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Designing transparent superamphiphobic coatings directed by carbon nanotubes

Xiaotao Zhu [a], Zhaozhu Zhang [a,*], Guina Ren [a,b], Xuehu Men [a,*], Bo Ge [a,b], Xiaoyan Zhou [a,b]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Tianshui Road 18th, Lanzhou 730000, PR China
[b] University of Chinese Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

Creating surfaces with superamphiphobic property and optical transparency simultaneously would have fundamental and practical significance but has been proven extremely challenging. Herein, we develop a transparent superamphiphobic coating using carbon nanotubes (CNTs) as the template by a facile approach. CNTs enwrapped with SiO_2 coating was produced by a sol–gel method and then sprayed onto the glass slides to form coatings. Subsequent thermal treatment and surface fluoration allowed the sprayed coating to exhibit enhanced transparency across a broad spectrum of ultraviolet and visible wavelengths and also display superrepellency toward water and a number of organic liquids, such as dodecane. The obtained transparent coating can sustain its superamphiphobicity even after thermal treatment at 400 °C. Separate experiment demonstrated that the CNTs-directed geometrical structure played a key role in establishing superamphiphobicity.

1. Introduction

There has recently been significant amount of research directed toward achieving superamphiphobic (namely superhydrophobic and superoleophobic) surfaces [1–8] due to their wide applicability in various fields, including the development of self-cleaning surfaces, liquid–liquid separation membranes, and anti-fouling materials [9–12]. For superamphiphobic surfaces use in applications of self-cleaning windows, optical devices, and solar panels, high optical transparency is additionally needed. However, producing transparent superamphiphobic surfaces has proved extremely challenging. The challenge results from the competitive relation between surface roughness and transparency and also the difficulty in producing superamphiphobic surfaces. Increasing surface roughness, which is an indispensable requirement for superamphiphobic establishment, often causes light scattering and thus makes the surface become translucent or even opaque [13,14]. Moreover, to design superamphiphobic surfaces, some special structures such as the re-entrant geometries or overhanging architectures have to be introduced into the surfaces [7,15–20], which poses another tough fabrication challenge. Thus, despite various types of transparent superhydrophobic surfaces [21–23], transparent superamphiphobic surfaces are extremely rare. Until recently, Zhang and Seeger developed transparent superoleophobic surfaces by combination of versatile organosilanes in a grow-from method [24]. Vollmer et al. reported a transparent superamphiphobic coating using candle soot as the template [25]. Nair et al. developed electrospun SiO_2 nanofibers as template to produce a transparent superamphiphobic coating [26]. However, the optical transparency of these obtained coatings is relatively limited or the fabrication process is laborious, and thus many aspects of transparent superamphiphobic coating have still to be explored.

In this study, we for the first time demonstrated that roughed surface texture directed by pristine CNTs, in conjunction with the low surface energy of fluorinated silane, can be used to produce transparent superamphiphobic coatings, and the designing strategy was shown in Fig. 1a. We firstly coated carbon nanotubes (CNTs) with SiO_2 by a sol–gel approach and used it to form coatings by spray coating. The sprayed coating became transparent toward a broad spectrum of ultraviolet and visible wavelengths after thermal treatment. Subsequent surface fluoration allowed this transparent coating to exhibit superrepellent toward water and numbers of extremely low surface tension liquids, such as dodecane (γ_{lv} = 25.3 mN/m). We also investigated the effect of pure SiO_2-directed and carbon black-directed geometrical structure on surface wettability, and such information allowed us to engineer coatings with specific liquid-repellency behavior.

* Corresponding authors. Fax: +86 931 4968098.
E-mail addresses: zzzhang@licp.cas.cn (Z. Zhang), xhmen@licp.cas.cn (X. Men).

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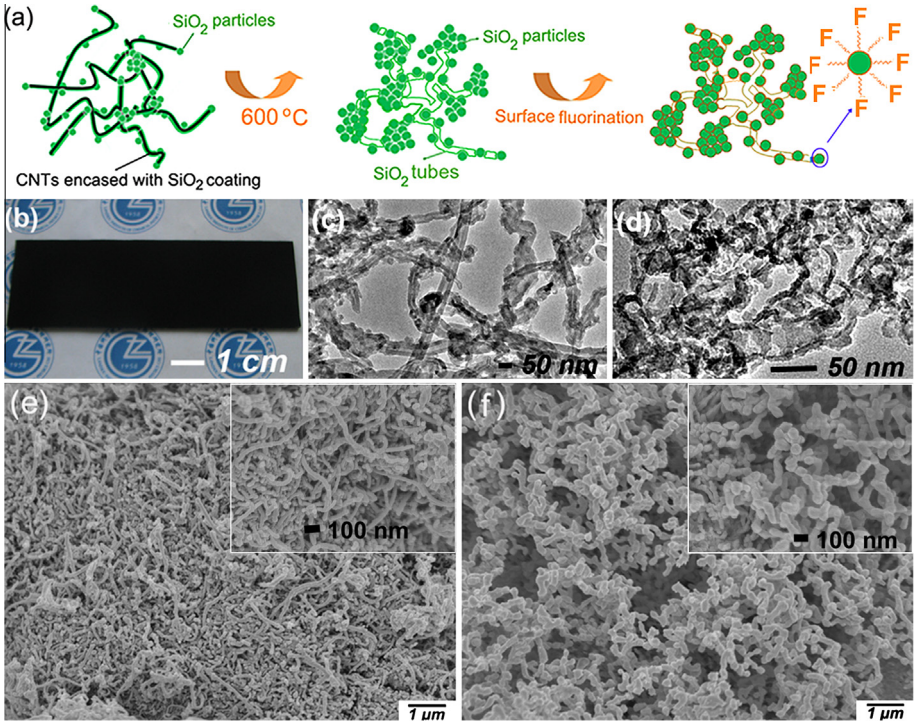

