Full Length Article

Fabricating superhydrophobic and oleophobic surface with silica nanoparticles modified by silanes and environment-friendly fluorinated chemicals

Ying Cai, Jing Li, Lingmin Yi *, Xiaojie Yan, Jiawei Li

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China
Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China

A B S T R A C T

Fluorinated polymers or fluorinated chemicals are often used to enhance the hydrophobicity and oleophobicity of surfaces. In this work, amphiphobic coating surfaces of silica nanoparticles modified by methyltrimethoxysilane (MTMS), ethyltriethoxysilane (ETES) or/and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (HFOTES) were fabricated via a sol-gel process. The results demonstrated that the surface wettability of coatings was greatly influenced by the type of silanes which were used to modify silica, and superhydrophobic and oil-repellent coating surface was obtained by using silica co-modified by MTMS and HFOTES (MF-SiO$_2$). The water contact angles of dip-coated MF-SiO$_2$ coatings could reach to 150.2° with the lowest angle of water hysteresis (3.3°) among all samples. One reason was that the addition of MTMS changed the holes structures of F-SiO$_2$, and the co-modified surface of MF-SiO$_2$ formed the multi-scale rough structures. Moreover, the percentage of fluorine at the surfaces for sample MF-SiO$_2$ was greatly increased due to the packing of —CF$_3$ groups on surface. In other words, the addition of MTMS influenced the outmost layer of coating and changed the distribution of fluorinated chemical groups for sample MF-SiO$_2$. Therefore, the coating for sample MF-SiO$_2$ could exhibit superhydrophobic and oil-repellent properties owing to the multi-scale surface roughness as well as the packing of —CF$_3$ groups on the outmost layer of surface.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Superhydrophobic surfaces exhibiting static water contact angles (CA) greater than 150° and extremely low water contact angle hysteresis (CAH) have aroused worldwide interest during the past few years [1–4], which was due to their peculiar properties and potential applications including self-cleaning [5–7], oil-water separation [8,9], anti-icing [10], anti-bacteria [11], corrosion resistance [12,13], and so on. It was reported that a fluorinated compound could reduce the surface tension down to 6.7 mJ/m^2 when the surface was enriched with —CF$_3$ groups, which was considered to be the lowest surface free energy of any solid [14]. Recently, extensive research has been conducted to develop superhydrophobic surfaces with different precursor such as fluorinated alkylsilane (FAS) [15,16] and any other nonfluorinated co-precursors.

Unfortunately, some products of long perfluoroalkyl chain, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), have caused global ecosystem pollution [17,18]. It was reported that perfluorinated carboxylic and sulfonate containing chains of six or less perfluorinated carbon atoms had substantially shorter half-lives bio-accumulation in the human body and were less toxic than long perfluoroalkyl groups [18–23]. But poor dynamic water-repellent properties and nonpersistent low surface energy limited the use of those short fluorinated chain chemicals [20–23]. The conventional strategy employed to improve coating persistent low surface energy typically involved hydrolyzing n-alkyl silane and short chains FAS. For instance, Lakshmi et al. [24] reported a sol-gel process to fabricate superhydrophobic and oleophobic nanocomposite coatings by embedding silica nanoparticles in methyltriethoxysilane (MTES) and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane. Tang et al. [10] recently synthesized a new fluorinated silane (3-[(perfluorohexysulfonyl) amino]propyltriethoxysilane, HFTES) by the reaction of perfluorohexanesulfonyl

fluoride with γ-aminoproyltriethoxysilane. Furthermore, superhydrophobic surface with anti-icing performance sol-gel colloid coatings were prepared via hydrolytic condensation of nanosilica sol, MTES and HFTES. However, neither of the above mentioned work further discussed the effects of the n-alkyl silane on surface reorganization of the colloid films, which would change the surface wetting behavior.

According to the reports [21,22,25–27], n-alkyl chain compound has been widely used as a co-modified component to prepare fluorinated materials. The surface free energy, surface reorganization and wettability of fluorinated copolymer films was affected by the various lengths of hydrocarbon side [25–27]. It was reported that the synergistic effect of the side chains in fluoroalkyl acrylate and crystal hydrocarbon pedant groups in stearyl acrylate restricted the surface molecular motion and caused stable dynamic water repellency [21]. Nevertheless, the orientation of fluorine-containing segments on the solid surfaces faces a challenge of effective arrangement. Therefore, it is interesting to fabricate superhydrophobic surfaces by modifying silica nanoparticles via n-alkyl silane and short-chain FAS sol-gel process, and study the relationship among geometrical structure, chemical compositions and the surface wettability.

In this study, we describe a superhydrophobic surface with nanocomposite structure via a simple sol-gel process, which was prepared by modification of nano-silica sol with n-alkyl silane (methyltrimethoxysilane (MTMS), ethyltriethoxysilane (ETES)) and low surface energy 1H,1H,2H,2H-perfluorooctyltriethoxysilane(HFOTES) via hydrolysis-condensation reaction. And then, the structure and morphology of nanoparticles, the surface properties, morphologies and surface compositions of composite coatings were investigated by fourier-transform infrared (FTIR), transmission electron microscopy (TEM), contact angle measurements (CAM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) analysis. According to the results of these measurements, this work could provide a new strategy to control the orientation of fluorinated groups to fabricate hydrophobic or oleophobic surface with low surface free energy.

