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A facile and novel emulsion for efficient and convenient fabrication of durable superhydrophobic materials

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HIGHLIGHTS

- A novel emulsion similar to paint was synthesized for superhydrophobic materials.
- This emulsion demonstrated a great versatility in matrix and processing method.
- The prepared materials kept original superhydrophobicity after repeated abrasion.
- The resultant materials had high resistance to strong acid and alkaline corrosion.
- These superhydrophobic materials also demonstrated excellence in self-cleaning.

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ABSTRACT

There are significant challenges related to practical applications of superhydrophobic materials due to their limited durability, difficult processing conditions, and complicated synthesis procedures. In this study, a facile and novel emulsion composed of nanopartilcles (i.e. SiO_2 or TiO_2) and epoxy resin was synthesized to produce superhydrophobic surfaces using spraying, dipping and brushing methods, mimicking ordinary household paints. The obtained superhydrophobic materials had a water contact angle (CA) of ~152° and a sliding angle (SA) of ~6° at the room temperature. Interestingly, the emulsion demonstrated a great versatility for application in type of materials and application methods. The hierarchical surface structure fabricated by the emulsion was found to be independent of the substrate type and processing method, resulting in similar water repellent performance among all surfaces obtained. The superhydrophobic surfaces also exhibited excellent durability even after sustaining a series of mechanical damages including finger wiping, tape peeling and sandpaper abrasion. Moreover, they were able to maintain their superhydrophobic performance after immersion in aqueous solutions of pH ranging from 1 to 13 and boiling in water at 100 °C. This study shows that the novel emulsion can be used to fabrication of superhydrophobic surfaces using a one-step method that is green, versatile, scalable and independent of operator skill, special equipment, and the type of substrate. It has an excellent promise for real life applications.

1. Introduction

Control of the wettability of solid surface has attracted a great interest in many fields for decades [1–4]. As a representative inspired by the lotus in nature, superhydrophobic surfaces with water contact angle greater than 150 °and sliding angle less than 10 °exhibit preferable anti-wettability and is considered as promising candidates in areas such as anti-icing [5–9], anti-fogging [10], self-cleaning [11–15], oil/water separation [16,17], microfluidics [18], and biofouling [19,20]. Typically for achieving surface superhydrophobicity, it requires a low surface energy coating layer with appropriate micro/nanoscale surface roughness characteristics [21]. Some researchers have obtained superhydrophobic surfaces via methods, such as etching and electrospinning, that had more than two treatment steps [22–26]. It was also reported that the complex processing procedures were simpli-

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fied into one-step approaches [27–33]. Evidently, materials with superhydrophobic surfaces can largely prolong their service life and extend their applications. However, practical applications of superhydrophobic materials is still a challenge due to their lack of stability and durability in real-life performance [34,35].

Mechanical damage is a key factor responsible for the loss of superhydrophobicity of these materials in real-life applications. Three approaches including self-healing, self-regeneration, and bonding medium have been used to improve the durability of superhydrophobic surfaces. Self-healing ability can protect superhydrophobic surfaces via spontaneous restoration [36-39]. However, this restoration will be out of work when the healing agents exhausted after multiple damage-restoration processes. Furthermore, the healing behavior always depends on external stimuli, like UV irradiation, humidity that may result in complex operations with a high maintenance cost. For superhydrophobic coatings with an adequate thickness, their self-regeneration effect can sufficiently allow them to tolerate mechanical damages [40,41]. Owing to self-regeneration, a new superhydrophobic structure will be rebuilt and demonstrate similar superhydrophobicity when the top superhydrophobic layer is abraded or damaged. Unfortunately, the self-regeneration may loss after repeatable abrasions. As a result, the introduction of bonding medium is deemed to be a promising method to enhance the stability of superhydrophobic materials. As a low cost commercial adhesive, epoxy resin has been widely used to bond the superhydrophobic coatings with substrates tightly [37,42–46]. However, it is a great challenge to generate desired roughness as the epoxy resin can readily wrap nanoparticles. Xiu [43] coated the substrate with epoxy resin layer embedded with silica nanoparticles and obtained superhydrophobic materials after a plasma etching treatment of the top composite coatings to remove epoxy resin that coated on the nanoparticles. In order to get rid of the requirement for special equipment, Tu [41] pretreated the wood substrates with a layer of epoxy resin which initially dispersed in tetrahydrofuran. By means of repeated immersion and drying processes, the superhydrophobic structure was finally created on the epoxy resin layer using the mixed solution contained fluorinated alkylsilane (FAS) functionalized silica nanoparticles and only a small amount of epoxy resin. It was reported that the introduction of a small amount of epoxy resin enhanced the compatibility between the superhydrophobic structure and the substrate that was pre-coated with the epoxy resin layer, as well as it also avoided covering the nanoparticles completely. They obtained superhydrophobic materials with high mechanical stability in this method. However, the preparation process was still complicated and time-consuming even though the usage of specialized equipment was avoided.

