

## Characterization of Transparent Hydrophobic Coating with Silica and Graphene Oxide Fillers by Sol-Gel Method

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Received 26 October 2017; Revised 11 December 2017; Accepted 17 January 2018

### ABSTRACT

*Transparent hydrophobic coating was prepared by using the sol-gel method. Two different roughness agents namely silica and graphene oxide, GO were used in this study. Surface contact angle, transmittance degree, IR spectroscopy and surface morphology were characterized for each sample. All samples show good transparency which was confirmed by UV visible spectroscopy. The hydrophobicity obtained for GO-containing sample is more significant as compared to silica-containing sample indicating that GO is the better candidate to be used as a hydrophobic coating in optically transparent applications such as solar cells, optical lenses and windows.*

**Keywords:** Transparent Hydrophobic Coating, Sol-Gel Method, Silica, Graphene Oxide

### 1. INTRODUCTION

Surface with water contact angle (CA) greater than 90° is commonly called as hydrophobic surface [1]. In nature, plants and insects including lotus leaf, water strider and penguin exhibit hydrophobic property. Developing hydrophobic surface with self-cleaning characteristics have enormous potential applications in automobile glass, building materials, bathroom mirrors, greenhouse glass and solar panel. Hydrophobic chemical composition and high surface roughness are the two factors that are responsible for this phenomenon [1-3]. Li and Amirfazli previously worked on the theoretical aspect of the effect of surface contact angle and hierarchical micro/nanostructures on the wettability of coated glass surface [4-6] and concluded that hierarchical structures with hydrophobic property affect not only the wettability of the surface but also the mechanical strength of the treated surface. However, report in literature indicates that it is difficult to obtain surfaces possessing both excellent hydrophobic property and high optical transparency. This is because the transparency and surface roughness are often competitive properties. Increasing surface roughness will increase the surface hydrophobicity but at the same time increase the scattering of light that falls on the surface (i.e. Mie scattering) [7]. Mie scattering occurs when the diameter of the scattering particles is close to the wavelength of the incident light and is seen as the primary factor in reducing the optical transparency of hydrophobic surface. To reduce Mie scattering, surface roughness must be reduced below the wavelength of the incident light. It has been proven that sub-100 nm roughness produces a low scattering intensity and will be effective in fabricating hydrophobic

surface with high optical transparency. Thus, to fabricate transparent hydrophobic surface, extra efforts should be paid to control the roughness dimension of the coated surface. To this end, Han *et al.* have employed silane modified carbon nanotube coating in preparing hydrophobic surface [8]. They fabricated transparent hydrophobic glass by sol-gel method using tetraethoxysilane as precursor and obtained CA > 150°. Recently, Bayindir *et al.* produced high hydrophobic surface by comparing single layer microporous coating with double layer micro/nanoporous coating of spin-coated ormosil colloid [9]. The CA that they obtained was close to 160°. Other methods of preparing hydrophobic surfaces that were reported included electrospinning, template method and CVD method [10-12].

Although several methods have been successful in synthesising surfaces with high hydrophobicity, however, most of them involve tedious sampling stages, processing procedures and the employment of special templates (microporous/nanoporous) that reduce their potency for scale-up purposes. On the other hand, the reliance on using silica as roughness agent for preparing hydrophobic surface is not feasible since it degraded at prolonged outdoor exposure and thus reducing the surface hydrophobicity [13].

It is well-known that graphene has excellent chemical, thermal and environmental stability [14-16]. Therefore, graphene has emerged as a prominent candidate to fabricate stable and transparent hydrophobic coating materials. It can be realized with the incorporation of functionalized graphene, namely graphene oxide, GO onto modified tetraethoxysilane that is initially prepared by sol-gel method. Pristine graphene seems inapplicable to be used as one of the hydrophobic components because of weak chemical interaction with other materials.

In this study, the transparent hydrophobic surface was prepared by a facile sol-gel method using tetraethoxysilane, TEOS as precursor and fluoroalkylsilane as hydrophobic agent *cum* modifier. Silica and GO were employed as roughness agents to enhance the surface roughness. Their properties were compared to determine whether the modified graphene-based coated surface will be able to rival the performance of the silica-coated surface and be a better candidate for applications requiring superhydrophobic property.

