



Synthesis of polymeric fluorinated sol–gel precursor for fabrication of superhydrophobic coating



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ABSTRACT

A fluorinated polymeric sol–gel precursor (PFT) is synthesized by copolymerization of 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate (FMA) and 3-methacryloxypropyltrimethoxysilane (TSMA) to replace the expensive long chain fluorinated alkylsilanes. The fluorinated silica sol is prepared by introducing PFT as co-precursor of tetraethyl orthosilicate (TEOS) in the sol–gel process with ammonium hydroxide as catalyst, which is then used to fabricate superhydrophobic coating on glass substrate through a simple dip-coating method. The effects of PFT concentrations on the chemical structure of the formed fluorinated silica, the surface chemical composition, surface morphology, wetting and self-cleaning properties of the resultant fluorinated silica coatings were studied by using X-ray powder diffraction (XRD), Fourier transform infrared spectrometer (FTIR), X-ray photoelectron spectrophotometer (XPS), scanning electron microscopy (SEM) and water contact angle measurements (WCA). The results show that the fluorinated silica sols are successfully obtained. The size and size distribution of the fluorinated silica particles are found greatly dependent on the concentration of PFT, which play a crucial role in the surface morphology of the corresponding fluorinated silica coatings. The suitable PFT concentration added in the sol–gel stage, i.e. for F-sol-1 and F-sol-2, is helpful to achieve both the low surface energy and multi-scaled microstructures, leading to the formation of the superhydrophobic coatings with bio-mimicking self-cleaning property similar to lotus leaves.

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1. Introduction

Super-hydrophobic surfaces inspired by the lotus effect have attracted tremendous attention in both fundamental research and practical applications due to their unique characteristics like self-cleaning [1,2], antifogging [3], anti-corrosion [4,5] and anti-icing [6–8]. On these surfaces, a sessile droplet shows apparent contact angle higher than 150° and a dynamic droplet does not stick to these surfaces [2]. Numerous studies attribute such wetting behavior to a combination of surface chemistry and surface roughness on multiple scales [9].

The roughness at two or more length scales is found to play a much more important role in the realization of superhydrophobicity [10–18]. The approaches that attempts to generate rough surfaces include sol–gel process [10,11], self-assembly technique [12,13], physical and chemical vapour deposition [14,15], lithographic patterning, chemical etching [16,17], anodic oxidation,

electrospinning [18,19], and so on. Most of these methods demonstrated require special or complicated equipment and rigorous experiment conditions, which are potentially costly and time-consuming for practical implementation in applications. In contrast, sol–gel process is considered as a convenient and economically favored strategy for up-scaling production of superhydrophobic surface due to its ability to engineer surface structure and roughness easily [20].

Typical roll-off superhydrophobic surfaces achieved based on sol–gel process generally involves separately making the topography at single or dual scale from the formation of silica nanoparticles, followed by applying a low surface energy coating on it [21,22]. Fluorinated alkylsilanes, especially the long-chain ones, such as perfluorooctyltrichlorosilane (PFOS) [23], dodecyl or octadecyltrichlorosilane (ODTS) [24], long-chain perfluoroalkyl-triethoxysilane (PFAS) [25], et al., are attractive to reduce the surface free energy (SFE) because of their particular characteristics provided by fluorine atoms. It is reported that a fluorinated compound can reduce the surface tension down to ~ 6.7 mN/m when the surface is enriched with $-\text{CF}_3$ groups, which is substantially smaller than that of water (~ 72.8 mN/m at room temperature) [26].

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However, these fluorinated alkylsilanes are very expensive, which greatly limits their wide applications in the industrial production.

To achieve the cost-efficient fabrication of superhydrophobic surfaces, a polymeric fluorinated sol-gel precursor, poly(dodecafluoroheptylmethacrylate-co-3-methacryloxypropyl-trimethoxysilane) (PFT) was designed and synthesized via solution polymerization by using dodecafluoroheptyl methacrylate (FMA) and 3-methacryloxypropyltrimethoxysilane (TSMa) as monomers, 2,2-azobisisobutyronitrile (AIBN) as initiator. A series of fluorinated silica sols were prepared through ammonium hydroxide catalyzed hydrolysis-condensation of the mixtures of tetraethyl orthosilicate (TEOS) and PFT. The superhydrophobic coatings on glass substrate were eventually fabricated through a simple dip-coating process followed by calcination at 110 °C for 2 h. The effects of PFT concentrations on the chemical structure of the formed fluorinated silica, the surface chemical composition, surface morphology, wetting property of the resultant fluorinated silica coatings were studied. The self-cleaning performance was also evaluated with black carbon as contaminated dust.

2. Materials and methods

2.1. Materials

2,3,4,5,5,5-Hexafluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate (FMA) was obtained from Xeogia Fluorine-Silicon Chemical Co. Ltd. (Harbin, China). 3-(Trimethoxysilyl)propyl methacrylate (TSMa) was purchased from Luosenbo Tech. Co. Ltd. (Xi'an, China). 2,2-Azobisisobutyronitrile (AIBN) was obtained from J&K Co. Ltd. (Qingdao, China). Tetrahydrofuran (THF), *n*-hexane and trichloromethane were dried and distilled over CaH₂. Tetraethoxysilane (TEOS) and ammonium hydroxide (25%) were commercially available and used without further purification.

