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Fabrication of a superamphiphobic coating by a simple and flexible method

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ABSTRACT

A facile and flexible method to prepare raspberry-like nanoparticles that can be used as a superamphiphobic coating is reported. Anatase TiO_2 nanoparticles were chosen as the core because of their irregular morphology and photocatalytic performance. Anatase TiO_2 nanoparticles were surrounded tightly by tiny functional fluoride–silica nanoparticles via the hydrolysis-condensation reaction of tetraethoxysilane and 1H, 1H, 2H, 2H-perfluorodecyl triethoxysilane. The obtained Si–F@TiO_2 nanoparticles can be sprayed or dipped directly onto various substrates. The coated film exhibited quite good liquid resistance, even when subjected to water jetting and sand abrasion. The photocatalytic effect of the coated anatase TiO_2 with respect to formaldehyde was also studied and discussed. This method will provide more opportunities and fast access to practical applications in surface, environmental, and energy engineering.

Introduction

Because of a combination of low-surface energy species and unique topographic features based on dual-size roughness, the surface of lotus leaves exhibits outstanding water repellent effects, known as the "lotus effect" (Jiang, Zhao, & Zhai, 2004; Jiang, Fang, Wang, Wang, & Ji, 2016; Marmur, 2004; Ming, Wu, van Benthem, & de With, 2005; Qian, Zhang, Song, & Liu, 2009; Yamamoto et al., 2015). In recent decades, inspired by the hierarchical morphology of the lotus leaf, many studies have been devoted to preparing superhydrophobic surfaces with multiple functions, including self-cleaning (Blossey, 2003; Lu, Sun, Chen, & Gao, 2017), anti-corrosion (Pan, Wang, Xiong, Deng, & Shi, 2016; Zhang, Xia, Kim, & Sun, 2012), anti-icing (Cao, Jones, Sikka, Wu, & Gao, 2009; Farhadi, Farzaneh, & Kulinich, 2011), and drag reduction (Venkateshan et al., 2016; Virk, 1975). In contrast to superhydrophobic surfaces, superamphiphobic surfaces extend these extreme anti-wetting properties to organic solvents, which have brought a much broader range of applications (Schlaich et al., 2016). However, fabrication of superamphiphobic surfaces is still an enormous challenge. The most commonly adopted method of fabricating superamphiphobic surfaces is the use of a rough surface structure, which is then decorated with low-surface energy materials. However, the established techniques for fabricating micro–nano-scale hybrid rough structures are complicated and costly; these include electrospinning (Ganesh et al., 2013), photolithography (Li et al., 2015), candle soot aggregation (Deng, Mammen, Butt, & Vollmer, 2012), and interfacial secondary growth (Tan et al., 2013). In addition, most techniques for fabricating superamphiphobic coatings rely on fairly specific substrate materials, such as metals (Gao, Qiu, et al., 2016; Li & Yu, 2016b), polymers (Fan et al., 2016; Wu et al., 2016), and glass (Lee, Kim, Lee, & Choi, 2013; Li, Zhang, Gao, & Wei, 2016). For instance, Li and Yu (2016a) fabricated a superamphiphobic ZnO film on an X90 pipeline steel surface via a combined approach using electrodeposition, hydrothermal treatment, and chemical modification. The contact angles of water and glycerol on this film were approximately 158° and 154°, respectively, and their sliding angles were <10°. Wong et al. (2016) created a superamphiphobic surface using a two-layer coating on a plastic sheet, demonstrated by a PMMA layer coated on a glass substrate. The PMMA sheet had superamphiphobic properties with high contact angles for water (154°), toluene (139°), and silicone oil (132°). The technologies mentioned above for fabricating superamphiphobic surfaces are limited and have a narrow application range because of their particular substrates. A practical, widespread, and more facile strategy to construct superamphiphobic layers on various substrates is still lacking and remains a challenge (Kim et al., 2016; Liang, Wang, Bao, & He, 2016).

The micro–nano structures of metals and oxide metals, such as TiO_2 (Lai et al., 2016), ZnO (Tao et al., 2013), and Ag (Gao, Gan, Xiao,

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Zhan, & Li, 2016), have broad applications in the fields of multifunctional materials, as well as distinct optoelectronic properties. In particular, TiO_2-based technologies have continued to mature and have attracted wide scientific attention for constructing novel nanostructured versatile surfaces in recent years. For instance, Lai et al. (2015) prepared multifunctional TiO_2-based particles and investigated the effect of fluorination degree and liquid surface tension on the wetting behavior. Chen, Guo, and Liu (2016) synthesized a superamphiphobic FOTS-TiO_2 powder with flower-like quasi-spherical structures, which can repel not only water but also various oils. However, the high-temperature conditions involved in the preparation process limit its large-scale application in industrial production.

In this study, we developed a simple and flexible method to prepare a superamphiphobic coating by constructing a Si–F@TiO_2 raspberry-like nanoparticle structure. An anatase TiO_2 nanoparticle was chosen as the central particle, and smaller Si–F nanoparticles was synthesized on the surface of TiO_2 nanoparticles via the hydrolysis-condensation reaction of tetraethoxysilane (TEOS) and 1H, 1H, 2H, 2H-perfluorodecyl triethoxysilane (HDFTES). The prepared coating also exhibited repellent effects for organic matter, such as ethylene glycol and toluene. Finally, because of the presence of titanium dioxide, the photocatalytic effect of the coating with respect to formaldehyde was also studied and discussed. The dispersions could be used to prepare superamphiphobic coatings on various substrates by spray-coating or dip-coating.

