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Ultrasonic atomization based fabrication of bio-inspired micro-nano-binary particles for superhydrophobic composite coatings with lotus/petal effect

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ABSTRACT

To mimic a superhydrophobic surface as found in nature, micro-nano binary surface structures with specific chemical properties are required. This type of special binary structure was usually realized by introduction of hierarchical inorganic microparticles; however, existing preparation methods are usually complex and difficult for scalable manufacture. In order to solve this problem, a facile ultrasonic atomization-based spray drying method has been developed in the present study for producing hierarchical silica microparticles for eventual fabrication of superhydrophobic coatings with either a lotus or petal effect depending on the required application. 3-aminopropyl-triethoxysilane (APTES) was used as a modifier for enhancing the binding between the silica nanoparticles. The hierarchical silica microparticles exhibited an diameter of around 10 μm and proper nano-roughness to realize a superhydrophobic effect. The prepared hierarchical silica microparticles/epoxy coating achieved a very high water contact angle up to 161° and a sliding angle as low as 5°. Both lotus and petal effects were achieved. Mechanical properties of the composite coating have also been enhanced by virtue of the modifiers. The interactions between $-NH_2$ groups from the APTES modifier and −OH groups from the silica led to a strong adhesive force with water molecules, while the introduction −F groups to the silica could reduce this affinity and result in a smaller sliding angle.

1. Introduction

Surfaces with a water contact angle greater than 150° are defined to be superhydrophobic [1–3]. A variety of superhydrophobic surfaces have been discovered in nature, such as plant leaves, insect wings and legs, among which two superhydrophobic states are observed in terms of lotus and petal effects [4–6]. These surface properties attribute to the combinational effect of both the micro-nano structure and the special chemical properties of the surfaces. The lotus effect, as observed in a lotus leaf, is characterized with a contact angle larger than 150°and a water sliding angle smaller than 10°, because water droplets are easily to roll off. Micro-sized papillae and cilium-like micro-nano structures with a mean diameter of ~7 μm are observed on the surfaces of lotus leaves, which are composed of wax like hydrophobic materials. The petal effect, as observed in the rose petal, is characterized with a contact angle greater than 150° and a high water sliding angle enabling water drops more likely to stick on its surface [6–10]. Hierarchical micropapillaes and nanorods with a mean diameter of ~10 μm are also observed on the surfaces of rose petals, which endow them with superhydrophobicity, but with have high water adhesion as reflected from a higher water sliding angle due to deficiency of hydrophobic materials. Superhydrophobic coatings on different substrates, especially on metals, have attracted substantial attentions for various applications, including self-cleaning, anti-fogging and anti-bacterial and anti-corrosion by virtues of their advantageous surface properties [11,12].

As inspired by these properties as observed in natural, both micro-nano hierarchical structure and special chemical properties are required for designing a superhydrophobic surface. Micro-

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nano-binary particles have been promising candidates to offer the required roughness for this type of the surface, because of their micro-nano dual-scale rough hierarchical morphologies [10,11,13,14]. Many artificial superhydrophobic surfaces have been fabricated with micro-nano binary particles and polymers through various methods such as self-assembly, emulsion polymerization and layer-by-layer method [15–22]. The self-assembly method [15,16] is generally based on a sol-gel reaction, but an extra surface modification process is also necessary. The emulsion polymerization [15,17] is characterized by distribution of inorganic particles on the surfaces of monomer emulsion droplets. However, the secondary structures of these particles are difficult to control precisely, because of their special requirements for a continuous and dispersed phase. For the layer-by-layer technique [16,18,19], the inorganic particles are deposited on selected templates, and a number of deposition cycles are required to obtain desired superhydrophobic effects. EI-Maiss et al. [20] developed superhydrophobic surfaces with both low and high water adhesion properties utilizing a mixture of monomers. Ke et al. [21] fabricated micro-sized and nano-sized silica particles filled polydimethylsiloxane superhydrophobic coatings with a maximum contact angle of 155° on a glass substrate by a two-step drop coating method. However, the complex procedures of these existing fabrication methods, such as multiple time-consuming preparation steps and harsh processing conditions, make them difficult for scale-up manufacture.

Spray drying technique has been widely adopted to manufacture particles in food, pharmaceutical and other industries owing to its simple, rapid and reliable processes, making it to be suitable for scalable manufacture [22]. The entire spray drying processes can be divided into three units: atomization, drying and particles collection. In the atomization unit, liquid phase is transformed into tiny droplets. These droplets are then conveyed to a drying chamber for solvent evaporation, which is known as the drying unit. In the particle collection unit, the dried solid particles are separated from the conveying air through collectors. In a conventional spray drying process, pressure based nozzles are applied for the atomization. However, the generated droplets were found to be heterogeneous. In order to solve this problem, ultrasonic atomization technique was introduced so as to produce uniform droplets from liquid phases by virtues of the capillary and cavitation effects of ultrasound [22–25]. Compared with the above-mentioned fabrication processes of inorganic particles for superhydrophic coating, this ultrasonic atomization based spray dying is advantageous because it is a rapid and scalable process. However, this process has rarely been applied on fabrication of hierarchical inorganic particles for superhydrophobic coatings, because proper designs on the material formulations as well as fabrication procedures are required.

