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SHORT COMMUNICATION

Preparation and properties of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric nanoparticles—A new approach to facile creation of a completely superhydrophobic coating surface with these nanoparticles

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Abstract Novel fluoroalkyl end-capped vinyltrimethoxysilane oligomeric nanoparticles were prepared by the hydrolysis of the corresponding oligomer under alkaline conditions. The size of fluorinated nanoparticles thus obtained is of submicrometer levels and is not sensitive to the refractive indices of a variety of solvents; however, the turbidity of the dispersed fluorinated nanoparticles is extremely sensitive to the refractive indices of these solvents. In particular, the solvents of which the refractive indices are from 1.378 to 1.408 were found to afford the transparent colorless dispersed particle solutions. More interestingly, the modified glass surface treated with fluorinated nanoparticles exhibited a completely superhydrophobic characteristic (a water contact angle: 180°) with a nonwetting property against water droplets.

Keywords Superhydrophobicity · Oleophobicity · Refractive index · Nanoparticle · Dispersibility · Surface modification · SEM · AFM

Introduction

Fluoroalkyl end-capped oligomers are attractive functional materials because they exhibit various unique properties such as high solubility, surface active properties, biological activities, and nanometer-size controlled self-assembled molecular aggregates that cannot be achieved by the corresponding nonfluorinated and randomly fluoroalkylated polymers [1–4]. From the developmental viewpoint of new fluorinated functional materials, it is of particular interest to explore new fluorinated polymer/silica nanocomposites that could exhibit improved properties superior to those of the parent polymers. In fact, considerable research effort has been hitherto devoted to organic/inorganic nanocomposites because of their potential application in a variety of fields such as inks, cosmetics, paints, adhesives, textiles, and electronics [5–9]. Very recently, we have succeeded in preparing new fluorinated polymer/silica nanocomposites possessing unique characteristics such as good thermal stability, surface active property, and good dispersibility in a variety of solvents imparted by both fluorine and silica nanoparticles by the use of fluoroalkyl end-capped oligomer as a key material [10–13]. In these fluoroalkyl end-capped oligomers, fluoroalkyl end-capped vinyltrimethoxysilane oligomers are in particular interest due to them exhibiting higher surface active characteristics compared to the traditional fluoroalkylated silane-coupling agents [R_F-$CH_2CH_2Si(OR)_3$; R_F = fluoroalkyl groups] [14]. From the applicable viewpoint of fluorinated oligomer/silica nanocomposites into a variety of fields, it is very important to prepare new fluoroalkyl end-capped vinyltrimethoxysilane oligomeric nanoparticles, including their application to the surface modification. In this paper, we would like to report the preparation of fluroalkyl end-capped vinyltrimethoxysilane oligomeric nanoparticles, with particular emphasis on the facile creation of a completely superhydrophobic coating surface by the use of these nanoparticles.

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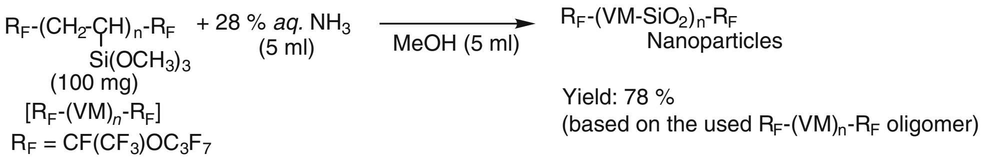
Scheme 1 Preparation of fluoroalkyl end-capped oligomeric nanoparticles



Experimental

Measurements

Fourier-transform infrared (FTIR) spectra were measured using Shimadzu FTIR-8400 FT-IR spectrophotometer (Kyoto, Japan). Dynamic light-scattering (DLS) measurements were measured using Otsuka Electronics DLS-7000HL (Tokyo, Japan). Scanning electron microscopy (SEM) images were measured by using JEOL JSM-5300 (Tokyo, Japan). The contact angles were measured by the use of Kyowa Interface Science Drop Master 300 (Saitama, Japan). Thermal analyses and atomic force microscope (AFM) were recorded on Bruker axs TG-DTA2000SA differential thermobalance (Kanagawa, Japan) and Keyence-VN8000 (Osaka, Japan), respectively.

Materials

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer was prepared by reaction of fluoroalkanoyl peroxide with the corresponding monomer according to our previously reported method [14].

