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Solvo-affinity property of glass surfaces modified by self-assembled monolayers of organic and/or inorganic chemicals

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ABSTRACT

Three ultrathin films consisting of dendrimer self-assembled monolayer (SAM), silica particle/dendrimer SAM and silica particles have been prepared on glass surface to develop solvo-affinity and surface roughness and to elucidate the anti-fingerprint effect. The solvo-affinity and surface roughness of the coated films on glass surface were characterized by contact angle measurement and atomic force microscope. The results showed that the fabrication of dendrimer SAM on glass revealed the significantly high hydrophobicity. The loading of silica particles also enhanced hydrophobicity. Thus, the roughness of the surface was enhanced, suggesting the meaningful relation of hydrophobicity and roughness. However, the probable relation of anti-fingerprint property with solvo-affinity and surface roughness was not necessarily found, although the highest anti-fingerprint property was observed for a SAM of 3-aminopropyltriethoxysilane on glass which displayed medium hydrophobicity.

1. Introduction

Recently, the demands for using touchscreen devices such as smart phones and tablet computers are greatly increasing, since they are easy and convenient to use in our daily life. However, since fingerprint oils, or dirt are easily attached on their surfaces, the anti-fingerprint materials which possess both hydrophobic and oleophobic properties have been developed and applied on the surface of such devices to supply the anti-fingerprint property to protect their surface from any kind of stains. Many researches have been done to provide anti-fingerprint coating on the surface of such devices. For example, surface modifications by using perfluoroalkyl-based compounds were performed to supply the solvophobic properties on surfaces [1]. However, these compounds are costly and environmentally unfriendly. Recently, silica particles have been used to supply roughness on many surfaces to make the surface hydrophobic [2–4]. It is known that the construction of surface roughness as well as the modification by hydrophobic chemicals can provide hydrophobic property on surfaces [2–4]. Hybrid films of fluoropolymers with different kinds of silica particles have been fabricated to generate strawberry-like or quincunx-shaped composite silica particles on glass slide surfaces to provide hydrophobic property [4].

Self-assembled monolayer (SAM) is an effective method to supply solvophobic property on surfaces [3,5,6]. In addition, the surface is scarcely affected by the formation of monolayer on it, since the thickness of SAM is in nanometer scale [7–9]. Moreover, the SAM can also provide the anchoring sites for the subsequent self-assembly of the next monolayer, if adequate SAM molecule is utilized [5,6,8–12]. Thus SAM consisting of materials that can provide the oleophobic property and the roughness could be effective to provide anti-fingerprint property on the surface. Dendrimers with well-defined molecular structure and surface functionality could be considered as promising materials to form such surface.

In the present work, three kinds of ultrathin organic and/or inorganic films consisting of dendrimer SAM, silica particle/dendrimer SAM and silica particle SAM were fabricated on glass surface by using sol–gel reaction to provide both hydrophobic and oleophobic properties. The contact angles with droplets of water, n-hexadecane and oleic acid were measured to evaluate the solvophobicity performance on the modified glass. Moreover, the

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surface morphology of the modified-glass was investigated by an atomic force microscopy (AFM). The solvophobicity and roughness of these ultrathin organic and/or inorganic films are assessed in connection with the anti-fingerprint property.