## **2. EXPERIMENTAL**

### **2.1 Materials**

The chemicals used in this study were tetraethoxysilane, TEOS (Merck), fluoroalkylsilane, FAS namely, heptadecafluorodecytrimethoxysilane (Gelest), silica, (Sigma), graphene oxide, GO (Graphenea) and ethanol (J. Kollins), hydrochloric acid (Merck) and distilled water. All chemicals were used as received.

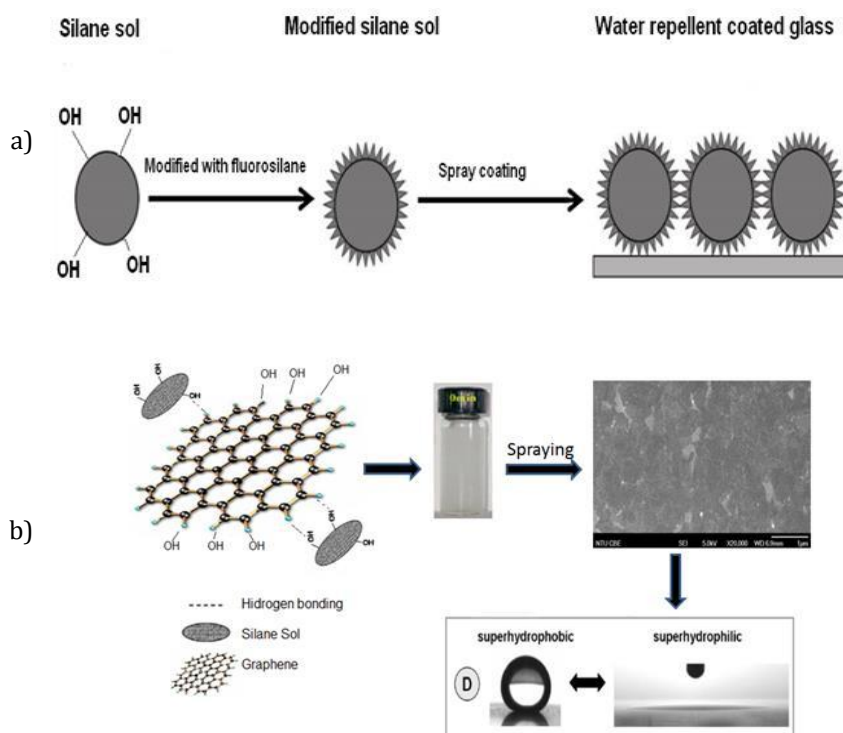
### **2.2 Pretreatment of Glass Substrates**

Pre-treatment of the glass substrate was an essential first step to ensure that dirt was removed and the glass surface is clean. Commercially available glass micro slides (Sail) were immersed in 0.5M HCl for 10 minutes, were washed with distilled water and finally were rinsed with ethanol. The glass micro slides were then dried in an oven at 60 °C for a few hours before using. This precautionary step assists in obtaining a homogeneous and uniform coating layer on the glass micro slides.

### **2.3 Preparation of Transparent Hydrophobic Coating**

A silane sol solution having a fluorinated group was prepared by mixing tetraethoxysilane, as a precursor, heptadecafluorodecytrimethoxysilane as co-precursor *cum* modifier, distilled water

and ethanol both were used as solvents and HCl which was used as a catalyst. The solution was kept stirring to reach sol-gel network. To enhance the surface roughness of the coating solution, silica nanoparticles (Sigma) or graphene oxide was added respectively at a concentration of 0.03 wt% with respect to the master batch of the coating solution (Scheme 1).