Preparation of fluoralkyl end-capped oligomeric nanoparticles

A typical procedure for the preparation of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric nanoparticles is as follows: To a methanol solution (5 ml) containing fluoroalkyl end-capped vinyltrimethoxysilane oligomer [100 mg; R_F-[CH_2CHSi(OMe)$_3$]$_n$-R_F: R_F-(VM)$_n$-R_F; R_F = CF(CF_3)OC_3F_7; n=2–3], 28% aqueous ammonia solution (5 ml) was added. The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. After centrifugal separation of this solution, the obtained products were well washed with methanol and dried in vacuo to achieve the expected white powdery product (78 mg). The expected product [R_F-(VM-SiO_2)$_n$-R_F] thus obtained was subsequently characterized by the use of FTIR [ν/cm^{-1}: 1,335 (CF_3), 1,242 (CF_2), 1,065 (Si–O–Si)] (Scheme 1).

Surface modification of glass with R_F-(VM)$_n$-R_F oligomeric nanoparticles: [R_F-(VM-SiO_2)$_n$-R_F]

The methanol solution (10 ml) containing R_F-(VM)$_n$-R_F oligomer [R_F = CF(CF_3)OC_3F_7: 200 mg] and 28% aqueous

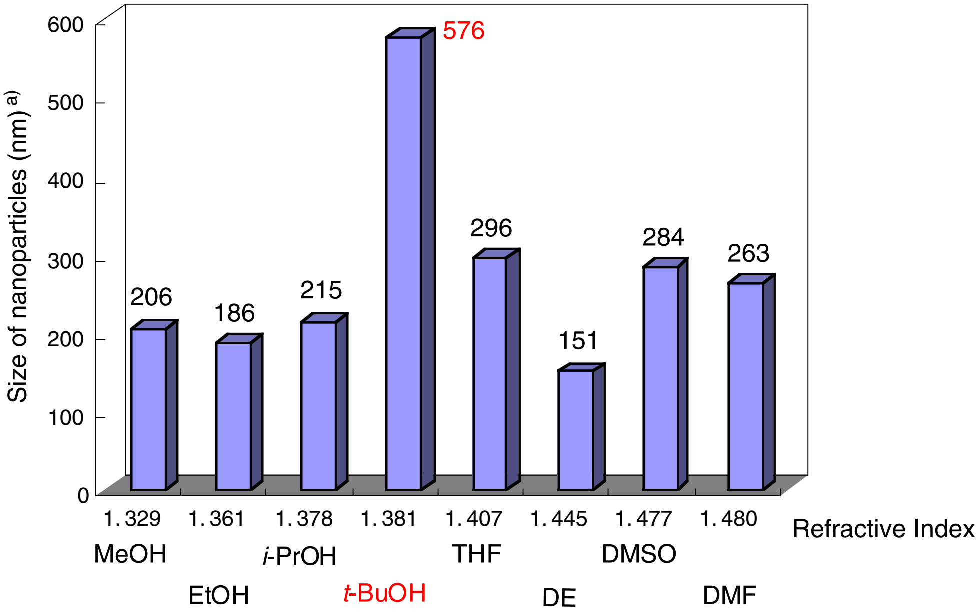


Fig. 1 Relationship between the size of R_F-(VM-SiO_2)$_n$-R_F nanoparticles (concentration of nanoparticles: 1 g/dm^3) and the refractive indices of a variety of solvents. *a* The size of R_F-(VM-SiO_2)$_n$-R_F nanoparticles was determined by dynamic light scattering measurements in each corresponding solvent

Fig. 2 Relationship between the turbidity (absorbance at 500 nm) of R_F-(VM-SiO_2)$_n$-R_F nanoparticles (concentration of nanoparticles: 1 g/dm^3) and the refractive indices of a variety of solvents