2. Experimental

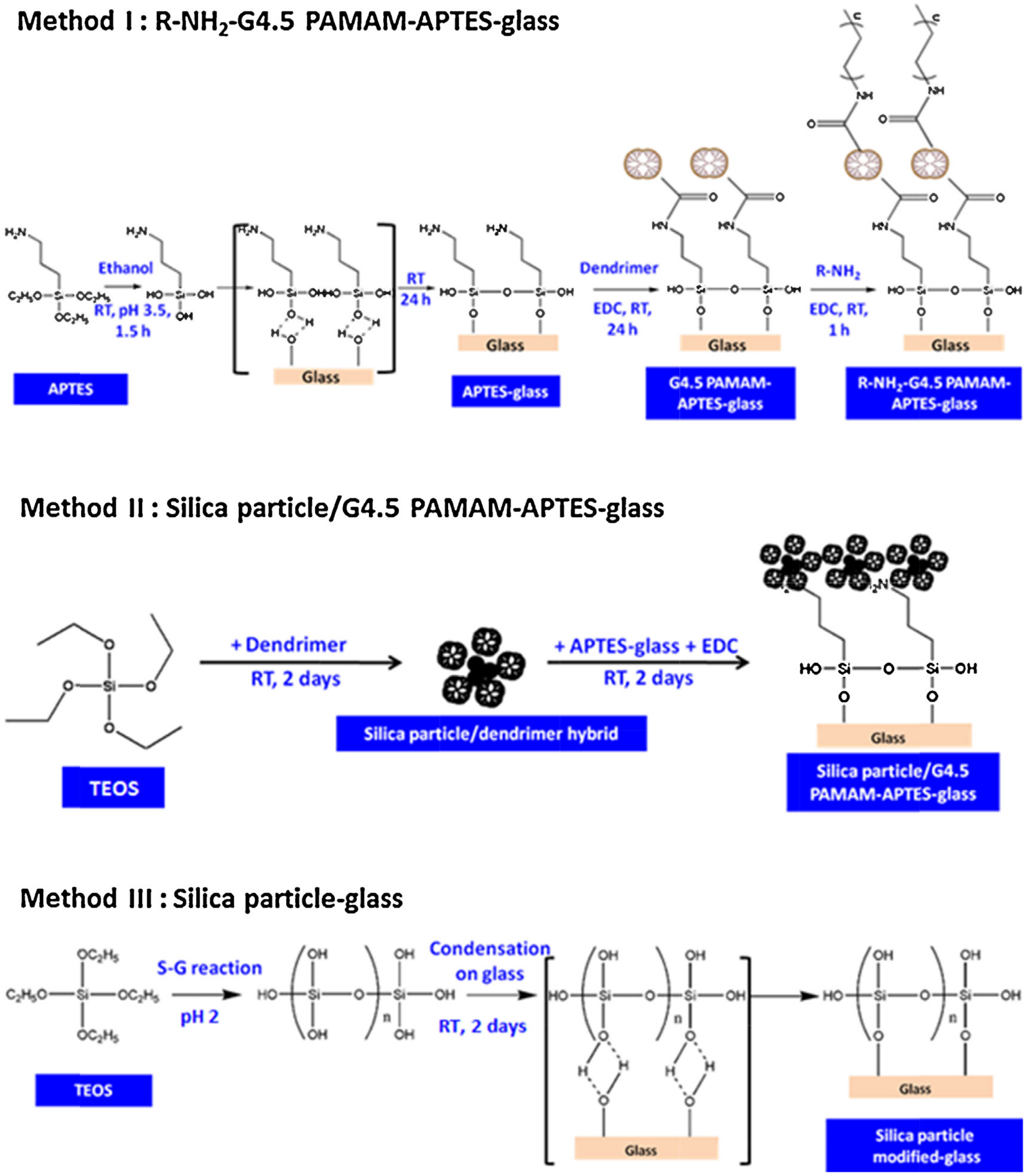
2.1. Reagents

Carboxyl-terminated 4.5th generation (G4.5) poly(amido amine) (PAMAM) dendrimer (5 wt% in methanol), propylamine (PA), hexylamine (HA), and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) were products from Aldrich Chemical Co. Tetraethyl orthosilicate (98%, TEOS), and 3-aminopropyltriethoxysilane (99%, APTES) were purchased from Acros Organics. Ethyl alcohol and hydrochloric acid were commercial products.

2.2. Modification of glass surface by dendrimer SAM

A SAM of APTES on glass was prepared as shown in Scheme 1 (Method I); the glass substrate was immersed into a piranha solution (H_2SO_4:H_2O_2 = 3:1) for 30 min to clean and introduce hydroxyl groups on the glass surface, and then rinsed with water several times. An aqueous solution of APTES (2%, v/v) was prepared by mixing APTES with water, ethanol (10%, v/v) and 0.1 M HCl (3.3%, v/v), and pH of the solution was adjusted to 3.5 for hydrolyzing APTES for 1.5 h at room temperature. After that, the glass substrate was dipped into the hydrolyzed APTES solution and the solution was stirred for 24 h at room temperature. The obtained APTES-SAM glass substrate was washed with ethanol to remove unreacted chemicals and dried overnight in an oven at 110 °C.

In immobilization of G4.5 PAMAM dendrimer on APTES-glass (Scheme 1 (Method I)), an aqueous solution of carboxyl-terminated G4.5 PAMAM dendrimer was prepared by diluting a



Scheme 1. Schematic representation of the procedures for surface modification on glass.

5 wt% methanol solution of dendrimer with water, and then EDC was added to a 0.15 mM dendrimer solution. After that, the APTES-glass was immersed into the mixture, and the solution was stirred for 24 h at room temperature to allow the amide-bond formation. An obtained G4.5 PAMAM-APTES-glass was rinsed several times with water to remove unreacted chemicals and dried in an oven at 110 °C for 4 h.

On functionalization of terminal group of G4.5 PAMAM dendrimer by PA or HA ($R-NH_2$) (Scheme 1 (Method I)), EDC was added to a 10 mM methanol solution of $R-NH_2$, and G4.5 PAMAM-APTES-glass was dipped into the mixed solution for 1 h at room temperature. Then the prepared $R-NH_2$-G4.5 PAMAM-APTES-glass substrate was washed several times with ethyl acetate to remove unreacted chemicals and dried in an oven at 110 °C for 4 h.

2.3. Modification of glass surface by SAM of silica particle/dendrimer hybrid

For fabrication of silica particle/dendrimer hybrid onto APTES-glass as shown in Scheme 1 (Method II), silica particle/dendrimer hybrid was prepared by mixing TEOS with G4.5 PAMAM dendrimer at a molar ratio of 1000:1 and pH of 2 and 10 and by performing sol–gel reaction at room temperature for 2 days. Then EDC was added to the silica particle/dendrimer hybrid solution, and the APTES-glass substrate was immersed into the mixtures and stirred for 2 days at room temperature to allow the amide-bond formation. The silica particle/G4.5 PAMAM-APTES-glass substrate was washed to remove unreacted chemicals and dried overnight in an oven at 110 °C.

2.4. Modification of glass surface by SAM of silica particle

Fabrication of silica particles on glass was carried out as follows (Scheme 1 (Method III)); the reaction solution was prepared by solving TEOS in an ethanol:water (20:80, v/v) mixture at different TEOS concentrations (15, 50, 100 mM). The pH of the reaction solution was adjusted by HCl to be 2. Then the glass substrate was dipped into the sol–gel solution and the solution was stirred for 2 days at room temperature to allow the condensation on glass. The obtained glass substrate was washed to remove unreacted chemicals and dried overnight in an oven at 110 °C.

2.5. Measurements

Transmission electron microscopic (TEM) images were taken using a Hitachi H-7000 equipped with a CCD camera, operating at a voltage of 100 kV. Infrared (IR) absorption spectra were recorded for sample powders on an FTIR absorption spectrometer (Nicolet, Nexus 670) with an attenuated total reflection (ATR) mode. Ultra violet–visible–near infrared (UV–VIS–NIR) absorption spectroscopic measurements were performed on a Jasco V-670 series UV spectrometer. AFM observation was performed using a Digital Instruments NanoScope III apparatus. Contact angle measurements with water, n-hexadecane and oleic acid were performed using the static sessile drop method by means of a conventional digital camera. An aliquot (10 μL) of test liquid was slowly dropped on the modified glass surface. Contact angle was measured at a few seconds after dropping.

3. Results and discussion

3.1. Dendrimer SAM on glass

SAM of APTES was fabricated on glass surface by the condensation of silanol groups of the hydrolyzed APTES with hydroxyl groups on glass surface to form a stable siloxane (Si–O–Si) bond [5,6,12–14] to provide functionality on glass surface (Scheme 1 (Method I)). The formation of SAM on the glass surface was confirmed by water contact angle as shown in Fig. 1. The water contact angle of bare glass was 37°, which reveals the bare glass surface to be rather hydrophilic. However, after SAM of APTES was fabricated on the glass surface, the water contact angle was increased up to 51°. This increase in the water contact angle indicates the improvement of the solvophobicity.

