

## SURFACE MODIFICATION OF SOL-GEL HYBRID FILMS USING FLUORINATED SILICA NANOPARTICLES

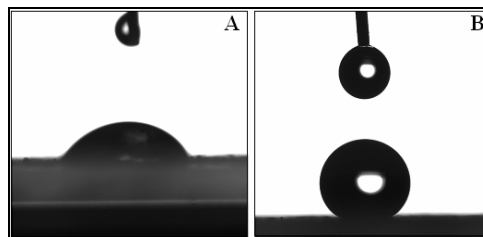
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Received September 24, 2012

Silica nanoparticles have been synthesized using the Stöber process with tetraethoxysilane (TEOS) and diethoxydimethylsilane (DEDMS) and further functionalized by adding fluorinated groups using fluoroalkylsilane (1H, 1H, 2H, 2H –perfluorooctyltriethoxysilane, FAS13) in a propanolic solution. The final dispersed solutions were used to deposit thin films on glass slides. The investigations of the prepared silica nanoparticles by DLS and ESEM, respectively, showed that they consisted mainly of particles with a diameter of 350-400 nm. The functionalization of silica nanoparticles by fluorinated groups has been confirmed by Fourier transform infrared spectroscopy (FTIR). The water contact angle of the thin film containing fluorinated silica nanoparticles is found to be higher ( $145\pm 3^\circ$ ) than the water contact angle of film prepared with silica particles without FAS13 ( $67\pm 2^\circ$ ).



### INTRODUCTION

Wettability is one of the important properties of solid surfaces, and is related to both the chemical composition and the geometrical microstructure of the surface.<sup>1,2</sup> Ultrahydrophobic surfaces have been fabricated by different methods such as sol-gel processing,<sup>3-9</sup> chemical etching,<sup>10</sup> electrochemical machining.<sup>11</sup> Sol-gel process still remains the most used method to obtain the hydrophobic surfaces because is a versatile method with its high process speed, suitability for continuous production and variety of chemical precursors.<sup>12</sup> Elucidation of the nature of various intermediates or precursors in solution should have potential for further advancement in various applications including

automobile glass, building materials, bathroom mirrors, and green-house glass. Perfluoroalkylsilane is one of the silane precursor proposed and used to form hydrophobic water-repellent films on the surfaces of various materials.<sup>13,14</sup>

The present work investigates the morphology and surface properties of hybrid materials prepared through the sol-gel technique, using TEOS as the particle precursor, diethoxydimethylsilane (DEDMS) as the modifying siloxane and fluorinated silica powder. The experiments are carried out in water-ethanol mixtures, in the presence of ammonium hydroxide aqueous solution. The silica nanoparticles dispersed solutions (with and without fluorinated silica powder) were deposited onto clean glass slides, using a small brush, to obtain thin films. Morphology

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and nanostructure of the silica nanoparticles is studied using dynamic light scattering (DLS), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR-ATR). The wetting properties of the prepared and functionalized nanoparticles coated glass surfaces were performed using the contact angle measurements.

## RESULTS AND DISCUSSION

### Particle size and morphology

The samples were characterized as sols through dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements (see Figs. 1 and 2).

The colloidal silica particles formed via the base-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) and diethoxydimethylsilane (DEDMS) in an aqueous mixture containing ethanol and ammonia were found to be colloidal stable, having a large size distribution (average diameter  $D = 592$  nm). In this sample, the size distribution was characterized by a lower polydispersity index ( $PdI = 0.2$ ). When, in synthesis the fluorinated silica nanoparticles were added to colloidal silica sol, the surface of silica nanoparticles was modified (see Fig. 1). The size's polydispersity was more pronounced and this was reflected, on one hand, by the higher value of the polydispersity index ( $PdI = 0.5$ ) and, on the other hand, by the much higher values of the average

diameter ( $D = 629$  nm), compared with the main peak ( $P_1 = 328$  nm). Although the recorded main peak ( $P_1$ ) of fluorinated silica particles indicated, in general, smaller particles' sizes than those measured for the sample with TEOS and DEDMS ( $P_1 = 555$  nm). The value of the average diameter ( $D$ ) is much higher for the sample with fluorinated silica nanoparticles and this effect could be explained by the entrapment of larger fraction of the particles in growing organic network, resulting in a shift of particle size distribution ( $P_1$ ) to smaller diameter.<sup>15</sup>

