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Full Length Article

Gradient structure based dual-robust superhydrophobic surfaces with high-adhesive force

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ABSTRACT

Dual-robust (mechanical and chemical robust) superhydrophobic surfaces with a high adhesive state have aroused lots of attention for their potential application in liquid transportation, biochemical separation and in situ detection devices. Herein, we design a gradient structure based multi-scale micro- and nano-structures (inorganic-organic interpenetrating structures, self-similar sacrificial structures and micro-nano structures) to realize dual robust superhydrophobic surfaces by spraying method. Upon changing the fabrication process, three kinds of superhydrophobic surfaces were made based on benzoxazine, mesoporous SiO_2 and imidazole. A rigorous sandpaper abrasion test, chemical resistance test (pH = 1–14, 12 h) and anticorrosion test were carried out to exhibit the environmental stability of the system. High adhesive properties of surfaces were demonstrated by adhering water test. The clear multi-scale structures are showed and its relationship with properties is built. Scanning electron microscope was used to examine different structures and the gradient structure in system. The gradient structure based dual-robust superhydrophobic surfaces give a promising prospect for water transportation application in their large-scale and low-cost fabrication method and super mechanical and chemical robust.

1. Introduction

Superhydrophobic surfaces have been researched intensively due to their wide applications [1–3]. Recent development in liquid transportation [4,5], biochemical separation [6] and in situ detection [7], makes superhydrophobic surfaces with a high adhesion become a new focus. Until now, various such smart surfaces have been prepared inspired by natural [8-10], like gecko [11,12] and rose petals [13,14]. In spite of the progress achieved in high adhesive superhydrophobic surfaces, there are still a lot of fundamental problems that impede the real application, such as mechanical [13,15–17] and chemical robustness [18,19], fabrication issues (require special devices, complicated conditions, small substrate size, etc.) [20,21], large area manipulation capability [22], and so on. To find an ideal method to perform a large scale robust superhydrophobic surface with a high adhesive for liquid transportation, biochemical separation and so on is still a challenge task.

As known, superhydrophobic surfaces are based on unique hierarchical surface structure and low surface energy materials [13]. However, micro-nano structures are mechanically weak and low surface energy materials are chemically unstable. A number of efforts for making mechanically robust superhydrophobic surfaces have been devoted, such as wearable metal surface/mesh [23], polymer-nanomaterial composites [24], and deposition of low-energy materials on fabrics [25] or porous silica [26]. During the research process, novel structures include microflower/nanorod structures, micro-bowl and micro-lens structures, nanorods, cacti, and periodic microstructures are developed. However, almost all mentioned works above proposed methods still have some limitations, for example, complicated processing methods (template method, chemical vapor deposition, sol-gel, plasma treating and electrospinning), tedious chemical treatments, strict conditions, and sophisticated equipment, which making superhydrophobic surfaces are potentially costly and time-consuming for practical implementation in applications. So, designing new structures which are mechanical and chemical robust, used as smart function (e.g., high adhesive for liquid transportation), low cost and suitable for industry scale application are needed. Gradient structures have evolved over millions of years and make the biological systems strong and tough

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which are greatly superior to homogeneous microstructures [27]. For example, multilayer structures which made by inorganic-polymer composites showed exceptional mechanical properties [28–30]. Mizuki [31] designed a novel superhydrophobic coatings with gradient density by movable spray method which showed excellent mechanical durability. However, putting gradient structures into superhydrophobic surface are seldom reported, which may be caused by the complex processing and difficult control in gradient structures especially to form a gradient structure with micro-nano structure at the same time.

On the other hand, for making superhydrohpobic surface, different kinds of low surface energy materials are tried, including metal oxide [32], hydrogenated diamond [33], carbon nanotube [34], polyvinylidene fluoride [35], polytetrafluoroethylene [36], etc. Compared with inorganic materials, organic materials possess a higher adhesion on substrate which is more favorable in reality. However, organic materials, such as F-rich coatings (for example, polytetrafluoroethylene) may cause a serious environmental problem. Furthermore, most polymer networks (such as polyurethane [37], poly(methyl methacrylate) [38]) still cannot satisfy the requirement to mechanical and chemical robust. Benzoxazines, a novel class of phenolic resins, have been gained a lot of attention because of its attractive characteristics, including rich raw materials, small shrinkage during curing, low viscosity [39,40]. And corresponding polymers have excellent properties including low water absorption, high thermal stability, good mechanical properties and low surface energy, which make them to be a good candidate for using as a superhydrophobic surfaces material [41,42]. Most fascinating thing for benzoxazine to use as superhydrophobic surfaces is tuning ability between intra to intermolecular hydrogen bonds through UV exposure which can result changing from superhydrophobic to superhydrophophilic [42,43]. These unique properties give benzoxazine a wonderful prospect in using as superhydrophobic surfaces, especially in smart superhydrophobic surfaces, such as transport liquid. As a new kind of material, benzoxazine's usage in smart devices is still at initial stage.