It has been reported that the possessing of both roughness and hydrophobicity would provide the surface with highly hydrophobic performance [2,3]. Thus carboxyl-terminated G4.5 PAMAM dendrimers with a globular shape were immobilized on the APTES-glass by using EDC as a condensing agent for amide-bonding between amine group on APTES-glass and carboxyl terminal group on the G4.5 PAMAM dendrimer (Scheme 1 (Method I)) to provide a "bumpy structure" on glass surface [14]. It was observed that after G4.5 PAMAM dendrimers were immobilized on APTES-glass, the water contact angle was significantly increased up to 71°. However, when the carboxyl-terminated groups of PAMAM dendrimers were functionalized by aliphatic amines (PA and HA) to enhance the hydrophobicity on the G4.5 PAMAM-APTES-glass as shown in Scheme 1 (Method I), the water contact angle of $R-NH_2$-G4.5 PAMAM-APTES-glass was decreased to 52° and 54°, respectively, for PA and HA (Fig. 1). It might be noted that the behavior of water contact angle on G4.5 PAMAM-APTES-glass is at least abnormal from the conventional behavior of the surface, if only the solvophobicity of chemical species on surface is considered.

Then the consideration of surface roughness should give us any suggestion on the explanation of abnormal behavior of water contact angle. Surface morphology of bare, APTES- and G4.5-APTES-glass was observed by using a contact mode AFM as shown in Fig. 2. AFM morphological image of APTES-glass revealed a smooth surface due to the formation of a three-dimensional polymeric network of APTES on an original fine rough surface (around 1 nm height) of bare glass. It has been reported that the thickness of APTES film is in the range of 3–5 nm [7,11]. Whereas, the AFM image of G4.5 PAMAM-APTES-glass displayed a lot of domains deposited on the APTES-glass surface, and the height of the domains was in the range of 2–7 nm (Fig. 2), indicating that G4.5 PAMAM dendrimers are inhomogeneously immobilized on the APTES-glass surface. It can be suggested that the fabrication of G4.5 PAMAM dendrimers could provide a "bumpy structure" on the APTES-glass and hence change the intrinsic hydrophilicity of the G4.5 PAMAM-APTES-glass which comes from hydrophilic G4.5 PAMAM dendrimer species as observed in Fig. 1(c).

For comparison, contact angle with a drop of hexadecane was measured for all surfaces. The contact angle with n-hexadecane was 14° for bare glass and this indicates that the bare glass surface has less oleophilic property. However, after the SAM of APTES was fabricated on the glass surface, the contact angle became 0°. This observation supports that the formation of APTES induced oleophilic properties of glass surface, being consistent with the behavior of water contact angle as described above. However, the 0° contact angle should be surprising, because the free terminal of APTES is amine. Convincible explanation is that amine terminal of APTES comes close to the hydrophilic glass surface to form hydrogen bonding with hydroxyl group on it and then hydrophobic propyl moiety is exposed on the modified glass surface [15]. Therefore, at the same time, water contact angle of APTES-glass also maintains similar angle to alkyl chain-terminated $R-NH_2$-G4.5 PAMAM-APTES-glass. On the other hand, after G4.5 PAMAM dendrimers were immobilized on APTES-glass, the hexadecane contact angle was significantly increased up to 18°. The increase in the oleophobicity of APTES-glass might come from the hydrophilic