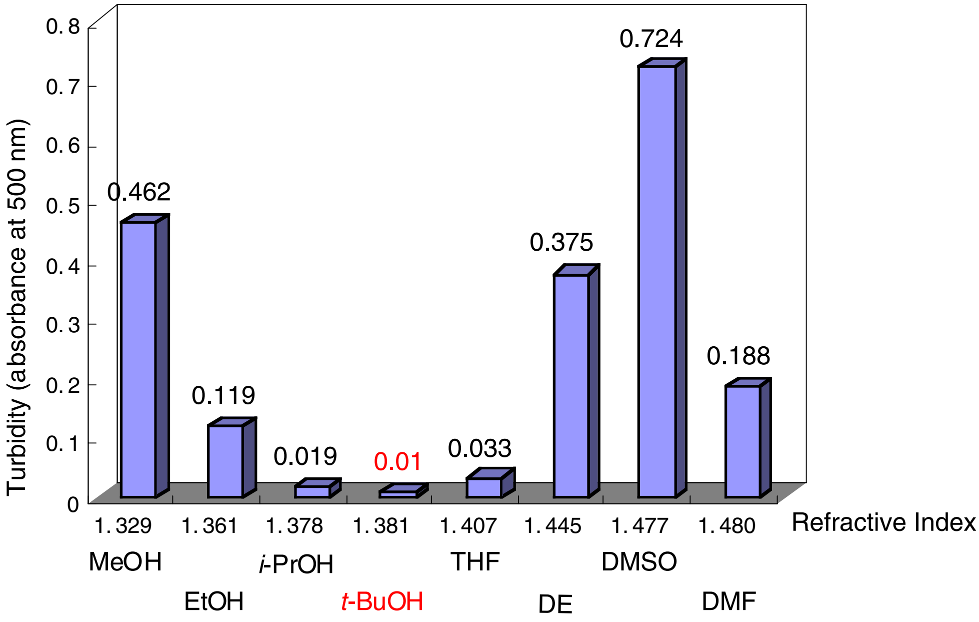


Fig. 3 Photograph of dispersed R_F-(VM-SiO_2)n-R_F nanoparticles (concentration of nanoparticles: 1 g/dm^3) in a variety of solvents

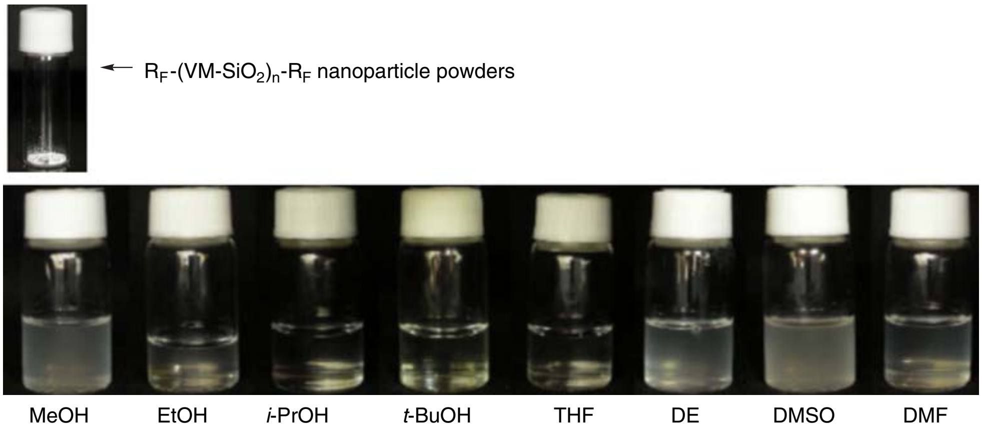


Table 1 Contact angles of dodecane and water on the modified glasses treated with R_F-(VM-SiO_2)n-R_F nanoparticles

Treatment conditions[a]	Contact angle (degree)	
	Dodecane	Water
Alkaline conditions	39	180
Acidic conditions	52	119

[a] See experimental part

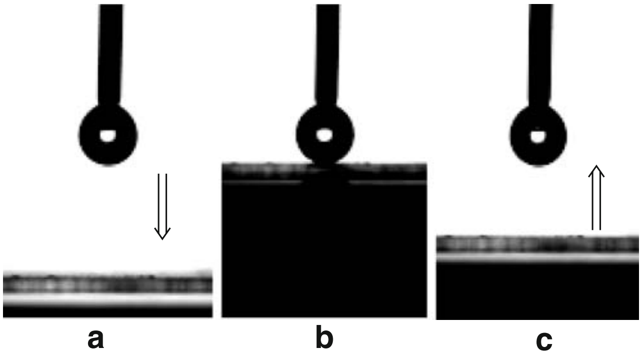


Fig. 4 Charge coupled device camera images of the water droplets: **a** water droplet that adhered to the needle tip (process before adhesion of the water droplet on the modified glass surface); **b** water droplet on the modified glass surface; **c** pull-up process of the needle from the modified glass surface