**Scheme 1.** Schematic formulation of hydrophobic coating using (a) silica and (b) GO by sol-gel method.

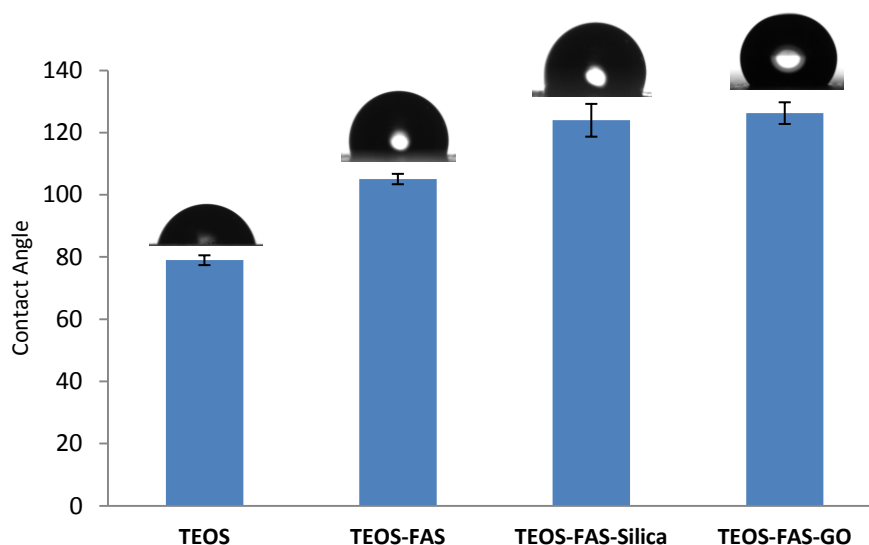
The fabrication of the hydrophobic surface was achieved by spray deposition using spray-coater (JSpray 125-A) with a fluid nozzle having a diameter of 0.3 mm. The glass substrate was heated at 60 °C prior to being used. The distance between glass substrates and spray coater were made constant at 25 cm as well as spray pressure which was set by default (0.1 MPa). The deposited hydrophobic coating then was cured at 100 °C in a vacuum oven for one and half hour to dry the samples and to remove any unreacted materials and excess solvent.

## 2.4 Characterization

The water contact angle was measured by using Attension Theta Lite Optical Tensiometer (Biolin Scientific, TL 100) by sessile drop method. The contact angles for five different droplets (5  $\mu$ l of water) were measured, and their average was taken as the contact angle value. The optical transparency was determined by using UV-Visible Spectroscopy (Shimadzu, UV-1800) in the visible light region. The surface chemical composition was measured using FTIR (Bruker Tension II) using ATR technique. The surface roughness was investigated by using Atomic Force Microscope (JPK Nanowizard 2) using contact mode method. The morphology of the samples was measured by using Field Emission Scanning Electron Microscope FESEM (Carl Zeiss, Gemini SEM 500).

### 3. RESULTS AND DISCUSSION

#### 3.1 Water Contact Angle Studies

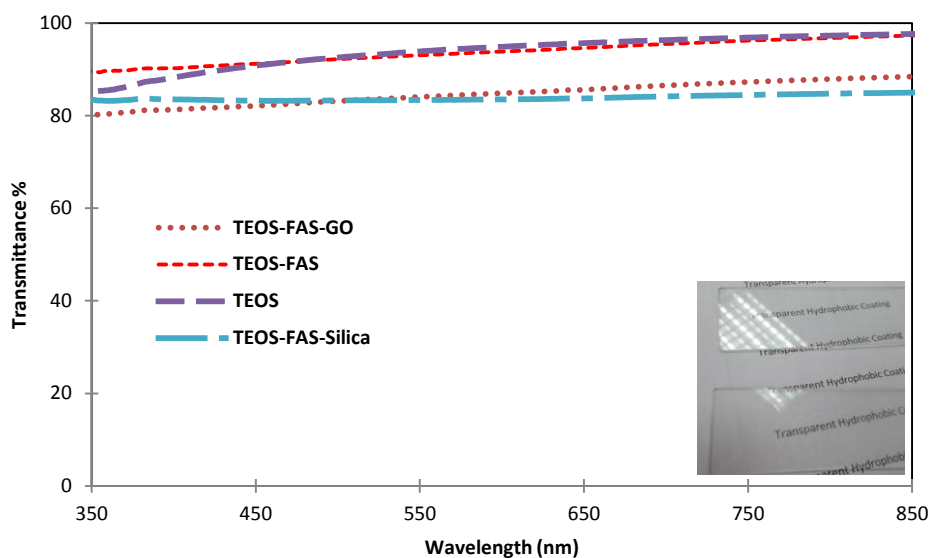


**Figure 1.** Contact angle for different hydrophobic coating surfaces.

Figure 1 shows the water contact angle for micro slide surfaces that have been treated with different hydrophobic formulations namely TEOS, TEOS-FAS, TEOS-FAS-Silica and TEOS-FAS-GO. As expected, due to the presence of two entities namely surface roughness (GO or silica) and hydrophobic agent (FAS), graphene oxide and silica-based hydrophobic coating surfaces show the highest contact angle of 126.3° and 124° respectively. TEOS-FAS sample also exhibits hydrophobicity, 105.1° due to the influence of FAS material that responsible to reduce the surface free energy of the sample [8]. As for TEOS sample, the surface contact angle was only in the hydrophilic range, 79° because of the absence of hydrophobic agent (e.g. FAS) as well roughness agent (e.g. silica and GO).

