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Micro–nano hierarchically structured nylon 6,6 surfaces with unique wettability

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ABSTRACT

A micro–nano hierarchically structured nylon 6,6 surface was easily fabricated by phase separation. Nylon 6,6 plate was swelled by formic acid and then immersed in a coagulate bath to precipitate. Micro particles with nano protrusions were generated and linked together covering over the surface. After dried up, the as-formed surface showed superhydrophilic ability. Inspired by lotus only employing 2-tier structure and ordinary plant wax to maintain superhydrophobicity, paraffin wax, a low surface energy material, was used to modify the hierarchically structured nylon 6,6 surface. The resultant surface had water contact angle (CA) of 155.2 ± 1.3° and a low sliding angle. The whole process was carried on under ambient condition and only need a few minutes.

1. Introduction

Immense attention has been given to surfaces with unique wetting phenomena in both the industry and scientific communities lately [1–11]. Water contact angle (CA) is used to characterize the wetting behavior of a water droplet on the solid substrate. Surfaces with CAs larger than 150° are commonly referred as superhydrophobic surfaces, while surfaces featuring CA lower than 10° are termed as superhydrophilic surfaces. In nature, a well-known example of superhydrophobic surface is the lotus leaf, which has micro-papilla covered with nano protrusions of waxy crystal. Water drops can bead up on a lotus leaf and roll off easily. This phenomenon has been named as the "lotus effect". It is a vivid illustration of the principle that the surface wettability is determined by both chemical composition and surface topography. When a material is defined, surface roughness can enhance the underlying wettability. On the other hand, for a certain micro structured substrate, surfaces possessing different chemical composition have dissimilar wetting phenomena. Because of the unique wetting behavior, both superhydrophobic and superhydrophilic surfaces are promising for many applications, such as self-cleaning articles [12–14], corrosion inhibition [15], drag reduction [16], microfluidic devices [17,18] and biological apparatus [19–23]. Up till now, numerous methods and techniques have been developed to produce surfaces with unique wettability [24–37]. In contrast to many multiple, time-consuming, chemically harsh processes, we now provide a facile way to fabricate micro–nano hierarchically structured superhydrophilic surfaces by phase separation. The whole process was carried out under ambient conditions in a short time, and can be used for large area fabrication.

Polyamide (PA), commonly known by its commercial name nylon, is one of the most popular engineering plastics and has a vast range of applications because of the excellent durability, chemical and abrasion resistance. Han et al. has reported reversible switching between superhydrophobic and superhydrophilic wettability could be achieved by biaxially extending and unloading an elastic polyamide film with triangular net-like structure [38]. Nylon 6,6, one of the most common commercial grades of nylon, is employed here to build a unique micro–nano hierarchical structure which can greatly enhance the wettability similarly to the lotus leaf. Based on the hydrophilic nature of nylon, the resulting surface is non-repellent to water. But after further surface modification with a low surface energy material, paraffin wax, the surface wettability was reversed to superhydrophobic. The process we use here can be applied to other hydrophilic polymers to produce superhydrophilic surfaces, thereby extending the use of such materials for super wetting applications.

2. Materials and methods

2.1. Materials

The nylon 6,6 boards provided by Badische Anilin und Soda Fabrik (BASF) were cut into small pieces about 1.1 × 1.1 cm in size and used without any other treatment. Formic acid (HCOOH ⩾ 88%) purchased from Xilong Chemical, ethanol, acetone, methanol and ethyl acetate of reagent grade purchased from Beijing

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Chemical Plants, and deionized water were used as received. Paraffin wax was purchased from Shanghai Paraffin Wax Company.

2.2. Preparation of nylon 6,6 surface with special wettabilities

The nylon board was coated by a layer of formic acid using a dropper and then left under ambient conditions to swell for 1 min. About 100 μL formic acid was coated on each piece of nylon board. Afterwards the board was immersed into ethanol bath, where the surface gradually turned white. After 1 min, the board was removed from the bath and dried under vacuum at room temperature for 12 h. The swelling–coagulating processes were carried on under different temperatures from 15 °C to 35 °C. For comparison, smooth nylon 6,6 board was cast with formic acid and left under ambient conditions letting the solvent evaporate completely. Hydrophobic surfaces were generated by putting the nylon plates in a Petri dish containing 0.8 mg/mL paraffin wax in ethyl ether. The Petri dish was half-sealed to make ethyl ether evaporate slowly. The evaporation of the solvent led to the formation of wax layer on the nylon surface.