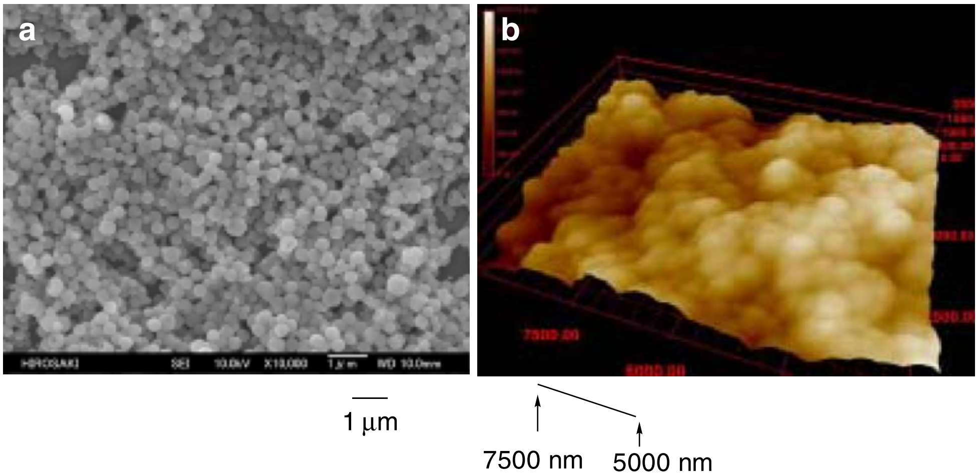


Fig. 5 SEM (**a**) and AFM topographic (**b**) images of the modified glass surface prepared under alkaline conditions

ammonia solution (5 ml) was stirred with a magnetic stirring bar at room temperature for 1 day. The glass plate (18×18 mm^2 pieces) was dipped into this methanol solution at room temperature and left for 1 min. This was lifted from the solution at a constant rate of 0.5 mm/min and subjected to the treatment for 1 day at room temperature; finally, it was dried in vacuo for 1 day at room temperature. After drying, the contact angles of water and dodecane for this glass plate were measured. Similarly, we prepared the sol solution by the use of 28% aqueous acetic acid solution (5 ml) instead of ammonia solution, and the glass plate was also modified by the use of this solution.

Results and discussion

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer suffered the hydrolysis under alkaline conditions to afford the corresponding fluorinated oligmeric nanaoparticles [R_F-(VM-SiO_2)$_n$-R_F] in good isolated yield: 78%.

The obtained R_F-(VM-SiO_2)$_n$-R_F nanoparticles have a good dispersibility in traditional organic solvents such as methanol, ethanol, *i*-propyl alcohol (*i*-PrOH), *t*-butyl alcohol (*t*-BuOH), tetrahydrofuran (THF), 1,2-dichloroethane, dimethyl sulfoxide, and *N*,*N*-dimethylformamide, except for water. We have measured the size of R_F-(VM-SiO_2)$_n$-R_F nanoparticles in these organic media by DLS measurements at 30 °C. These results are shown in Fig. 1.

As shown in Fig. 1, we could not obtain a good relationship between the size (151–576 nm: number-average diameter) of R_F-(VM-SiO_2)$_n$-R_F nanoparticles and the refractive indices of the solvents. However, the turbidity of the well-dispersed nanoparticle solutions is extremely sensitive to the refractive indices of these solvents, as shown in Fig. 2, and the effective decrease of turbidity was observed in *i*-PrOH, *t*-BuOH, and THF to afford the transparent colorless solutions. Especially, the lowest turbidity was observed in *t*-BuOH, indicating that the refractive index of our present fluorinated nanoparticle is around 1.38 (see Fig. 3).