#### 3.2 UV Visible Spectroscopy

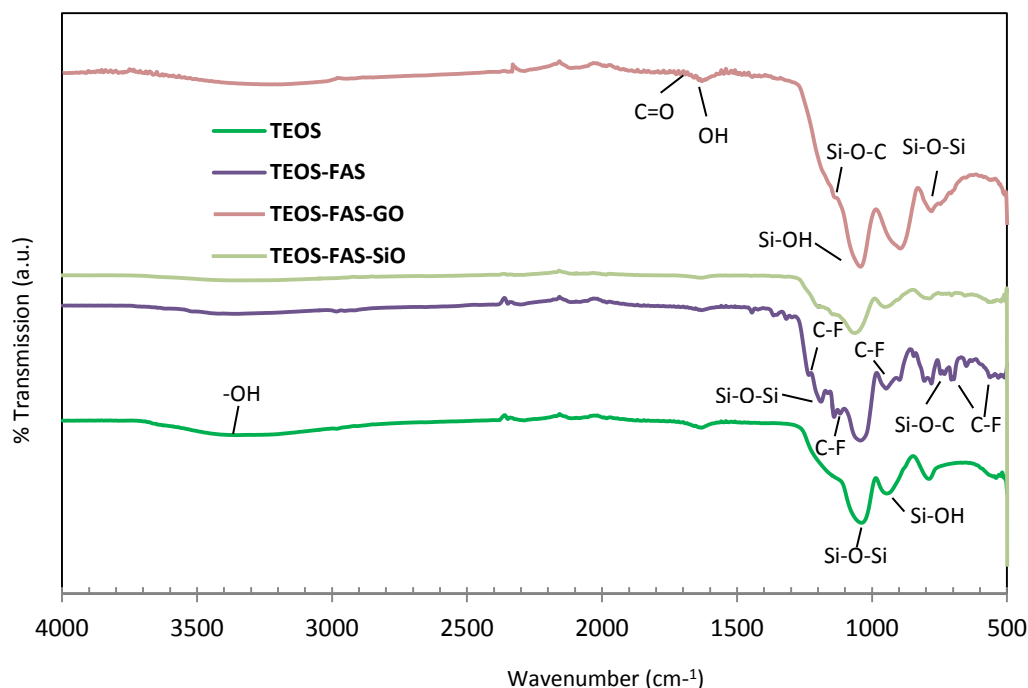
Optical transmission of the samples was measured, and the result is depicted in Fig. 2. All samples show high transmittance which is in the range of 80-95% indicating that the samples are optically transparent. TEOS and TEOS-FAS samples have the highest transparency because they are less influenced by Mie scattering in which mostly present in the samples containing roughness fillers [7]. TEOS-FAS-GO and TEOS-FAS-Silica contain GO and silica respectively in which they are crosslinked in the coating network. With the addition of fillers e.g. GO or silica, the coating samples tend to become translucent because both fillers induce light scattering thereby decreasing the intensity of visible light [17]. However, as discussed in the previous section, with no incorporation of fillers the hydrophobicity will drop. Therefore the amount that should be incorporated into the coating is very crucial so that the water contact angle and transparency values could be optimised.



**Figure 2.** UV-Visible spectra for different hydrophobic coating surfaces. The inset photo shows the transparency of hydrophobic coating micro slides.