Beside the DLS technique, the ESEM image also made possible to see that the size distributions became polydisperse, in case of silica solution with fluorinated silica powder (see Fig. 2). The ESEM images of silica sols obtained from both syntheses (see Table 2) are shown in Fig. 2. According to Fig. 2A, when the sol-gel reaction is carried out with TEOS and DEDMS (without fluorinated silica powder), monodisperse particles with an average diameter of about 400 nm are generated. In case of sample with fluorinated silica nanoparticles (Fig. 2B), can be observed that the silica nanoparticles are distributed into a consistent organic medium. These observations explain the results obtained through DLS measurements, showing that the average diameter obtained for sample with fluorinated silica nanoparticles is not for single particles, but for aggregates. The larger average diameter in the sample with fluorinated silica nanoparticles can be due the presence of outer shell of fluorinated silane bonded around the silica spheres.<sup>16</sup>

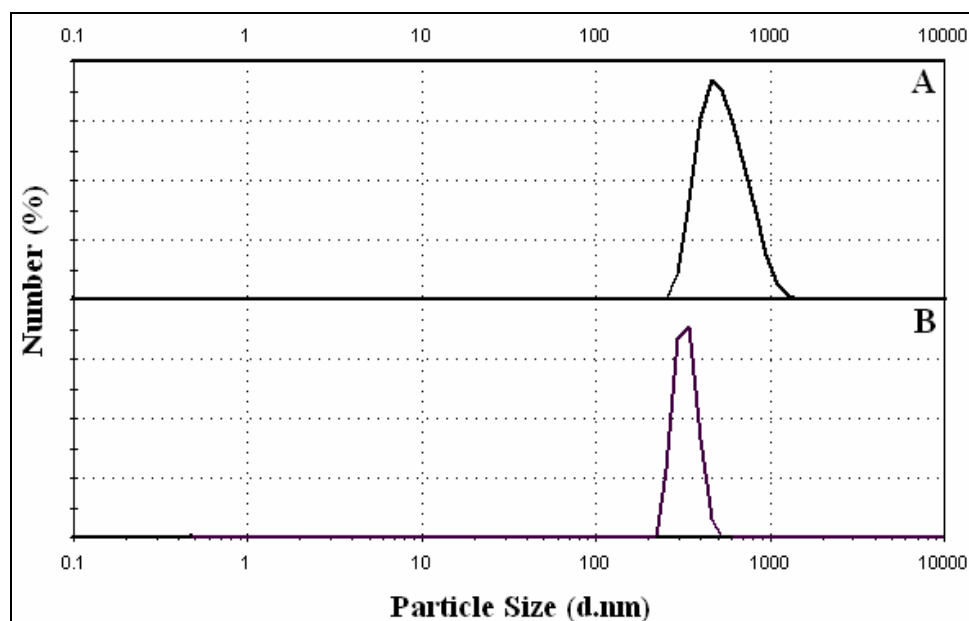


Fig. 1 – The particle size distribution data of the silica sols: (A) silica nanoparticles with TEOS+DEDMS and (B) silica nanoparticles with TEOS+DEDMS+functionalized silica nanoparticles by FAS13.

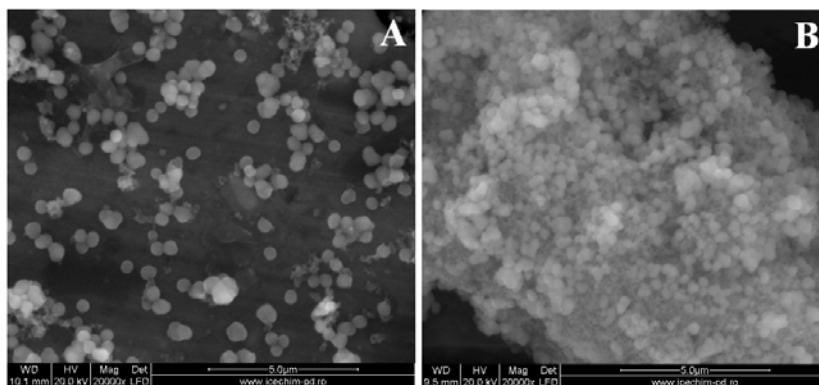


Fig. 2 – ESEM images of the silica sols: (A) silica nanoparticles with TEOS+DEDMS and (B) silica nanoparticles with TEOS+DEDMS+functionalized silica nanoparticles by FAS13.