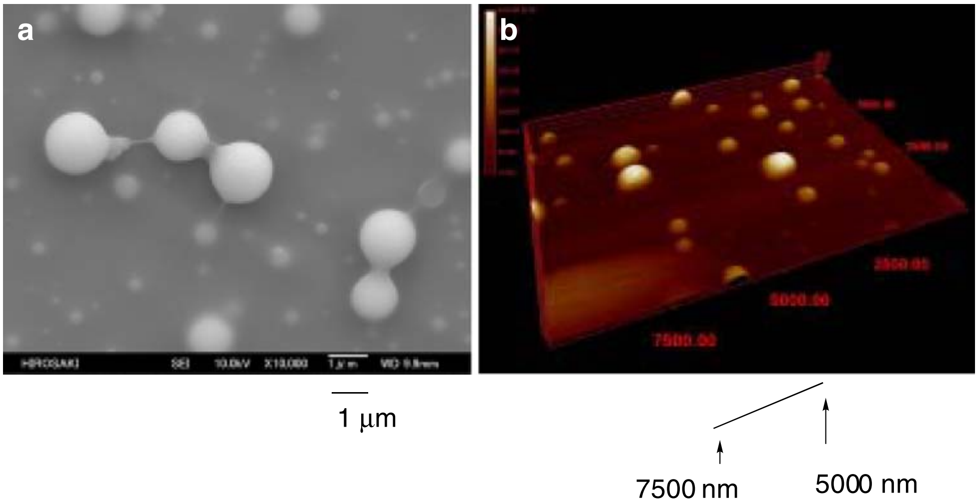


Fig. 6 SEM (**a**) and AFM topographic (**b**) images of the modified glass surface prepared under acidic conditions

In this way, our fluorinated oligomeric nanoparticles can afford a good dispersibility not only in organic solvents but also in transparent colorless solutions in *t*-BuOH, *i*-PrOH, and THF. Thus, it is of particular interest to apply our present fluorinated nanoparticles to the surface modification of glass. We have prepared the modified glass treated with R_F-(VM-SiO_2)$_n$-R_F nanoparticles, and the contact angles of dodecane and water on the modified glasses were measured. The contact angles of dodecane and water on the modified glass surfaces treated with R_F-(VM-SiO_2)$_n$-R_F nanoparticles are shown in Table 1.

As shown in Table 1, the contact angle of dodecane on each modified glass surface showed significantly large values: 39–52 degrees, which exhibit a good oleophobicity imparted by fluoroalkyl segments in nanoparticles on the modified glass surface, compared to that (0 degree) of the nontreated glass. Quite interestingly, we have succeeded in preparing the completely superhydrophobic coating surface, which can exhibit a water contact angle of 180° on the modified glass surface treated with the sol solution prepared by the hydrolysis of R_F-(VM)$_n$-R_F oligomer under alkaline conditions. Figure 4b shows the shape of water droplet on the surface. Unexpectedly, we could not deposit water droplets on this modified surface due to the extremely higher water contact angle: 180°. Thus, when we pulled up the needle in the contact angle measuring instruments from the modified surface, we could not get this modified surface wet in the water droplet, as shown in Fig. 4c.

Hitherto, it is well-known that superhydrophobic surfaces (a water contact angle greater than 150°) are fabricated by combining appropriate surface roughness with hydrophobic (low-surface-energy) materials (contact angle of water >90°) [15–27]. For example, Tsuji et al. reported the formation of a superhydrophobic fractal surface by the use of an alkylketene dimer [28, 29]. The topographic images of the modified glass surface illustrated in Fig. 4 were determined by AFM, and they are displayed in Fig. 5.

R_F-(VM-SiO_2)$_n$-R_F oligomeric nanoparticles are confined to a nanosized space on the surface, and fluoroalkyl groups in nanoparticles are located at a rough surface to decrease the surface free energy effectively (see Fig. 5b). In addition, Fig. 5a shows a typical SEM image of the substrate coated with well-dispersed R_F-(VM-SiO_2)-R_F nanoparicles with a mean diameter of 309 nm.

In contrast, a water contact angle of 119° was observed on the modified glass surface treated with the sol solutions prepared by the hydrolysis of R_F-(VM-Si)$_n$-R_F oligomer under acidic conditions. AFM and SEM images in Fig. 6 show that a fractal surface that exhibits superhydrophobic characteristics was not formed on this modified glass surface, and we could observe the relatively smooth surface with the formation of partially agglomerated R_F-(VM-SiO_2)$_n$-R_F particles. Especially, we failed to prepare very fine R_F-(VM-SiO_2)$_n$-R_F particles under acidic conditions. The formation of this smooth surface would afford a water contact angle value similar to that (108°) of poly (tetrafluoroethylene).

In conclusion, our new R_F-(VM-SiO_2)$_n$-R_F nanoparticles possessing a good dispersibility, which were prepared by the hydrolysis of the corresponding oligomer under alkaline conditions, were applied to the surface modification of glass. The modified glass surface with this nanoparticle was found to exhibit a completely superhydrophobic characteristic (a water contact angle of 180°). Therefore, we could not get this modified surface wet in the water droplet due to its completely superhydrophobic characteristic. We believe that this completely superhydrophobic characteristic is the first example on this modified glass surface. Further studies are actively in progress.

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