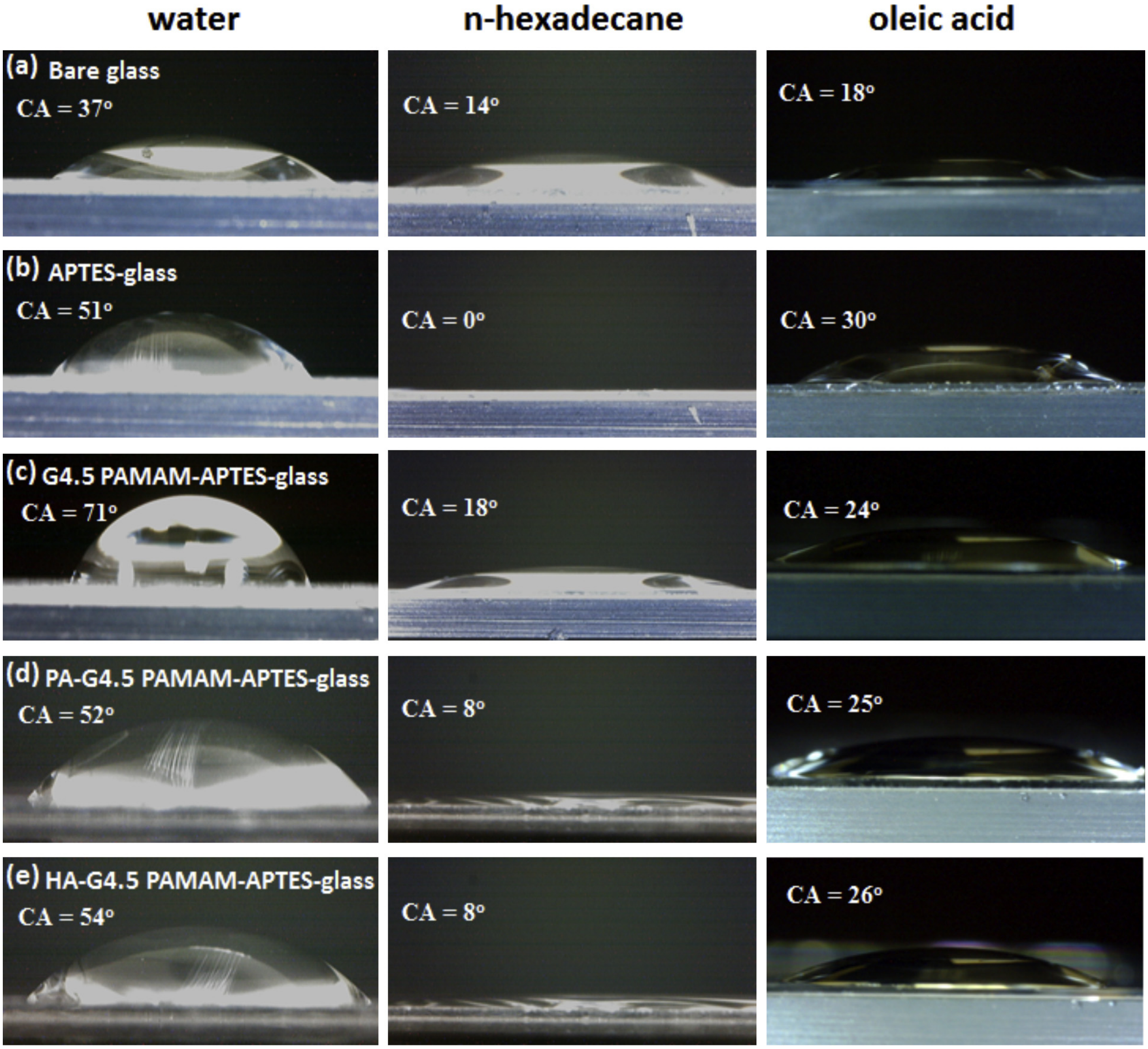


Fig. 1. Contact angles with water, n-hexadecane and oleic acid of (a) bare glass, (b) APTES-glass, (c) G4.5 PAMAM-APTES-glass, (d) PA-G4.5 PAMAM-APTES-glass and (e) HA-G4.5 PAMAM-APTES-glass.

chemical structure of G4.5 PAMAM dendrimers. In addition, it was observed that the hexadecane contact angle of R-NH_2-G4.5 PAMAM-APTES-glass was decreased to 8°, after G4.5 PAMAM dendrimers were functionalized by aliphatic amines (PA and HA), indicating the creation of oleophilic periphery. It can be referred that the hexadecane contact angle mainly behaves depending on solvophobicity of the surface, different from the behavior of water contact angle as described above.

Meanwhile, oleic acid was also used to verify the properties of the modified surfaces in connection with anti-fingerprint property, because oleic acid and its derivatives are main chemicals of fingerprint component [16]. The contact angle with a drop of oleic acid was lowest for bare glass (18°), medium for G4.5 PAMAM-APTES-glass and R-NH_2-G4.5 PAMAM-APTES-glass (24–26°) and highest for APTES-glass. This order is completely independent of the orders of oleophobicity from water and hexadecane contact angles. This means that the affinity of oleic acid on surface does not necessarily obey on oleophobicity of surface and roughness on it. The affinity should originate in the specified interaction of amphiphilic oleic acid on each modified surface.

3.2. Silica particle/dendrimer SAM on glass

For gaining a further insight into the contribution of surface roughness on anti-fingerprint property, in the present work, two kinds of surfaces including silica particles were fabricated. First, silica particles were used as so-called fillers in dendrimer SAM to introduce a hard structure on the glass surface. Silica particle/dendrimer hybrids were prepared by the sol–gel reaction using G4.5 PAMAM dendrimers as a stabilizer, and then applied onto the APTES-glass surface (Scheme 1 (Method II)). The formation of the silica particle/dendrimer hybrids was confirmed by IR absorption spectroscopy, as shown in Fig. 3. The hybrids prepared at both acidic and basic conditions exhibit a new IR absorption band at 1085 cm^{-1} attributed to the Si–O–Si stretching vibration mode of a silanol bond, which is not observed in spectra of TEOS and dendrimer [5,6,12–14]. These results strongly indicate the formation of silica particle/dendrimer hybrid by using carboxyl-terminated G4.5 PAMAM dendrimers as a stabilizer.

The TEM images of silica particle/dendrimer hybrids prepared at basic and acidic conditions are shown in Fig. 4(1). It has been reported that the silica particles prepared by acidic- or basic-catalyzed sol–gel

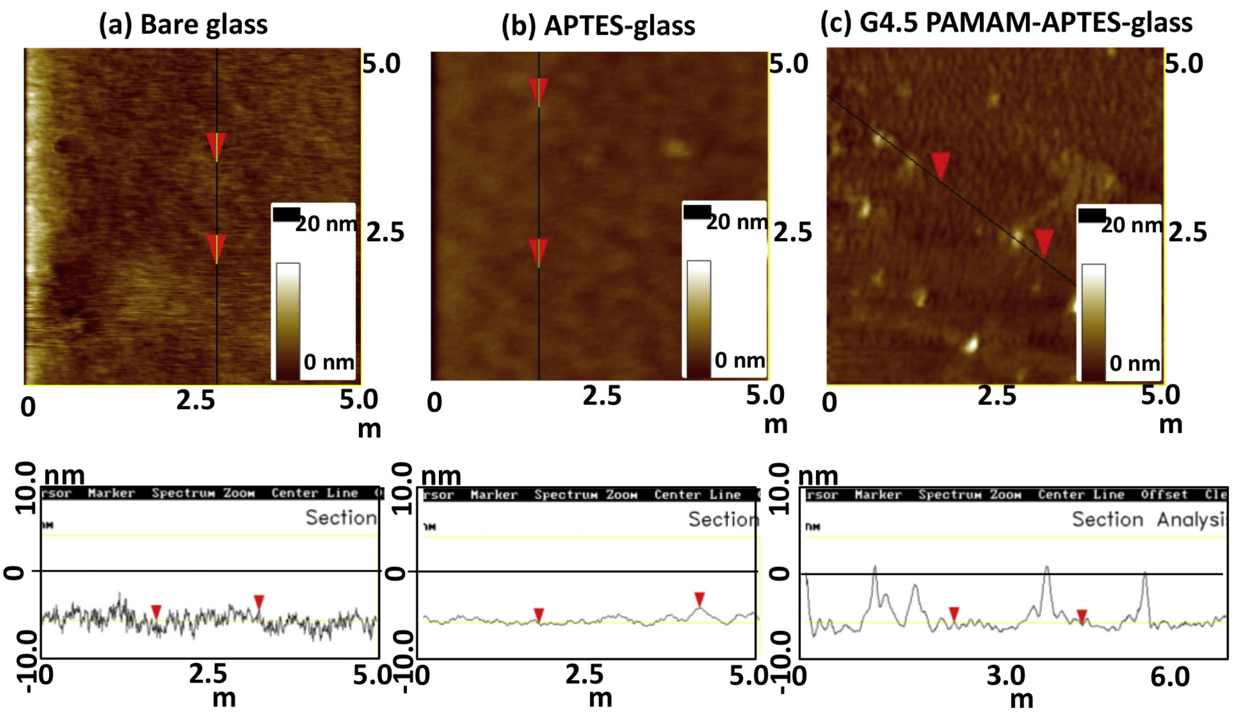


Fig. 2. AFM images of (a) bare glass, (b) APTES-glass and (c) G4.5 PAMAM-APTES-glass.

