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A novel method for the fabrication of superhydrophobic nylon net

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HIGHLIGHTS

- This method utilizes adhesive solely to construct roughness on substrates.
- This approach is successfully applied to filter paper, fiberglass cloth and glass slide.
- The superhydrophobic nylon net maintained its water repellency even after 60 cycles of oil-water separation.

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ABSTRACT

In this study, we demonstrate a facile, cost-effective, and scalable method to fabricate superhydrophobic nylon net surface based on textured adhesive coating in combination with hydrophobization. The nylon net was immersed into an N-Methyl-2-pyrrolodone solution containing one-component polyurethane adhesive and then directly transferred into a glycerol aqueous solution to form a textured adhesive coating spontaneously. The silanization was further achieved through polar groups on the adhesive coating with alkylsilane compounds, forming self-assembled monolayers on the surface of nylon net. This resulted in our ability to tune the surface properties of the nylon net from being hydrophilic (18°) to superhydrophobic. The silanized adhesive coating endowed the nylon net with a water contact angle of 152° and a sliding angle less than 5°. When applied to oil-water separation, the superhydrophobic nylon mesh maintained its water repellency even after 60 cycles of oil-water separation and the separation efficiency (n-hexane) was over 95%. The method developed was also successfully applied to construct superhydrophobic filter paper, fiberglass cloth and glass slide. Moreover, this method can be simplified when applied to construct superhydrophobic filter paper. Therefore, this cost-effective, easily-operated and environment friendly method offers great technological promise in the field of constructing superhydrophobic coatings on a large scale.

1. introduction

It is well-known that the superhydrophobic property with water contact angle (WCA) greater than 150° and sliding angle (SA) less than 10° [1–3] has motivated enormous interest because of its potential value in practical application. There are many useful properties about superhydrophobic surfaces, such as oil-water separation [4–8], self-cleaning [9,10], anticorrosion [11], water repellency [12,13], mechanical robustness [14,15] and so on. The key point to fabricate superhydrophobic surface is the combination of micro-nano hierarchical structure with materials having low surface free energy [16,17]. Up to now, kinds of methods have been developed to construct superhydrophobic surface, such as layer-by-layer assembly [18,19], laser process [20,21], solution-immersion method [22,23], sol-gel technique [24,25], chemical etching [26,27], vapor deposition [28] and so forth. Nevertheless, some of the fabrication approaches are potentially costly, environmentally harmful and time-consuming in practical areas.

With the development of offshore oil exploitation, water pollution has been a major threat to ecosystem. Therefore, researchers keep a watch eye on oil-water separation materials to solve the problems of oil pollution. The separation materials for spilled oil disposal are being developed, such as activated carbon [29], separators [30], film membranes [31,32], porous materials [33], and waste barley straw [34]. However, because of some common weaknesses: high cost, non-renewable, time-consuming, low separation performance, new materials with high separating efficiency, inexpensive and reusable capacities are urgently needed.

In the new research, superhydrophobic surfaces have been designed with various properties such as low-cost, mechanical robustness, excellent separation performance and easy operation

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in terms of oil-water separation [35,36]. Wang et al. [37] manufactured superhydrophobic fabrics and sponges with nanocrystals and thiols, which presented excellent features in oil-water separation. Wu et al. [38] adopted a chemical vapor deposition method to bind Fe_3O_4 nanoparticles onto polyurethane sponge surface and then the sponge was modified by tetraethoxysilane. Finally, the superhydrophobic sponge was successfully used for oil absorption and oil-water separation.

In reality, most of studies utilize adhesives to bond substrates and inorganic particles together for constructing robust textured surfaces [39,40]. However, there were no reports on utilizing adhesive solely to construct roughness on substrates, which will be easier to texture surfaces and reduce particle pollutants remarkably. In this study, a kind of commercial adhesive (one-component PU) with waterproof and anti-corrosion properties was applied to create a textured coating on nylon net surface and then the as-prepared sample was modified by Octadecyltrichlorosilane (OTS) to decrease surface free energy. The alkylsilane covalently bonded to the nylon net surface for the reason that the as-prepared nylon net surface treated by one-component PU possessed many polar groups. This novel technology of preparing superhydrophobic surfaces more simple compared to those traditional methods [41] and is also economical practical owing to the accessible and low-cost materials. When applied to oil-water separation, the superhydrophobic nylon net showed excellent separation performance. Moreover, this method is successfully applied to filter paper, fiberglass cloth and glass slide.