In our previous research [44,45], novel superhydrophobic surfaces were built based on meso-porous SiO_2 and benzoxazine. The inorganic-organic interpenetrating structures, self-similar sacrificial structures and micro-nano structures not only gave a mechanical robust superhydrophobic surface, but also showed a bright prospect in application because of spray method using. Compared with meso-porous SiO_2/benzoxazine, improved mechanical properties can be obtained after adding imidazole into system. However, the reasons for improved mechanical properties had not been clearly illustrated even though possible gradient structures' formation had been proposed. Furthermore, chemical robust and other possible smart devices usage had not shown as a communication.

In this paper, we prepared superhydrophobic surfaces by tuning mixing styles of meso-porous SiO_2, benzoxazine and imidazole through spray coating. Three different superhydrophobic surfaces not only show mechanical and chemical robust, but also exhibit a high adhesive state, especially for the gradient structure-based system, which makes us believe it is the most applicable superhydrophobic surface until now. Our results indicate that mixing meso-porous SiO_2 and imidazole before mixing with benzoxazine can give most excellent mechanical and chemical robust superhydrophobic surface with a high adhesive state. The different thermal stabilities of surfaces illustrated the coexistences of two kinds of cured structures in benzoxazine/meso-porous SiO_2/imidazole. The density of cured polymers of BA-a and cured BA-a/imidazole (6 wt% imidazole) is 1.183 g/cm^3 and 1.189 g/cm^3, respectively, which showed possible formation of gradient structures. In meso-porous SiO_2/benzoxazine/imidazole system, gradient structures are successfully introduced and explained in superhydrophobic surfaces and clear correlations between morphology and properties are established.

2. Experimental section

2.1. Materials.

All the chemicals were used as received except mesoporous material (SBA-15), which was purchased from Nanjing Xianfeng Nanomaterials Technology Co., Ltd. (China) and calcination treatment at 400 °C for 2 h was done before using. Its pore size is 6–10 nm and the specific surface area is 550–600 m^2/g. Bisphenol A based benzoxazine (BA-a, mp: 113 °C) was synthesized and purified according to previously reported procedure [46]. Imidazole was kindly provided by Shanghai QianFeng Chemical Co., Ltd. (China). Tin plates were supplied by Hua Electronic Instrument Co., Ltd. Bisphenol A, aniline, aqueous formaldehyde solution and acetone were provided by Xinghua Chemical Reagents Corp. (China).

2.2. Sample preparation

Three different blends were made by solution blending. SBA-15/BA-a blend (S/B, weight ratio was 1:3), SBA-15/Imidazole/BA-a blend (S/M/B, weight ratio was 1:0.2:3) were prepared (materials added successively and stirring for one night) using acetone as a mutual solvent; For S(M)/B preparation, 1 g of SBA-15 was dispersed in water (concentration is 20 wt%) by stirring and 0.2 g imidozale was then added, and the mixture was dried at 70 °C in an oven for one night. After that, mixed SBA-15 and imidazole was put into BA-a (3 g) acetone solution (S(M)/B, weight ratio was 1:0.2:3).

The concentrations of all three different solutions were kept at 20 wt% and stirred for a whole night. During spray coating, the distance between the spray nozzle and the substrates was kept at 30 cm and a steady airflow was kept to get a uniform film on tin and glass substrates. All coatings cured at 120 °C for 2 h and 220 °C for 2 h to get superhydrophobic surfaces.

2.3. Sample characterization

The surface structures before and after abrasion were measured on a SU8010 field emission scanning electron microscope (FESEM). The surface topography and surface roughness was measured by a Brüker Contour GT-X optical profilometer. The BET test was examined by a JW-BK132F Autosorb gas sorption system, the sample weight was 0.3 g. Nano Measurer 1.2 software was used to get size statistics of the hole in surfaces, and at least ≥150 points were chose. Sandpaper abrasion test (based on literature[45] made by ourselves) and a high-frequency, linear-oscillation tribometer (GF-I High Temperature Reciprocating Friction And Wear Testing Machine, Lanzhou Zhongke Kaihua Technology Development Co.) were adopted to evaluate the mechanical robustness of surperhydrophobic surface. For abrasion test, the prepared surface was loaded with 200 g force, facing 120 grid SiC sandpaper as an abrading surface, and moved forward in one direction at a rate of 5 $cm\,s^{-1}$. The gravity of weight was calculated as 3.2 kPa (including weight of the sample). The tribometer was operated under a normal load of 30*g* for 5 mins with a 6 mm traverse length at a speed of 200 turn/min. Water contact angles (WCAs) were measured with a goniometer (KRÜSS DSA 20, Germany). Droplets of distilled water with a volume of 2–5 μL were placed gently onto the surface at room temperature and pressure. WCAs were measured five times at different locations. Cyclic voltammetry measurements were carried out with a VoltaLab-PST050 instrument using a saturated calomel electrode as the reference electrode and a carbon rod as the counter electrode. Electrochemical impedance spectroscopy (EIS) curves were recorded with an Auto Lab FRA2 instrument. After coating samples of $1 \times 1\ cm^2$ were soaked in 3.5% NaCl solution for 30 min, they were then electrochemically tested according to the ASTM D-4752 test. The density of cured polymers without meso-porous SiO_2 was measured based on ASTM D792 at 24 ± 1 °C. The chemical resistance of blended coatings