reaction are different in morphology and size [17]. Even for the present silica particle/dendrimer hybrids, their morphology and size depended on the pH. It was found that the silica particle/dendrimer hybrid obtained from the acid-catalyzed TEOS solution (pH ~ 2) may start from polymerization of TEOS into small spherical particles (2–3 nm), then such small particles were aggregated into larger particles (200–300 nm) and the aggregates were further agglomerated into condensed particles with a size larger than 1 μm. On the other hand, the size of the hybrid prepared under basic condition was also micrometer scale in size as well, but its density appears to rather homogeneous in a particle and lower than that of the hybrid prepared under acidic condition, since only small particles seem to be aggregated into larger particles. Synthesis of silica by the sol–gel process involves the formation of a colloidal suspension of siloxane groups (Si–O–Si) by the condensation reaction of silanol (Si–OH) with water. The presence of acid or base catalyst brings about a profoundly distinctive effect on the mechanism of the reaction and the final morphology of the silica particles [12,14].

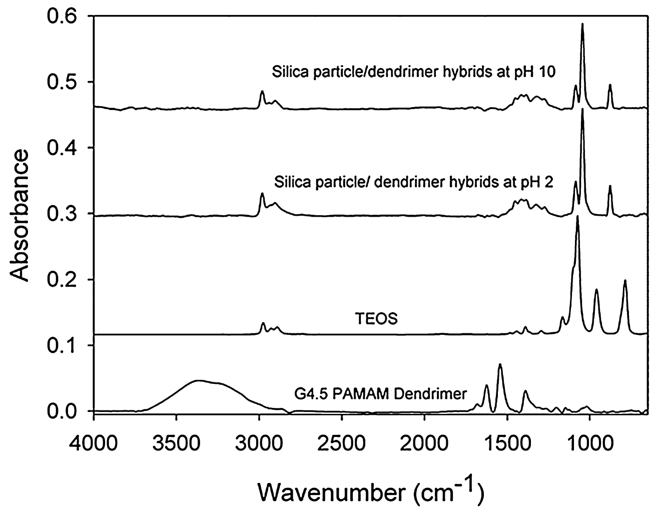


Fig. 3. FTIR spectra of silica particle/dendrimer hybrids at pH 2 and 10, G4.5 PAMAM dendrimer and TEOS.

The as-prepared silica particle/dendrimer hybrids were fabricated on APTES-glass by using a coupling agent to form an amide bonding between dendrimer in the hybrid and APTES on the glass. The fabrication was confirmed by AFM: Fig. 4(2) shows AFM images of the silica particle/G4.5 PAMAM dendrimers prepared at two pHs on APTES-glass. It was clearly seen that silica particle/dendrimer hybrids existed onto the APTES-glass surface. These observations indicate that the hybrids are successfully fabricated on the APTES-glass. AFM images elucidated that silica particle/dendrimer hybrid at pH 2 and 10 displayed height difference of 10–50 nm.

The surface of the porous structure with deep valleys could promote air trapping beneath the liquid drop and hence enhance hydrophobic and/or oleophobic performance [18]. It is also known that the water contact angle is extremely high on a bumpy structure, like the lotus leaf [19]. Fig. 4(2) shows that the fabrication of the silica particle/dendrimer hybrid provides the bumpy structure on the APTES-glass surface. The results from water contact angle in Fig. 6 revealed that the surface of the silica particle/dendrimer-APTES-glass (contact angle 60–64° for pH 2 and 10) were more hydrophobic than APTES-glass (contact angle 51°). In addition, it was also indicated from the contact angles with n-hexadecane (Fig. 5) that the surface properties of the silica particle/G4.5 PAMAM dendrimer hybrids on APTES-glass were highly oleophilic, since a drop of hexadecane immediately spread after dropping it on the surface. According to the water and hexadecane contact angles and AFM images, it can be suggested that the bumpy structure is one of the most important factors which affect the hydrophobicity of the surface.

In the present work, oleic acid was used to verify the anti-fingerprint properties of the modified glass surfaces, since the surface tension of oleic acid is 31.8 mJ/m^2 [20] which is in the range of human fingerprint of 20–50 mJ/m^2 [18]. The results of the contact angle with oleic acid (Fig. 5, contact angle 21–22°) defined