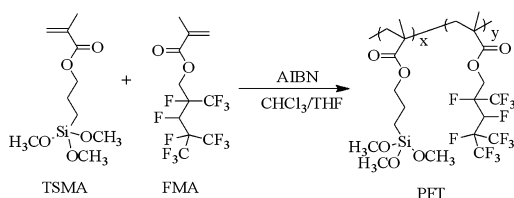
2.2. Synthesis of PFT

The random polymer PFT was prepared by conventional free radical copolymerization of FMA and TSMa. Briefly, 5.6 g (14 mmol) of FMA and 1.5 g (6 mmol) of TSMa were dissolved in 100 mL of mixed solvent consisting of tetrahydrofuran (THF) and chloroform (CHCl₃) with volumetric ratio of 1:1 under N₂. The copolymerization was initiated by AIBN (1.0 wt% of the total weight of the monomers) and reacted at 75 °C for 24 h. The resultant PFT was purified by co-precipitation method with *n*-hexane as precipitant and dried at 40 °C for 24 h under vacuum (Scheme 1).

2.3. Fabrication of superhydrophobic coatings by sol-gel process

In a typical procedure, glass substrate was ultra-sonicated in deionized water, 5wt% NaOH and ethanol for at least 30 min, respectively, then treated by oxygen plasma for 90 s (200 W, 30 Pa).

2.5 mL of ammonium hydroxide was slowly added into the mixture of 2.5 mL of TEOS and 50 mL of ethanol under vigorous magnetic stirring at room temperature. A fluorinated silica sol was prepared by subsequently dropping PFT solution (The formulation



Scheme 1. Synthesis of PFT.

was described in Table 2) into it and reacting for 2.5 h, which was then used to coat the clean glass slides via a simple dip-coating method. The wet coating was dried at room temperature and then heated at 110 °C for 2 h to remove residual solvent and solidify the coating. The corresponding fluorinated silica coatings were named according to the PFT concentration.

2.4. Characterization

The chemical structure of PFT was confirmed by proton and fluorine nuclear magnetic resonance (¹H NMR, AvanceIII 400, Bruker, Germany) using CDCl₃ as solvent and Fourier transform infrared spectrometer (FTIR, Tensor27, Bruker, Germany). The weight-averaged and number-averaged molecular weights (*M_w* and *M_n*, respectively) of PFT was determined by gel-permeation chromatography (GPC, Dionex Ultimate 3000, Dionex, America) with poly(methyl methacrylate) as standards and THF as mobile phase.

Surface elemental analysis of the resultant fluorinated silica coatings was carried out by X-ray photoelectron spectroscopy (XPS) (K-Alpha Thermo Electron Corporation, USA) with monochromatic Al K radiation (200 W, 12 kV, 1486.68 eV). The electron take-off angle from coatings was 90° from the surface. The vacuum in the spectrometer was kept at 10⁻⁷ Pa. Binding energies were calibrated relative to the C1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of the substrate. X-ray powder diffraction (XRD) was also recorded on a Bruker D8 Focus X-ray diffractometer using Cu Kα radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA.

The hydrophobicity of the fluorinated silica coatings was performed by using a video-based OCA 20 contact angle goniometer (Dataphysics, Germany) with a titling plate. All samples were measured with 5 μL of deionized water and repeated at least three times.

Scanning Electron Microscopy (SEM) images were obtained on a Quanta 600 FEG Field emission Scanning Electron Microscope (FEI, America). All samples were covered by an ultrathin layer of gold before SEM measurement.

3. Results and discussion

3.1. Characterization of polymeric sol-gel precursor PFT

To replace the expensive long chain fluoroalkylsilane (FAS) molecule as hydrophobic surface modifier, a polymeric sol-gel precursor PFT was designed and synthesized through free radical polymerization by using cheaper raw materials, 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate (FMA) (680 RMB/kg) and 3-(trimethoxysilyl)propyl methacrylate (TSMa), as monomers. A molar ratio of FMA and TSMa in feed as 70:30 was chosen to avoid the self-crosslinking reactions among methoxysilyl groups during the free radical polymerization. The chemical structure of PFT was characterized by FTIR, ¹H NMR and ¹⁹F NMR (Fig. 1). FTIR spectrum of PFT was shown in Fig. 1A. 2995 cm⁻¹ and 2954 cm⁻¹ were the characteristic stretching peaks of C-H (CH₃, CH₂). 2845 cm⁻¹ was assigned to the representative stretching vibration of C-H on Si-O-CH₃ group in TSMa unit [27]. 1750 cm⁻¹ was stretching vibration of C=O. 1238 cm⁻¹ and 706–675 cm⁻¹ were the stretching vibration and wagging vibrations of C-F bonds in FMA unit, respectively [28]. These results in combination with the disappearance of stretching vibration of C=C at 1635 cm⁻¹ indicated the successful copolymerization of FMA and TSMa. In the ¹H NMR spectrum of PFT (Fig. 1B), the peak at the chemical shift, δ of 3.59 ppm, originates from the hydrogen atoms on -Si(OCH₃)₃ moiety in TSMa unit. The peaks observed at

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