Fig. 1. (a) Schematic diagram illustrating the fabrication procedure of the transparent superamphiphobic coating; (b) digital image of the CNTs–SiO_2 coating sprayed onto glass slide; TEM images of the sprayed CNTS–SiO_2 coating before (c) and after (d) thermal treatment; FESEM images of the sprayed CNTS–SiO_2 coating before (e) and after (f) thermal treatment.

2. Materials and methods

2.1. Materials

Pristine multiwalled CNTs with a diameter of 30–50 nm and a length of about 30 μm were purchased from Chengdu Organic Chemicals Co., Ltd., China (synthesized by a CVD process; purity >99.9%). Trichloro(1H,1H,2H,2H-perfluorooctyl)silane and tetraethyl orthosilicate (TEOS) were purchased from Sigma–Aldrich. Ammonia solution (25–27 wt%) was analytical grade and used as received.

2.2. Preparation of CNTs coated with SiO_2

0.1 g CNTs was ultrasonically dispersed in 100 mL ethanol, and 5 mL ammonia solution was added into this suspension under stirring at room temperature. Subsequently, a 30 mL mixture of TEOS and ethanol (volume ratio 1:5) was added dropwise to the CNTs suspension (the total adding time was about 10 min), and the mixture was kept stirring for 12 h to hydrolyze TEOS completely. The resulting CNTs–SiO_2 suspension was sprayed onto glass slides with 0.2 MPa nitrogen gas using a spray gun.

2.3. Thermal treatment and surface fluorination

To realize transparency, the sprayed coatings were annealed in air at 600 °C for 90 min, and then the transparent coatings were modified with fluorosilane by chemical vapor deposition. The coatings and an open glass vessel containing about 0.1 ml of fluorosilane were put in a sealed desiccator with high vacuum for 2 min at room temperature. Afterward, the samples were placed in a vacuum oven at 80 °C for 20 min to remove untreated fluorosilane residues.

2.4. Characterization

Contact angle (CA), sliding angle (SA), and contact angle hysteresis (CAH) measurements were performed using a KRÜSS DSA 100 (KRÜSS Company, Ltd., Germany) apparatus at ambient temperature. CAH was observed by measuring the difference between advancing angle (θ_A) and receding angle (θ_R) on room temperature on the KRÜSS DSA 100 apparatus. θ_A and θ_R were collected with adding and withdrawing from the droplet, respectively. The volume of water and oil droplet in each measurement was approximately 5 μL. Scanning electron microscopy measurements were carried out using a JSM-6701F field-emission scanning electron microscopy (FESEM, JEOL, Japan). Transmission electron microscope (TEM) measurements were carried out using a FEI Tecnai F 30 transmission electron microscope. UV–visible absorption spectroscopy date was acquired using a HITACHI U-3010 UV–vis spectrophotometer. Surface roughness analysis was conducted on an Atomic force microscopy (AFM, AIST-NT, Smart SPM, USA).

3. Results and discussion

Thin coatings were obtained by spray coating the CNTs coated with SiO_2 (henceforth denoted as CNTs–SiO_2) onto glass slides, as shown in Fig. 1b. The sprayed coating surface is not flat, and CNTs wrapped around with SiO_2 coating and particles are exposed outside the coating surface (see Fig. 1c and e). The average thickness of silica shell and the average size of the silica particles are 20–30 nm and 100–200 nm, respectively. The CNTs–SiO_2 is probably formed through the nucleation and growth of silica nanoparticles which are deposited on the CNTs surfaces. In this sol–gel process, alkaline condensation of the impregnated silane leads to bonded oligomeric siloxane species that afford ultrafine silica nanoparticles deposited on CNTs [27]. Thermal treated the sprayed coating at 600 °C in air caused combustion of CNTs and generated a rough