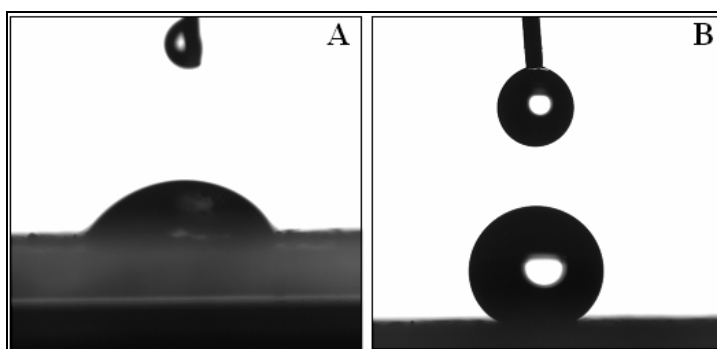


Fig. 3 – Images of water drops on coatings surfaces with: (A) silica nanoparticles with TEOS+DEDMS and (B) silica nanoparticles with TEOS+DEDMS+functionalized silica nanoparticles by FAS13.

### Static contact angle measurements

The silica nanoparticles dispersed solutions (with and without fluorinated silica powder) were deposited onto glass slides to obtain silica films (see Fig. 3). These films were investigated in order to verify their wettability. The hydrophobicity of coatings was shown by the water/coating contact angle.

This experimental series showed that the hydrophobicity is reached on the material having fluorinated silica particle. The low contact angle of a water droplet on the silica films is obtained for the film surface with TEOS+DEDMS ( $67 \pm 2^\circ$ ) (Fig. 3A). For the film containing TEOS+DEDMS and fluorinated silica particle (see Fig. 3B), the water contact angle increase at  $145 \pm 3^\circ$  and can be concluded that the coating film is ultrahydrophobic and have excellent water-repellency.<sup>17</sup> It can be deduced from the results that the coating film is covered with perfluoroalkyl group.<sup>7</sup>

### FT-IR studies

FT-IR spectra of dried hybrid materials (silica sols dried at room temperature) prepared with

silica nanoparticles and with addition of fluorinated silica powder, respectively, are shown in Fig. 4. From this figure, it can be observed a strongest peak at  $\sim 1050 \text{ cm}^{-1}$  with an accompanying asymmetric broad shoulder that is due to the asymmetric stretching vibration of Si-O-Si bonds in the silica nanoparticles. Another two significant peaks of silica appears at  $800 \text{ cm}^{-1}$  and  $\sim 945 \text{ cm}^{-1}$ , associated with the bending mode of Si-O-Si bonds and due the presence of Si-OH bonds, respectively.<sup>16</sup> The FT-IR spectra of the hybrid material prepared using fluorinated silica powder (Fig. 4B) reveals the new peak at  $848 \text{ cm}^{-1}$  as compared to sample prepared using only silica nanoparticles shown in Fig. 4A. This peak can be assigned to the C-H bonds, arising from FAS13 molecules<sup>18</sup> and confirms that the nanoparticles of silica are functionalized by fluorine from FAS13 molecules. These results indicated that the hybrid material with fluorinated silica powder was successfully made from the solution of alkoxides of TEOS and FAS13.