Experimental

Materials

TEOS was purchased from Pharm Chemical Reagent Co. (Shanghai, China). Ammonium hydroxide (NH_4OH) and ethanol were purchased from Sibo Pharm Chemical Reagent Co. (Nanjing, China). HDFTES ($C_{16}H_{19}F_{17}O_3Si$) was obtained from Ark (Fo Gang) Chemical Materials Co, Ltd. (Guangdong, China). TiO_2 (Titanium dioxide) (99.8%, anatase, hydrophilic) nanoparticles were purchased from Aladdin Industrial Co. (Shanghai, China). None of the reagents were subjected to further treatment.

Fabrication of F–Si@TiO_2 nanoparticle dispersion

First, a set amount of weighed anatase TiO_2 nanoparticles was dispersed into 80 mL of ethanol solvent as the central particles. Then, ammonia hydroxide (6 mL) and DI water (6 mL) were added and mixed by stirring at 1000 rpm at room temperature for 30 min, causing the nanoparticles to disperse evenly. Second, the packet particles were grown along the surface of the central particles. A set volume of a mixture of TEOS and HDFTES in a suitable ratio was added to the suspension while stirring for 36 h at room temperature to obtain the F–Si@TiO_2 structure. At the end of the reaction, the obtained mixture was kept in a sealed spray bottle before dip-coating.

Preparation of superamphiphobic film on various substrates by dip-coating

Various substrates were coated with the obtained dispersions by dip-coating. Afterward, the coated film was placed in oven at 60 °C to remove ethanol and water.

Characterization

Transmission electron microscopy (TEM) experiments were conducted on a Tecnai G20 electron microscope (FEI, USA) with an acceleration voltage of 200 kV. A total of 1 mL of the obtained sample was diluted with 30 mL of ethanol by stirring for 15 min. Then, the dilution was loaded onto a copper grid. The grid was allowed to air-dry for at least 15 min on a clean bench. The morphology of the sample surfaces was observed using field-emission scanning electron microscopy (SEM, Quanta 200, FEI, Holland) operated at 12.5 kV. The dispersion was sprayed onto a newly cleaved mica surface and dried in a dryer. The water and oil contact angles (CAs) were measured using a home-made contact angle goniometer in sessile drop mode at ambient temperature. The roll-off angle (RA) was obtained using a tilting stage method with a roll-off contact angle goniometer at ambient temperature. The volumes of the droplets used for the CA and RA measurements were 10 and 15 μL, respectively. For each sample, at least five tests were performed to obtain the average value at different locations. Optical properties of the material were characterized by UV–vis diffuse reflectance spectroscopy (UV–vis DRS, Beijing Purkinje TU-190, China) with an integrating sphere attachment, in which $BaSO_4$ was the reference. X-ray diffraction (XRD; Bruker D8 Advance, Germany) was employed to analyze the crystal structures of all samples by applying a graphite monochromator with Cu Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range from 5° to 80° and a position-sensitive detector using a step size of 0.021° and a scan rate of 41 min^{-1}.

Mechanical measurement of the coatings

Water resistance and sandpaper abrasion experiments were conducted. First, the coated film was placed at a 45° inclined angle and rinsed for 10 min using a water jet with variable pressure (10–90 kPa) (Verho et al., 2011). Second, spray adhesive was utilized to firmly bond the superamphiphobic coating onto hard glass substrates. The surface of the coated film was placed face-down on sandpaper and abraded under a pressure of a 100-g weight. A total of 10 cm of abrading along the longitudinal and transverse directions was defined as 1 cycle, and 20 cycles of mechanical abrasion tests were carried out on the coated film. CA and RA were measured after each cycle of abrasion (Su & Yao, 2014; Zhang et al., 2016).

Photocatalytic degradation of formaldehyde

The coated glass was immersed in an open beaker containing 15 mL of a formaldehyde solution of known concentration. The beaker was placed in a closed box with a UV lamp ($\lambda = 254$ nm). Under the irradiation of the ultraviolet lamp, 3 mL of formaldehyde solution was extracted to measure the change in the formaldehyde concentration using an acetyl acetone spectrophotometer every 12 h. The change in the concentration of formaldehyde solution against the radiation time was plotted.

Results and discussion

The mechanism of the reaction is shown in Fig. 1. Anatase TiO_2 nanoparticles were chosen as the core to obtain a coarse structure because of their unique shape and optical properties. Then, a mixture of a set ratio of TEOS and HDFTES was added to the TiO_2

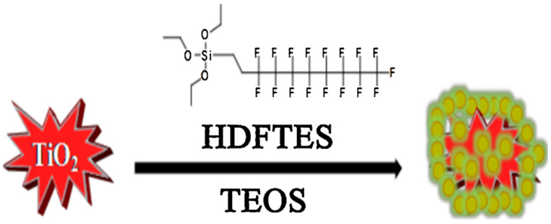

Fig. 1. Mechanism of Si–F@TiO_2 nanoparticle preparation.

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