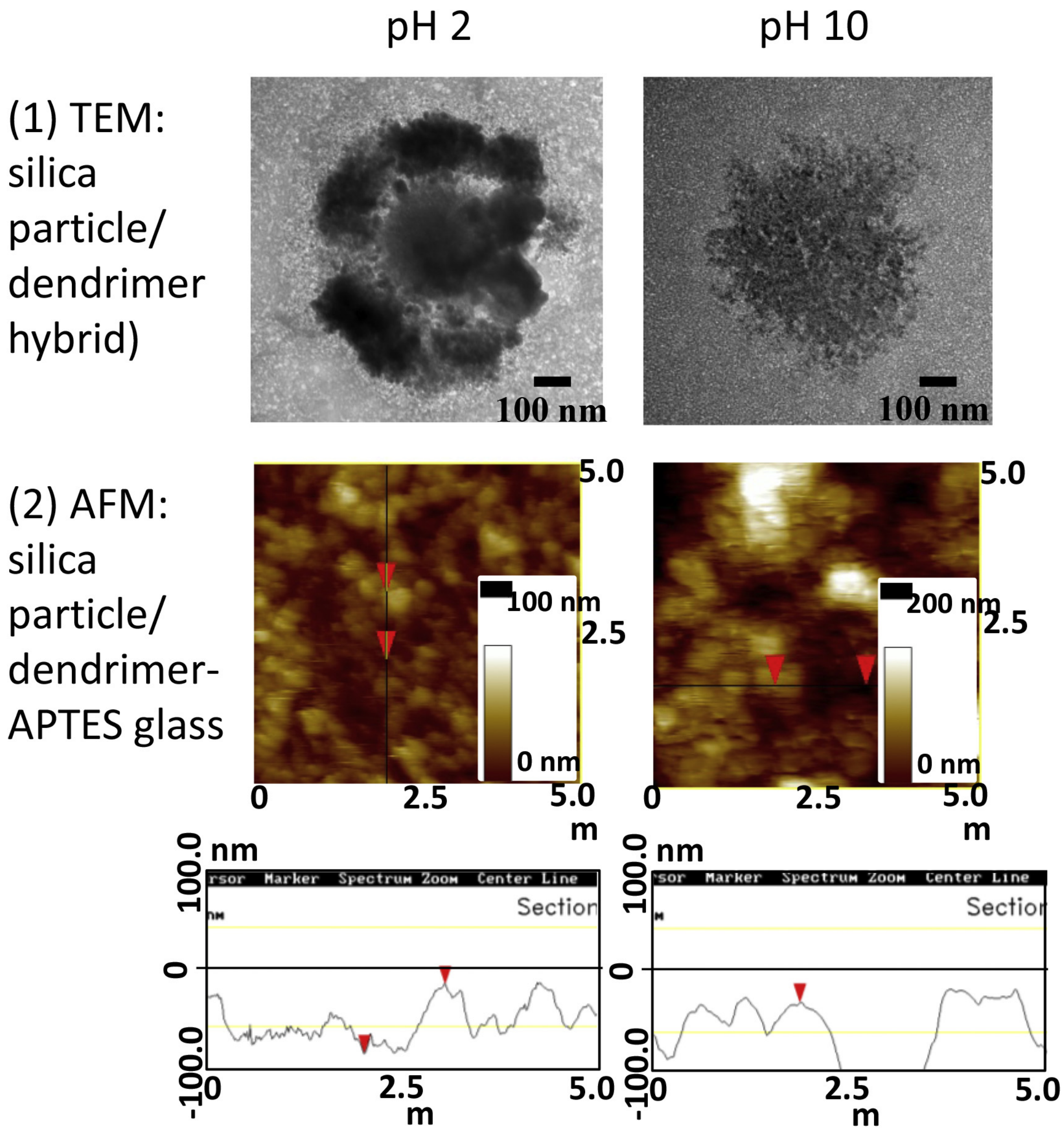


Fig. 4. (1) TEM images of silica particle/dendrimer hybrids and (2) AFM images of silica particle/dendrimer-APTES-glass at pH 2 and pH 10.

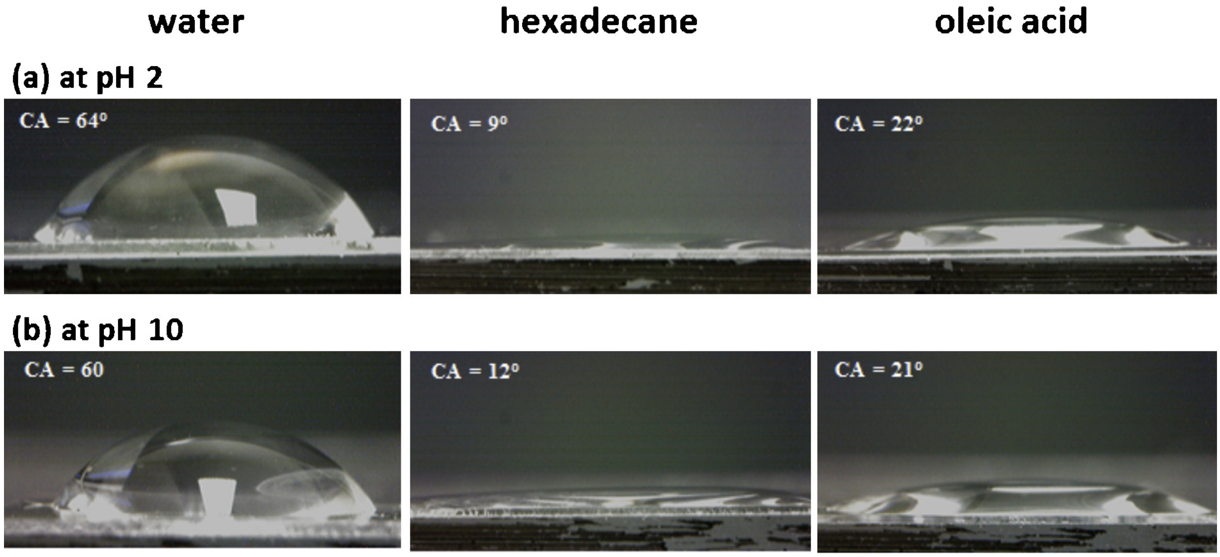


Fig. 5. Contact angles with water, n-hexadecane and oleic acid of silica particle/dendrimer-APTES-glass at (a) pH 2 and (b) pH 10.

that the surface of the silica particle/G4.5 PAMAM dendrimer hybrids on APTES-glass is repellent to oleic acid but the repelling ability is still weak. It can be suggested that the fabrication of the silica particle/dendrimer hybrids on APTES-glass could allow hydrophobicity but not enough anti-fingerprint property on the grass surface, despite of the bumpy structure (rough surface).

3.3. Silica particles on glass

The hard silica particles were directly attached on the glass surface through the acid-catalyzed sol–gel reaction to provide a bumpy structure. Stable siloxane (Si–O–Si) bonds were formed by the condensation of the silanol group from TEOS with hydroxyl group on the glass surface. Fig. 6(1) displays TEM images of silica particles in the sol–gel reaction solution at three different TEOS concentrations. The as-prepared silica particles were fairly uniform in size and shape. In addition, the sizes of the silica particles increased with TEOS concentration and were in the range of 3–10 nm. This is consistent with the report that with increase in the molar ratio of TEOS against base catalyst, the size of silica particles was increased [12].