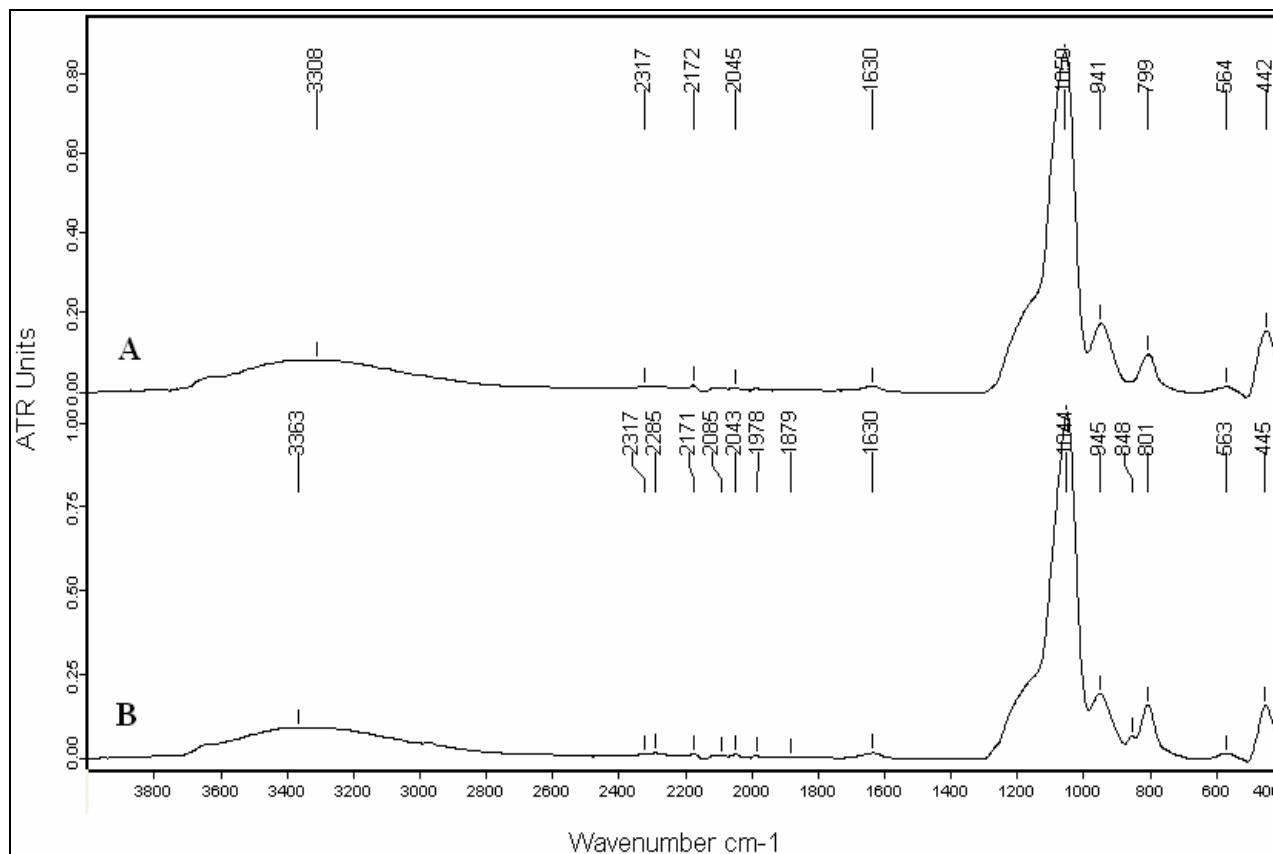


Fig. 4 – FTIR spectra of dried hybrid materials containing: (A) silica nanoparticles with TEOS+DEDMS and (B) silica nanoparticles with TEOS+DEDMS+functionalized silica nanoparticles by FAS13.

## EXPERIMENTAL

### Materials

For the synthesis of silica particles, tetraethoxysilane (TEOS, Merck-Schuchardt), diethoxydimethylsilane 97% (DEDMS, Sigma-Aldrich) and 1H, 1H, 2H, 2H - perfluorooctyltriethoxysilane (FAS13, Aldrich) were used as purchased. Ethanol and 2-propanol were obtained from Merck (99.9%). Ammonium hydroxide solution (33%) was purchased from Sigma-Aldrich. The chemicals were used as received.

### Preparation of water-repellent films

Silica sol was prepared by a base catalyzed sol-gel process. In the first step (S1), ammonium hydroxide solution (0.54 ml), ethanol (5 ml) and distilled water (0.6 ml) were stirred together for 10 minutes, and heated at 50°C. We used tetraethyl-orthosilicate (TEOS) as silica particle precursor and diethoxydimethylsilane (DEDMS) as particle coating precursor. As a second step (S2), an alcoholic solution of tetraalkoxysilane (TEOS) (0.5 ml) in ethanol (0.4 ml) was rapidly added, and stirring at 50°C was continued until a slight opalescence appeared (approximately 10 minutes). Diethoxydimethylsilane (0.078 ml) was then added drop-wise to the reaction mixture (S3). The molar ratio between TEOS and DEDMS was 5:1. Stirring and temperature were maintained for another 30 minutes.