2. Materials and method

2.1. Materials

One-component polyurethane (PU) was purchased from Shanghai Changcheng Fine chemistry Co., Ltd. N-Methyl-2-pyrrolodone (C_5H_9NO, NMP, Analytical reagent) was purchased from Tianjin Bodi Fine chemistry Co., Ltd. N-hexane was purchased from Tianjin Fuyu Co., Ltd. Octadecyltrichlorosilane (OTS) was provided by New Jersey. Glycerol was purchased from Tianjin Hengxing chemical manufacturing Co., Ltd. Sudan III was provided by Sinopharm Chemical Reagent Co., Ltd. Deionized water was self-made. Nylon net, glass side and fiberglass cloth were purchased locally. Filter paper was purchased from Hangzhou Special Paper Co., Ltd. All of the chemicals were used as received without further purification.

2.2. Synthesis of superhydrophobic nylon net

In order to obtain textured surface, nylon net samples were immersed into an N-Methyl-2-pyrrolodone solution with the solute one-component PU (5 g/L) for 2 h, and then it was taken out and suspended in air about 30 s before being immersed into a mixture of glycerol and deionized water (glycerol aqueous solution, 7/3, v/v). After 6 h, the nylon net was taken out and rinsed with abundant deionized water to remove surface impurity and then dried at 60 °C for 2 h. Finally the treated net was dipped into OTS/n-hexane (1%, v/v) for 2 h and subsequently the washed material was dried thoroughly to endow it with superhydrophobicity.

2.3. Characterization

The surface morphology was observed by a scanning electron microscopy (SEM, FEI QUANTA200) operating at 15 kV. A PicoPlus II AFM system from Molecular Imaging Inc. was used. AFM images were obtained at 512 × 512 resolution. The surface chemistry composition was investigated by Fourier transform infrared spectroscopy (FT-IR, Thermo Fisher Scientific, Nicolet 6700). For contact angles (CAs) measurements, 5 μL deionized water dropped on the surface of the sample at room temperature, which was detected on a contact angle meter (Hitachi, CA-A) in at least five different places of the surface.

2.4. Oil-water separation and stability experiment

Nylon net samples are 4 mm × 5 mm in size. An as-prepared nylon net covered the top of vial bottle. The separation method was to pass an immiscible mixture of n-hexane and water (1/1, v/v) through 80 mesh nylon net covering the bottle. The volumes of n-hexane before and after the Oil-water separation were measured as V_0 and V_1 by a graduated measuring glass cylinder with an accuracy of 0.1 ml respectively. The oil recovery efficiency is defined as Q (%) and calculated with Eq. (1):

$$Q = \frac{V_1}{V_0} \tag{1}$$

where V_0 is the initial volume of the n-hexane and V_1 is the final volume of the n-hexane.

Chemical durability and structural stability of nylon net was investigated to ensure its practical use. Chemical durability was assessed by measuring contact angle of the synthetically sample which had been immersed into aqueous solution with pH values range from 1 to 13 for 12 h. The structural stability of superhydrophobic product through cycling experiments of oil-water separation.

3. Results and discussion

3.1. Mechanism and surface morphology

The mechanism for the formation of a superhydrophobic coating on nylon cloth fiber is showed in Fig. 1. As shown in Fig. 1a: Firstly, when nylon net was immersed into a liquid mixture of one-component PU and NMP, it was coated with the mixture because of the capillarity of the net and the stickiness of the adhesive. Secondly, when the PU-treated nylon net was immersed into glycerin aqueous solution, the NMP solvent on nylon net surface was removed with water while the polymer gel particles grew up radially [42]. The chemical reaction was shown in Fig. 1b. Thirdly, two reactions simultaneously occurred in the third step: I) direct hydrogen bonding between the —Si—OH groups of the hydrolyzed silane and the —N—H groups on the coated fiber; II) condensation of the —Si—OH groups to form a siloxane polymer, which interact with N—H via hydrogen bonding. Finally, during the drying step, the —Si—O—Si— groups became bound to the fiber surface via a polycondensation.

Since isocyanate compounds in PU solution are sensible to water, it is easy to synthesize polyurethane in an organic system. Therefore, in this paper, one-component PU was firstly prepared in a NMP solution which was water-soluble and non-aqueous. And then the soaked nylon net was immersed into glycerin aqueous solution in order to obtain polymer gel particles. As shown in Fig. 1b, during the curing process, the reaction of isocyanate with water (main reaction) leads to the formation of urea with release of CO_2[43]. As Fig. 1b shows, the rate of the chemical reaction between one-component PU and deionized water is fast. Therefore, to obtain suitable surface morphology, the ratio of water in glycerin solution has to be well controlled. Glycerol, a kind of inert solvent for one-component PU, could reduce the rate of the chemical reaction between one-component PU and deionized water and affect the formation of the micro-nano particles.