### 3.3 FTIR

The chemical composition of different hydrophobic coatings coated on glass micro slides was studied by FTIR spectroscopy using ATR technique in transmission mode. As depicted in Fig. 3, the absorption peaks were observed in the range of 4000 – 500  $\text{cm}^{-1}$ . The wide peak at 3389  $\text{cm}^{-1}$  and 1669  $\text{cm}^{-1}$  indicates the asymmetric stretching vibration and bending vibration correspond to hydroxyl group that attribute to silanol and adsorbed water respectively [18-20]. The peak at around 1211, 1071 and 805  $\text{cm}^{-1}$  is the typical absorption of Si-O-Si asymmetric bending vibration whereas at 974  $\text{cm}^{-1}$  is ascribed to the bending vibration of Si-OH [18-20] which is attributed to unfunctionalized silica nanoparticles. Other interesting absorption peaks can be found very clearly especially for TEOS-FAS at around 1243, 967, 725 and 610  $\text{cm}^{-1}$  correspond to CF,  $\text{CF}_2$  or  $\text{CF}_3$  from C-F bonds [18, 22]. Weak broad absorption peak can be detected for TEOS-FAS-GO sample at 1722  $\text{cm}^{-1}$  corresponds to C=O vibration attributed to carbonyl or carboxyl group in GO [18, 23]. This peak is not so significant due to less amount of GO used in the sampling. The most important peak appears at 1136  $\text{cm}^{-1}$  representing Si-O-C bond which gives confirmation that fluoroalkylsilane, FAS is attached covalently to silanol particles which are apparent for TEOS-FAS-GO and TEOS-FAS-Silica.



**Figure 3.** FTIR spectra for different hydrophobic coating surfaces.

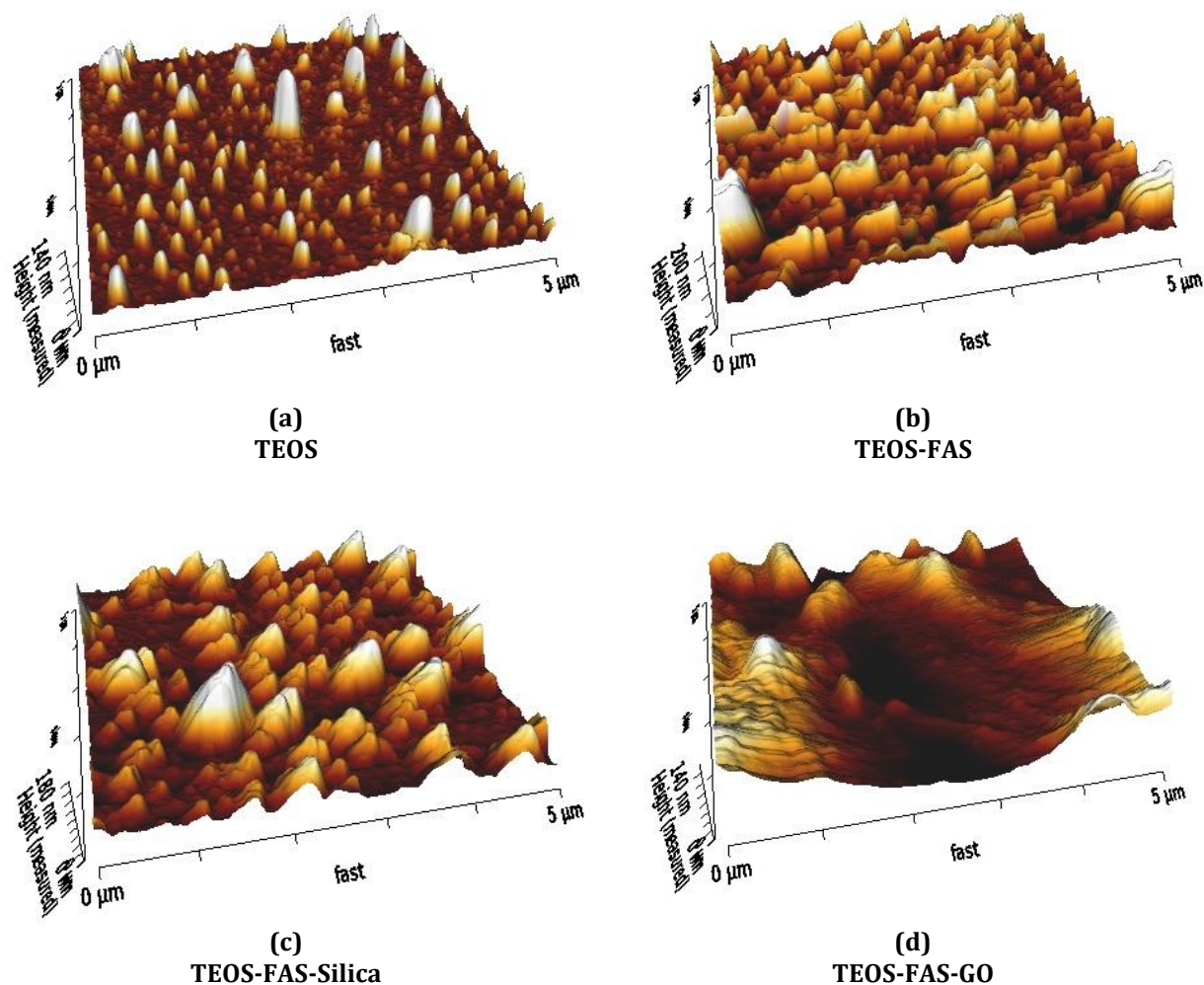
**Table 1** Infrared bands identified in hydrophobic coating surfaces from FTIR measurements