Therefore, the present work is amongst the first attempt to design and fabricate micro-nano-binary hierarchical silica particles for superhydrophobic composite coatings using a facile and scalable ultrasonic atomization-based spray drying method. The micro-nano-binary hierarchical silica particles were designed to microparticles with nano-roughness realized through aggregation of surface modified silica nanoparticles. Epoxy resin was selected to be the polymer matrix of the superhydrophobic composite coating due to its favorable characteristics, such as excellent adhesion to metals, rapid curing ability and chemical resistance [26–28]. Two modifiers were also applied for functionalization of the silica nanoparticles with 3-aminopropyl-triethoxysilane and 1H,1H,2H,2H-perfluorooctyltriethoxysilane. Influences of the functional groups of the modifiers on the morphologies of the hierarchical silica particles were investigated. Performances and mechanical properties of the superdrophobic composite coatings on the stainless steel substrates were also evaluated.

2. Experimental

2.1. Materials

Silica nanoparticles (mean diameter: ~15 nm) were obtained from the Beijing DK nano technology Co., Ltd. 3-aminopropyltriethoxysilane (APTES) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFTES), serving as the modifiers for adjusting the surface chemical property of the microparticles, were purchased from the Sigma-Aldrich. Hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), ethanol and acetone were supplied by the Merk & Co. Distilled water was used in all experiments. Potassium Bromide was acquired from the Sinopharm Chemical Reagent Shanghai Co., Ltd. The stainless steel with a grade of 304 was supplied from the Hip Yick Industrial Co. Ltd.

2.2. Fabrication of superhydrophobic composite coatings on metal substrates

Entire fabrication process of the superhydrophobic composite coating can be divided into two parts: preparation of micro-nano-binary silica particles and composite coatings.

Preparation of the micro-nano binary silica particles were performed by the ultrasonic atomization based spray drying process. Briefly, 3.0 g silica nanoparticles were ultrasonically dispersed into 100 ml ethanol for 30 min. Acidity of this silica suspensions were adjusted to a pH value of 2.5 using 1.0 mol/L HCl solution. APTES (0.025mol) or a mixture of APTES (0.025mol)/PFTES (0.005mol) were added dropwise into the silica suspension under mild agitation for 24 h at ambient temperature. No modifier was added for control samples. Before transferring to spray drying process, pH value of the suspension was adjusted to 7.0 using NH_4OH solution. Spray drying of the as prepared suspension was performed by a tailor-made spray drying system (Shanghai Shunyi Tech. Co., Ltd, China) equipped with a 50 KHz ultrasonic nozzle as an atomization unit and a cyclone as a powder collecting unit. The operating parameters were set as follow: inlet drying air temperature:100 °C drying air flow rate: 175–200 L/h, feed rate of suspension: 50 ml/h. Hierarchical silica microparticles were obtained after the spray drying process, because the silica nanoparticles in each atomized droplets were agglomerated during evaporation of ethanol as shown in Fig. 1. Three types of hierarchical silica microparticles were prepared by adopting different modifiers: APTES/PFTES-modified, APTES-modified and non-modified particles. The modification scheme is shown in Fig. 2.

Preparation of the superhydrophobic composite coatings on stainless steel substrates was realized via a two-step coating process. The stainless steel substrates (4 cm × 4 cm) were firstly polished by 240- and 400-grit sand papers, and then ultrasonically cleaned in distilled water and rinsed with ethanol. Epoxy resin (4.0 mL) and epoxy hardener (2.0 mL) were added into 16 mL acetone and stirred for 30 min to form a homogeneous polymer solution. The pretreated steel substrates were dipped into this

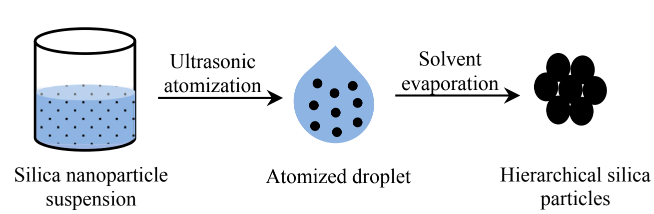

Fig. 1. Schematic formation of micro-nano-binary silica particles through ultrasonic atomization based spray drying process.