The formation of silica particles on glass surface and the morphology of silica particle-modified glass surface were confirmed by AFM, as shown in Fig. 6(2). It was elucidated that silica particles were successfully formed on the glass surface and that silica particles were attached with the "bossy fine structure" on the glass surface. In addition, as the TEOS concentration increased up to 100 mM, more "bossy fine structure" of silica particles was inhomogeneously formed on the glass surface. The height of the boss fine structure was in the range of 10–50 nm and the size and the population of the silica particles increased with TEOS concentration, depending on the TEOS concentration.

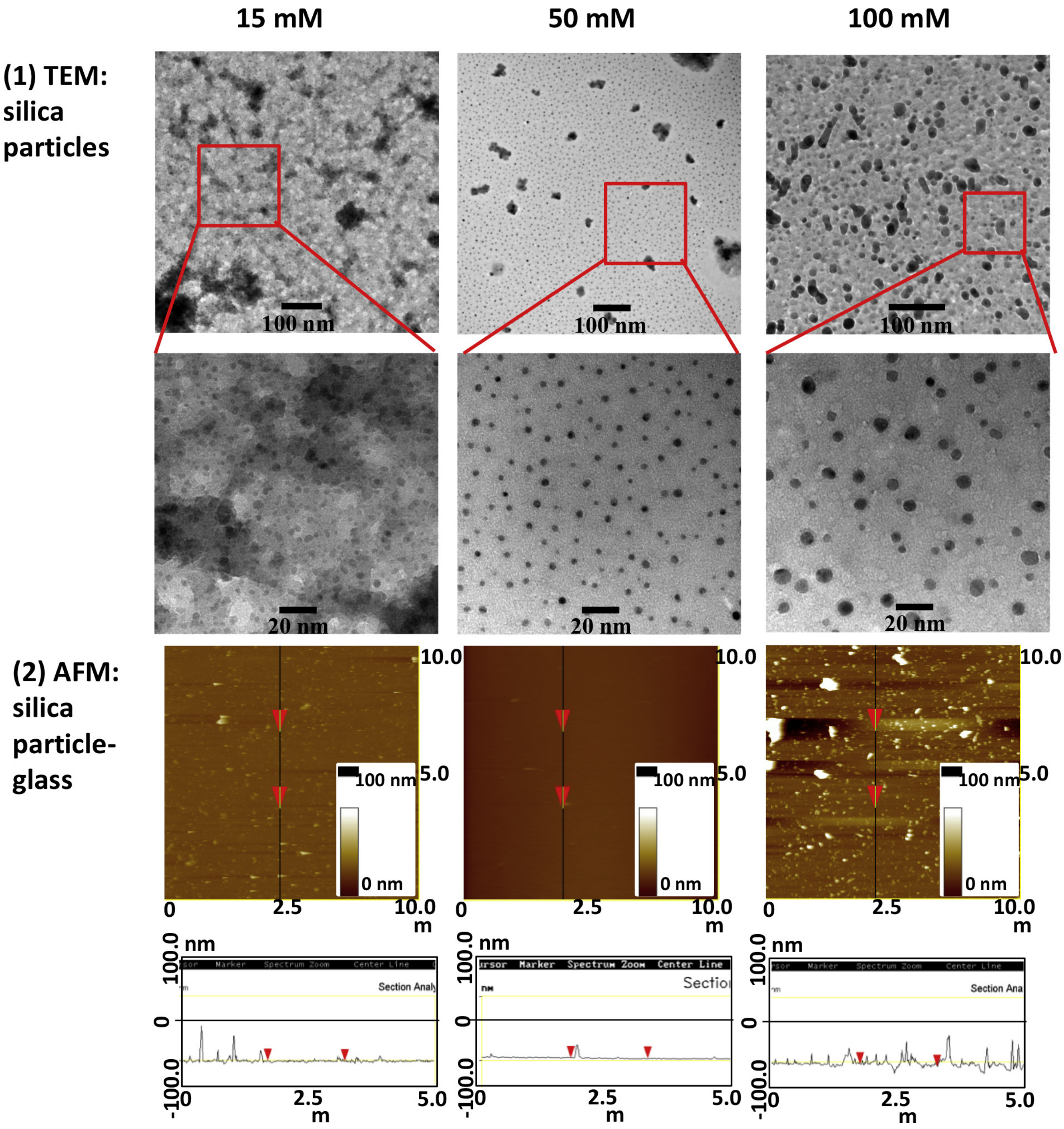


Fig. 6. (1) TEM images of silica particles and (2) AFM images of silica particle-glass at different TEOS concentrations of 15, 50 and 100 mM.

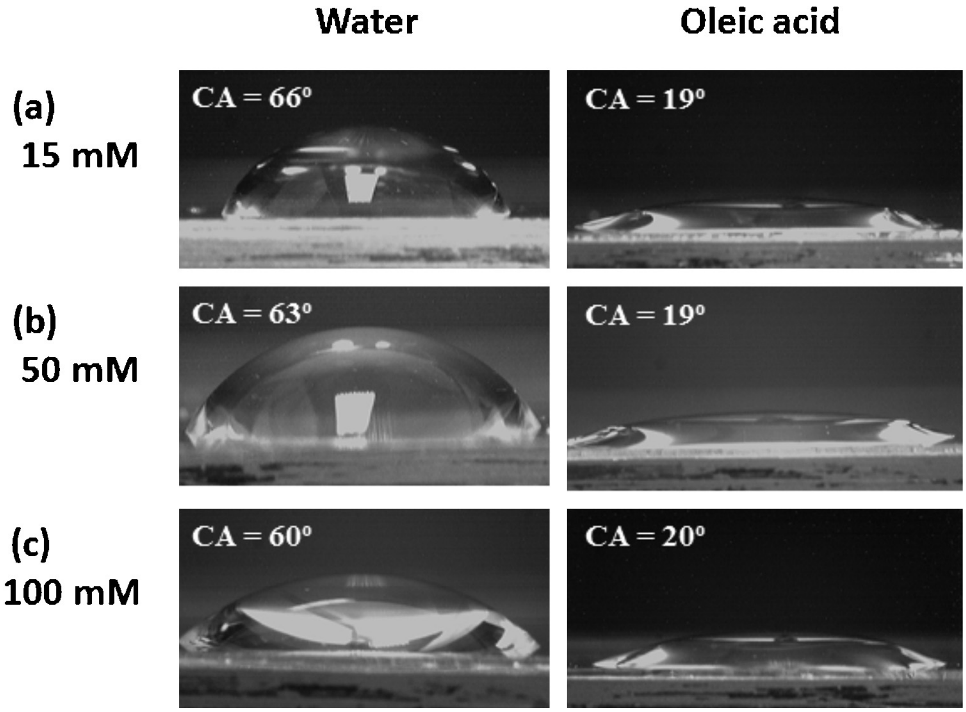


Fig. 7. Contact angles with water and oleic acid of silica particle-glass at different TEOS concentrations of (a) 15 mM, (b) 50 mM and (c) 100 mM.