Chemical bond	Wavenumber (cm <sup>-1</sup> )
-OH	3389 and 1669
Si-O-Si	1211, 1068 and 805
Si-OH	974
Si-O-C	1136 and 771
C-F	1243, 967, 725 and 610
C=O	1722

### 3.4 AFM Studies

The surface topography of coatings from TEOS sol, TEOS-FAS, TEOS-FAS-Silica and TEOS-FAS-GO as measured by Atomic Force Microscope, AFM is shown in Fig. 4. The images were taken at  $5 \times 5 \mu\text{m}^2$  planar via contact mode method. Different shapes of topography were obtained for the different samples. The rms roughness,  $R_q$  value obtained for each sample are 9.59 nm, 21.53 nm, 24.97 nm and 27.65 nm for TEOS sol, TEOS-FAS, TEOS-FAS-Silica and TEOS-FAS-GO respectively. The lowest hydrophobicity obtained for TEOS-sol (Fig. 4a) can be explained by the separated silica island distributed within the substrate surface [23]. When FAS is introduced in the formulation of TEOS-FAS (Fig. 4(b)), the morphology is rougher as can be seen in the image. In addition,  $R_q$  value is also higher as compared to TEOS sol surface. The sharp, compact and homogenous silica island is obtained for TEOS-FAS-Silica (Fig. 4(c)) with greater  $R_q$  value. This is due to the presence of silica particle that was introduced in the formulation to enhance its hydrophobicity. A different topography is obtained for TEOS-FAS-GO (Fig. 4(d)). This is a combination from the image of silica that was formed via sol-gel process and GO which is crosslinked with FAS [18]. The  $R_q$  value measured, 27.65 nm is also high in comparison with other samples and it indicates that GO is capable to be a roughness agent to enhance the hydrophobicity of glass surfaces.