More recently, a simplified approach that could enhance the durability of superhydrophobic materials using epoxy resin was reported. Si [44] firstly coated the substrate with epoxy resin layer via the casting method and then carefully covered the epoxy resin with stearic acid-$Mg(OH)_2$ powder(STA-MH) using a sieve. Finally, a durable superhydrophobic material with epoxy and STA-MH superhydrophobic coating was obtained using a process of only two steps. Simovich [45] reported a superhydrophobic resin coating with high mechanical stability via a one-step spraying method. The spraying composite solution was prepared by adding epoxy resin and silica nanoparticles into acetone and then stirring at ~70 °C for several hours. The glass slide was heated to 150 °C and then was intermittently sprayed with the composite solution. After cured at 130 °C for 24 h, the durable superhydrophobic glass was obtained. Zhang [46] prepared durable flowerlike ZnO/epoxy resin superhydrophobic coating via a simple immersion method. A ZnO/epoxy resin coating was firstly fabricated on metal substrate and then immersed in stearic acid to generated a desired roughness. After modification by acetic acid, a superhydrophobic coating was obtained.

Even though these studies have made good progresses in improving of durability of superhydrophobic materials, significant limitations and disadvantages still exist that include: 1) the need for toxic chemical reagents e.g., acetone, 2) the demand for energy due to long heating process, 3) the lack of systematical and comprehensive durability test data, 4) the process reliance on professional operators and drying equipment. As a result, there is a strong need to develop an efficient, green, safe, professional-independent method to prepare durable superhydrophobic materials.

Herein, a green, versatile, one-step method that is independent of operators, special equipment, and the type of substrate has been developed for obtaining durable superhydrophobic coatings at the room temperature. Specifically, an emulsion has been efficiently synthesized using nanoparticles (i.e. SiO_2 or TiO_2), PTES, waterborne epoxy and ethanol via a one-step method at the room temperature. The employment of waterborne epoxy resin helps the formation of homogeneous solution. The nanoparticles and the epoxy resin modified by PTES have low surface energy, effectively avoiding the nanoparticles to be fully covered by the epoxy resin. The balance between the amount of epoxy resin and the nanoparticles also ensures the optimum surface roughness and the bonding strength to be achieved, simultaneously. Ethanol serving as a solvent facilitates the as-prepared coating to be rapidly dried at room temperature. By simply spraying, brushing, dipping the synthesized emulsion, superhydrophobic surfaces can be easily created on different substrates without the need of any pretreatment process and the subsequent heating process. The flexibility in fabrication methods and simple operation conditions enable any non-skilled personal to rapidly and conveniently obtain different types of superhydrophobic materials using the emulsion, just like the usage of any ordinary house paints. Also, the emulsion can be stored for a long period of time by storing curing agent separately. As a result, the emulsion may be deemed as a type of paint that is mainly used to fabricate superhydrophobic surfaces and thus may be called as “superhydrophobic paint”.

In this study, the effect of process methods on the microstructure and wettability of the emulsion coated substrate surfaces has been thoroughly investigated. Moreover, the durability of the obtained superhydrophobic materials has been systematically and comprehensively evaluated via a series of performance tests e.g., sandpaper abrasion, knife scratches, tape stripping, and chemical corrosion. Furthermore, the superhydrophobic surface prepared on a large house wall with self-cleaning ability has been demonstrated. The application of the obtained superhydrophobic material in oil/water separation has also been explored.

2. Experimental section

2.1. Materials

The wood samples for this study were obtained from a Chinese fir grown in Guangzhou, Guangdong province, China. Filter paper was provided by Chuandong Chemical Industry Co., Ltd. (Chongqing, China). Glass was purchased from Shunhe Teaching Instrument Co., Ltd. (Jiangsu, China). Silica nanoparticles with a diameter of 15 nm were obtained from Aladdin (Shanghai, China). 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane ($C_8F_{13}H_4Si(OCH_2\text{-}CH_3)_3$, PTES) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Epoxy resin and curing agent (E-44) were purchased from Zhuoyue Chemical Reagent Co, Ltd (Yichun, China). Absolute ethanol was purchased from Ante Food Co, Ltd. (Anhui, China). All chemicals in the work were used as received without further purification.