2. Experimental

2.1. Materials

Acidic nano-silica sol (R900, pH = 3, solid content 35 wt%, water dispersion solution) was purchased from Akzo Nobel Co., Ltd. The diameter of nano-silica sol, as determined by transmission electron microscopy, was about 25 nm. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (HFOTES, Harbin) was obtained from Xuejia Fluorine-silicon Chemical Co., Ltd. methyltrimethoxysilane (MTMS) and ethyltriethoxysilane (ETES) were purchased from Aldrich Chemical Co. Acetic acid (36–38% aqueous solution, Hangzhou Chemical Reagent Co., Ltd.), Diiodomethane (99%, Sigma-Aldrich Co., Ltd), salad oil (99%, Meryer Chemical Technology Co., Ltd.), formamide and absolute ethanol (99%, Tianjin Yongda Chemical Reagent Co., Ltd.) were used without further purification.

2.2. Synthesis of modified silica particles

At first, 3.0 g acetic acid solution was added in the mixed solution of H_2O (1.55 g) and absolute ethanol (6.20 g) with a mass ratio of 1:4 until the pH value was about 3. And then, MTMS, ETES or/ and HFOTES (1.75 g) was added to the solution and stirred constantly for 30 min. After this, a pre-hydrolysis solution of silane was obtained. Finally, the obtained pre-hydrolysis solution was dropwise added into the acidic nano-silica sol and stirred at 25 °C for 24 h. The weight percent of silane in modified silica was 10 wt%, and the silica modified by MTMS, ETES or HFOTES was labeled as $M-SiO_2$, $E-SiO_2$ or $F-SiO_2$. The silica modified by 5 wt% MTMS and 5 wt% HFOTES was labeled as $MF-SiO_2$, and the silica modified by 5 wt% ETES and 5 wt% HFOTES was named as $EF-SiO_2$. In comparison, the silica modified by only 5 wt% HFOTES was labeled as $F'-SiO_2$ and was prepared by the same procedure.

2.3. Preparation of organic-inorganic nanocomposite coatings

Aluminium plates or glass slides of 2 cm × 4 cm were used as film substrates. The surface of all substrates were ultrasonicated with acetone for 30 min in order to clean grease, and then rinsed by a large amount of distilled water after ultrasonicated about 30 min in ethanol. After this, the prepared solution of modified silica was spin-coated onto the aluminium substrates at room temperature using a spin coater. A rotational speed of 3000 rpm and a holding time of 1 min were chosen. For the dip-coating method, the modified silica solutions were aged at 45 °C for 6 h, and then dip-coated on glass slides. The samples were evaporated slowly overnights and then thermally treated at 150 °C for 12 h.

2.4. Characterization

2.4.1. Fourier-Transform Infrared (FTIR)
FTIR spectra of the modified silica were recorded on a Bruker Vertex 70 FTIR using the KBr tabletting method. The measurements were used to qualitatively study the functional groups grafted on the modified silica surfaces and were carried out in the range of 4000–400 cm^{-1}. Silica powder for detection was obtained by using centrifugation-redispersion elution cycles to remove unreacted silane coupling agent, and then allowed to dry under vacuum at 100 °C for 24 h after freeze-drying.

2.4.2. Dynamic Light Scattering (DLS)
The particle size and distribution of silica sol was analyzed by dynamic light scattering (Malvern Instruments Zetasizer Nanos-6, UK) at 25 °C using ethanol as the dispersant. The silica sol was highly diluted (c ≤ 0.1 wt%) and ultrasonicated before testing to prevent multiple scattering.

2.4.3. Transmission Electron Microscopy (TEM)
To visually observe the size and morphology of original and modified silica, a small drop of highly diluted sol solution with ethanol was drop-deposited onto a carbon-coated copper grid and dried under ambient conditions, and then analyzed by transmission electron microscopy (JSM-1200EX, JEOL, Japan) in conventional transmission mode using 80kVacceleration voltage.

2.4.4. Contact Angle Measurements (CAMs)
The surface wettability of the composite coatings was evaluated by contact angle goniometry using a DSA20 contact angle measurement device (Kruss, Germany) at room temperature and ambient humidity. The static CA was measured through the sessile drop method which all liquids were dropwise added to the coatings surface, and the contact angles were determined by the average of at least five measurements on different positions. The coatings for CAMs were prepared by spin or dip-coated on clean aluminium platesor glass slides from a concentration of 10% (w/w) in modified solution, and then annealed at 150 °C under vacuum over 12 h. Four liquids, de-ionized water (72.8 mN/m, 3.0 μL), formamide (58.0 mN/m, 2.6 μL), diiodomethane (50.8 mN/m, 0.8 μL), salad oil (33.0 mN/m, 2.4 μL) and mineral oil (28.9 mN/m, 2.4 μL) were used to determine the surface wettability of coatings. The contact angle hysteresis or roll-off angles of liquids on the surface of coatings were investigated by dynamic contact angle (DCA) measurements using the method as the literature [28]. After a liquid