Meanwhile, the water contact angle of the modified glass surface was high like 60–66°, although it slightly decreased with increasing the TEOS concentration, as shown in Fig. 7. This reveals a hydrophobic property of the surface, which is derived from a bossy fine structure of silica particle-glass surface. However, it is confirmed from the rather low contact angle with oleic acid (19–20°) that the silica particle-modified glass displays less repellent to oleic acid. It is obvious that the fabrication of the silica particles could impart hydrophobic property but not fingerprint free on the modified glass surface. In other words, it can be suggested that the in situ fabrication of silica particles provides "boss fine structure" on glass substrate, but this structure is unsatisfactory to provide enough anti-fingerprint effect on the modified glass surface.

3.4. Comparison among modified glass surfaces

The affinity of surfaces with water and hydrophobic liquids can be estimated from contact angle with a drop of such liquids. It is obviously seen in Table 1 that the hydrophobic (oleophilic) chemical species in periphery of the surface has the profound effect on the hydrophobic (oleophilic) properties of the surface. When the bare (hydrophilic) glass surface becomes hydrophobic after the surface modification by hydrophobic alkyl molecules, the water contact angle of bare-glass (37°) increases, as seen in R-NH-G4.5 PAMAM-APTES-glass (52–54°). The same tendency to oleophilicity is observed from hexadecane contact angle. However, it should be noted that the similar behavior toward hydrophobicity (oleophilicity) is obtained even for APTES-glass despite of hydrophilic amine terminal of APTES on the surface. The possible explanation is that amine terminals are turned to hydrophilic glass surface and make the interaction like hydrogen bonding and then alkyl moiety is exposed on the periphery. Another attention point is the peculiar surface behavior of G4.5 PAMAM-APTES-glass. The surface with hydrophilic amine periphery on G4.5 PAMAM-APTES-glass possesses oleophobicity (hexadecane contact angle = 18°) but hydrophobicity (water contact angle = 71°) at the same time. When the roughness of the surface is considered, this behavior can be explained: the affinity with water is affected by the surface roughness, although the affinity with hexadecane is not so influenced by it. This difference could come from the variation of the surface tension between water and hexadecane. The effect of roughness is investigated using the glass surface loaded silica particles. When silica particles are loaded on G4.5 PAMAM-APTES-glass or bare glass, the roughness is increased, and at the same time the water contact angle or hydrophobicity is increased as expected. Therefore, it can be remarked that the surface roughness plays

Table 1
Contact angles with water, n-hexadecane and oleic acid and roughnesses of various surfaces.

Method	Sample	Contact angle			Roughness (nm)
		Water	n-Hexadecane	Oleic acid	
I	Bare glass	37°	14°	18°	1–2
	APTES-glass	51°	0°	30°	1–4
	G4.5-APTES-glass	71°	18°	24°	1–7
	R-NH-APTES-glass	52–54°	8°	25–26°	–
II	Silica/DEN hybrid	60–64°	9–12°	21–22°	10–50
III	Silica	60–66°	–	19–20°	5–50

an important role on creating the hydrophobic property on the surface.

On the other hand, the contact angle with oleic acid can be regarded as a barometer of anti-fingerprint effect, but the relationship of oleic acid contact angle with other parameters cannot be confirmed, since the contact angle with oleic acid was 18° for hydrophilic bare glass, 19–22° for hydrophobic silica particle-loaded glass with rough surface, 21–26° for hydrophobic G4.5 PAMAM dendrimer-loaded glass, and 30° for APTES-glass (see Table 1). This indicates that the anti-fingerprint property is not directly relevant to the hydrophobicity, oleophobicity and moreover the surface roughness. It should be noticed that the targeted surfaces concerned in the present work are fabricated by nonfluorinated chemicals and the contact angle with oleic acid is at most 30°. Anti-fingerprint property may be related to the chemical species which is exposed in the periphery of the surface, since oleic acid is an amphiphilic chemical with hydrophobic oleyl moiety and hydrophilic carboxylic acid moiety. Therefore, further investigations should be required to elucidate the factors for controlling anti-fingerprint property and the chemical species for optimizing these factors to improve the anti-fingerprint ability on the surface.

4. Conclusions

Three kinds of ultrathin organic/inorganic composite films, that is, dendrimer SAMs, silica particle/dendrimer SAMs and silica particles were successfully fabricated on the glass surface by using facile techniques. A fabrication of dendrimer SAMs on the glass revealed a significant increase in surface hydrophobicity, although it did not provide enough roughness on the glass surface. In addition, it was found that the fabrication of the silica particle/dendrimer hybrids and silica particles allowed an increase in surface roughness besides surface hydrophobicity. The results from contact angle measurement with water and hexadecane indicated that the silica particle/dendrimer-APTES-glass and silica particle-glass had hydrophobic properties. Especially, the in situ fabrication of silica particles on glass surface is more preferable than the others, since this technique is simple and provides “boss fine structure”. Concerning anti-fingerprint property, contact angle with oleic acid was examined for differently modified glass surfaces. Anti-fingerprint property was not found any relation to hydrophobicity (oleophilicity) and/or surface roughness. APTES-glass, which possesses medium hydrophobicity and high oleophilicity, displayed higher anti-fingerprint ability. The chemical species which is exposed in the periphery of the surface and repel amphiphilic oleic acid must be further searched.

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