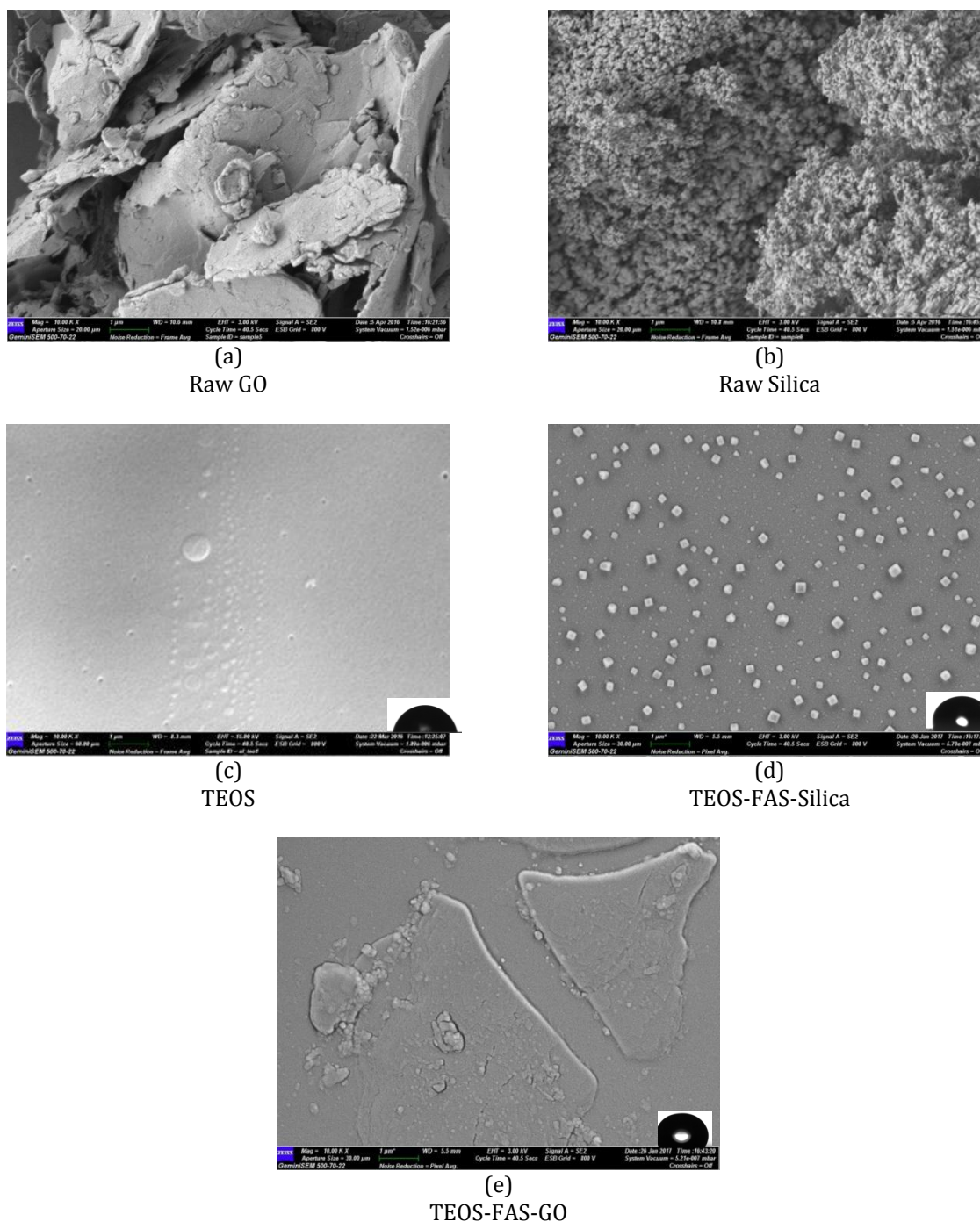


**Figure 4.** Atomic force microscopy for different hydrophobic coating surfaces (a) TEOS sol, (b) TEOS-FAS, (c) TEOS-FAS-Silica and (d) TEOS-FAS-GO.

### 3.5 FESEM

The surface morphologies of GO powder, silica nanoparticles and coatings derived from TEOS sol, TEOS-FAS-Silica and TEOS-FAS-GO are shown in Fig. 5. The morphology of coating obtained from TEOS sol presented in Fig. 5(c) shows microsized particles that were scattered and irregular on its surface. These microsized particles represent silica that was formed from sol-gel reactions. This is in contrast with the coating resultant from TEOS-FAS-Silica as presented in Fig. 5(d) where the microparticles are more uniformly distributed on the on the substrate. This type of morphology is believed to be responsible for trapping air on the surface of the coating and prevent water penetration and enhancing the hydrophobicity of the surface of the coating [24].

On the other hand, different observation can be seen for TEOS-FAS-GO as shown in Fig. (5e). It is shown that silica microstructures deposited on the substrate as well as on the graphene lattice. TEOS and FAS capable of reacting chemically with GO surface by targeting carboxylic and epoxide at edges and basal respectively [18] and form a covalent bond. In this way, hydrophilic nature of GO transforms into hydrophobic property thus increases the contact angle.



**Figure 5.** Field emission scanning electron microscopy for different hydrophobic coating surfaces (a) TEOS sol, (b) TEOS-FAS, (c) TEOS-FAS-Silica and (d) TEOS-FAS-GO and insets in Fig. 5(c)-Fig. 5(e) represent water contact angle.

#### 4. CONCLUSIONS

Transparent hydrophobic coatings using silica and GO fillers as roughness agents are successfully synthesized by using facile sol-gel method. The water contact angle shows that GO filler containing coating possesses slightly higher hydrophobicity in comparison with the coating using silica nanofiller. UV-Visible spectra show that all samples are transparent while FTIR shows the successful grafting of silica and graphene onto the FAS-TEOS chain with the appearance of Si-O-C peak due to the reaction between Si-OCH<sub>3</sub> group and OH group. Finally,



AFM demonstrates the roughness is increased with the addition of silica and GO fillers in which GO hydrophobic coating gives relatively greater roughness whereas FESEM shows the presence of silica microparticles and its deposition onto the substrate whereas it also confirms the growth of silica particle onto the graphene lattice.

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