2.3. Characterization

The surface microstructures were observed by field emission scanning electron microscopy (Hitachi, S-4300) operating at 15 kV. Contact angles were measured on a self-made instrument under ambient conditions by a sessile water drop method. Reported data are averages of five measurements at different places on the sample. For advancing and receding contact angle measurements, the volume of a water drop on the surface was increased and then decreased through a syringe and the whole process was recorded by a CCD at a speed of 25 frames per second. The crystal structure was examined by wide angle X-ray diffraction (Bruker D8 Discover-GADDS). Cu Kα radiation was used as the X-ray source, operated at 40 kV, 200 mA. X-ray were directly irradiated onto the nylon 6,6 board surface.

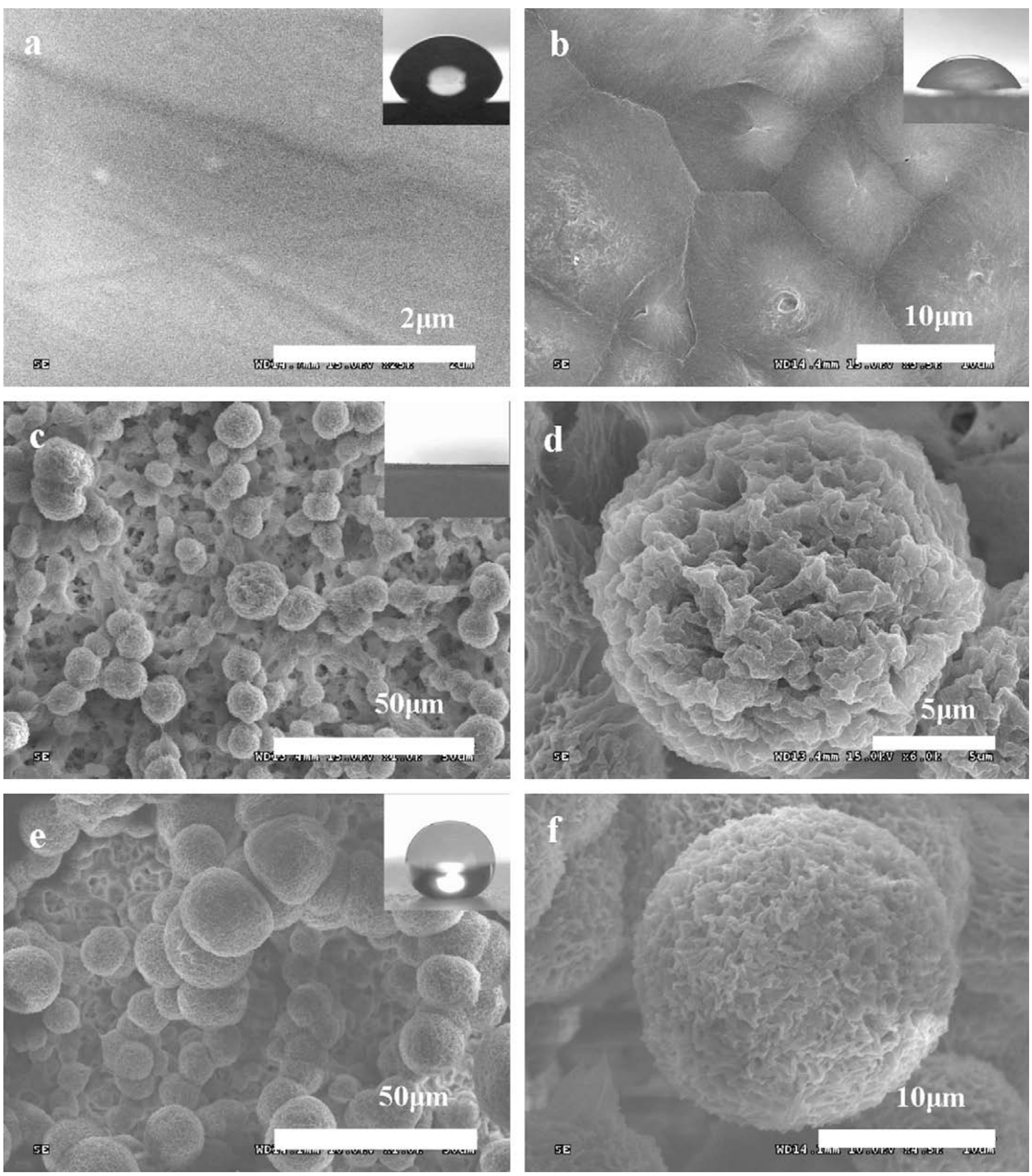

Fig. 1. SEM images of: (a) untreated smooth nylon 6,6 surface, (b) nylon 6,6 treated by formic acid and left evaporated under ambient condition, (c) hierarchically structured nylon 6,6 surface, (e) the hierarchical nylon surface modified by paraffin wax. (d) and (f) are high-magnification images of (c) and (e) respectively. The inserts are pictures of a 5 μL water drop placed on the corresponding surfaces.