed as a function of the particle structure according to the following scenario. Distinct particle aggregates embedded over the continuous binder C_{16}TMS/TMOS hybrid can be observed at the surface of the deposited film when low silica particle concentrations are used (Fig 5c, d, e, f - samples 1,2,4,7).

Like in Fig. 5a, the modified SiO_2 NP are aggregated at the surface of the binder with same non-uniformity (not presented).

5. Conclusions

Investigating the modifications to the maximum decreasing rate of d_n/d_x (the derivatives with the mole fraction), the driving force for the structure of the organic–inorganic hybrids was determined to be the self-assembly of the long hydrocarbon chains.

The FT-IR spectrometric measurements confirmed the existence of the alkyl groups over the silica surface. The intensity of the C-H stretching bands was the highest in the case of silica modified with longest alkyl chain (C_{16}); substitution with a shorter alkyl chain was characterized by a modified absorption maximum and a reduced intensity of the bands.

The thermal stability of the hybrids measured in He atmosphere showed that the weight loss occurred stepwise.

The SEM images were in agreement with our predictions, namely, the surface of the samples obtained by SiO_2 NP deposited on glass substrates as layer-by-layer deposition were mainly composed of particles. In contrast, in the case of "filler-binder" film it was observed a very smooth and fairly ordered arrangement of silica hybrid but also an almost continuous rough surface.

This new method used for the surface design allows the obtaining of a new class of hybrid films with superhydrophobic behavior, obtained from silica modified nanoparticles with alkyl chain length starting from C_3 up to C_{16}.

The method offers future perspectives in mechanically durable superhydrophobic structures.

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