Silica sol was also synthesized with fluorinated silica powder (0.01 g) redispersed in 2-propanol (2 ml), which was added to the end of the reaction mixture, and prepared in a similar way to that containing only TEOS and DEDMS. The fluorinated silica powder was obtained as follows: a mixture of 2-propanol (6.5 ml), ammonium hydroxide solution (0.54 ml) and distilled water (0.6 ml) was employed as reaction environment. This mixture was heated at 50°C, under continued stirring. A solution of TEOS (1 ml) in 2-propanol (0.5 ml) was rapidly added to the solution, and stirring at 50°C was continued until a slight opalescence appeared (approximately 10 minutes), confirming the formation of silica nanoparticles. The synthesized silica nanoparticles are further functionalized in a propanolic fluoroalkylsilane (FAS13,  $C_{14}H_{19}F_{13}O_3Si$ , (0.14 ml) dissolved in 2-propanol (0.5 ml)), and stirring at 50°C was continued another 40 minutes. The molar ratio between TEOS and FAS13 was 10:1. The functionalized silica nanoparticles were dried at room temperature (25°C), resulting in a white fluorinated silica powder. The composition of the fluorinated silica powder is summarized in Table 1. An amount of fluorinated silica powder (0.01 g) was used for the functionalization of silica sol.

The compositions of the coating solutions prepared (with and without fluorinated silica powder) and used in this study are presented in Table 2.

The final silica dispersed solutions (with and without fluorinated silica powder) were deposited onto clean glass slides, using a small brush and dried at room temperature before being used for further investigations.

Table 1

The composition of the fluorinated silica powder used for the synthesized of silica sol

Reagent	Amount (ml)
FAS13	0.14
TEOS	1
2-propanol	7.5
NH <sub>4</sub> OH	0.5
Water	0.6

Table 2

The compositions of the coating solutions

Reagent	Sample (heated at 50°C)					
	A			B		
	S1 (5 min)	S2 (10 min)	S3 (30 min)	S1 (5 min)	S2 (10 min)	S3 (30 min)
Ethanol (ml)	5	0.4	-	5	0.4	-
NH <sub>4</sub> OH (ml)	0.54	-	-	0.54	-	-
Water (ml)	0.6	-	-	0.6	-	-
TEOS (ml)	-	0.5	-	-	0.5	-
DEDMS (ml)	-	-	0.078	-	-	0.078
2 - propanol (ml)	-	-	-	-	-	2
Fluorinated silica powder (g)	-	-	-	-	-	0.01

### Characterizations

The samples were characterized both as sols and as films deposited onto clean glass slides. The analysis of the sols was carried out through dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements. Particle size distribution was measured through *Dynamic Light Scattering (DLS)* technique, with a Zetasizer Nano ZS (Malvern Instruments Ltd.) device, in the range of 0.6nm - 6µm. Morphology and shape of silica sols were studied by *Environmental Scanning Electron Microscopy (ESEM)*, using a FEI-Quanta 200 microscope. The silica sols were deposited on conductive stubs and dried at room temperature. The ESEM images were obtained in low vacuum mode.

The wetting properties of the hybrid films (obtained from the silica sols deposited onto clean glass slides and dried at room temperature) were performed using the contact angle measurements (KSV CAM 200). FT-IR spectra of the dried hybrid materials (silica sols dried at room temperature), in the range 400-4000 cm<sup>-1</sup>, were measured using a *Fourier transforms infrared spectrometer* (Tensor 37 from Bruker) in ATR mode using Golden.

### CONCLUSIONS

Fluorinated silica nanoparticles have been prepared by sol-gel process and used to prepare hydrophobic films on glass slides. FAS13 molecules are used for the fluorination of the silica nanoparticles. The water-repellent glass prepared with fluorinated silica nanoparticles is very hydrophobic and has excellent water-repellency. With proper experimental conditions same roughness can be obtained by sol-gel process for

industrial applications of the derived-fluorinated silica nanoparticles as engineering materials.

*Acknowledgements:* Cristina Nistor acknowledges the financial support of European Social Fund – “Cristofor I. Simionescu” Postdoctoral Fellowship Programme (ID POSDRU/89/1.5/S/55216), Sectoral Operational Programme Human Resources Development 2007–2013.

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