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One pot synthesis of opposing 'rose petal' and 'lotus leaf' superhydrophobic materials with zinc oxide nanorods

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ABSTRACT

The synthesis in *one pot*[1] of opposing 'rose petal' and 'lotus leaf' superhydrophobic materials from commercially available superhydrophilic cloth substrates of varying texture is described for the first time. Surfaces of 'rough' textured cloth and 'smooth' textured cloth were simultaneously rendered superhydrophobic by growing zinc oxide (ZnO) nanorods by a hydrothermal process in the same chemical bath. Contact angle hysteresis and water pendant drop tests revealed strong water adhesion to ZnO microrod-treated rough cloth. The combination of water contact angle >150° and *strong adhesion* is indicative of the 'rose petal effect' with potential for water pinning. Smooth cloth with ZnO nanorods exhibited *no adhesion* to water droplets with facilitative roll-off. The combination of water contact angle >150° and weak to no adhesion with water is indicative of the 'lotus leaf effect' with potential for self-cleaning. Pendant water drop tests indicated cohesive failure of water on rough cloth coated with ZnO nanorods. Natural rose petals demonstrated adhesive failure between the petal surface and water droplet. A parsimonious explanation is presented. We also describe the development of superhydrophobic clothes without the need for special conditions or further chemical modification.

1. Introduction

The ability of scientists to control the fluid adsorption/repellent character of surfaces is an important factor in the design of bio-inspired advanced materials [1–3]. The micro and nanostructure of plant leaves and flower petal surfaces have led scientists to develop new materials that offer a wide array of wetting properties[4–9] Two natural superhydrophobic phenomena in particular have attracted significant attention from the surface science community: (1) the 'lotus leaf effect', based on the superhydrophobic behavior of the common lotus (*Nelumbo nucifera*) [2] in which water droplets have minimal to no adhesion with the surface and easily roll off for self-cleaning; and (2) the recently designated 'rose petal effect' or 'petal effect', based on the superhydrophobic behavior of flower petals like those of the red rose (*Rosea rehd*) [10] in which the surface has strong adhesion to water that results in pinning or moisturizing behavior. Although both phenomena exhibit superhydrophobic behavior with water contact angle (WCA) greater than 150°, they differ dramatically with regard to water adhesion properties. The microstructure of the lotus leaf reveals the presence of a dual hierarchical structure consisting of micron-scale bumps (nubs) of about 10 μm diameter decorated with waxy nano-fibers (e.g. micropapillae with nanofolds) [11]. Micro/nano-embossed template structures acquired by fabricating replicas of the rose petal surface were able to demonstrate superhydrophobic behavior with strong water adhesion [10].

Self-cleaning (stain free) and water repellent garment technology has received significant attention from the textile industry. Superhydrophobic cotton fabrics have since been developed by modification with silica nanoparticles followed by treatment with fluorosilane [12,13]. Specifically, treating cotton textiles with calcium carbonate ($CaCO_3$) in SEBS-g-maelic anhydride solutions yielded superhydrophobic cotton textiles with WCA 150–154° [14]. Others have also reported on chemical modification of cellulose fibers with low surface energy materials [15,16]. For example, plasma treatment [17] of silica coated fabrics followed by application of a low surface energy material [18] led to highly water repellent surfaces. Furthermore, application of self-assembled poly (butylacrylate) treated carbon nanotubes on the surface of cotton fibers produced superhydrophobic surface [19]. Recently, azido-containing silica nanoparticle–polycation multilayers resulted in durable superhydrophobic cotton clothes [20].

ZnO is a semiconducting material that is naturally hydrophilic [21]. Due to its versatility, ZnO can be used in many applications

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[1] One-pot synthesis indicates that the two-step chemical synthesis on cloth surfaces was accomplished simultaneously for each cloth in one vessel (or one beaker).

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[22–24]. For example, superhydrophobic surfaces resembling the lotus leaf were synthesized by modification of cotton fabrics by with micro and/or nanostructured ZnO layers [25]. Electroless deposition of ZnO resulted in multifunctional surfaces that showed superhydrophobicity with switchable wetting properties [26]. Superhydrophobic ZnO nanowire (d = 15–100 nm, l = 500 nm) thin films produced by annealing Zn films on glass at 500 °C demonstrated WCA ca. 150° [27]. Growth of ZnO micro- and nanorods by hydrothermal process was shown to be a simple direct route to forming superhydrophobic surfaces [21]. It is known that fabrics consisting of fibers with multiscale roughness can lead to textiles with superhydrophobic properties [28,29]. Recently, Ates and Unalan described the application of ZnO nanowires to enhance multifunctionality of coatings for cotton with superhydrophobic nature [30].

In this work, we describe, for the first time, whole scale synthesis with ZnO in one pot– under identical chemical and ambient conditions– of opposing lotus leaf effect and rose petal effect superhydrophobic materials. Secondly, we reveal a significant difference in water drop behavior in the pendant drop test between a natural rose petal and the rough textured fabric surface. Finally, we show how to treat clothes with ZnO to produce superhydrophobic surfaces that show WCA greater than 160° by a simple and economical hydrothermal method without further chemical modifications.

2. Experimental

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (Merck, Germany), sodium hydroxide (NaOH) (Merck, Germany) and isopropanol ($(CH_3)_2CHOH$) (Lab Scan) were used for the synthesis of ZnO nanoparticles [31]. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (APS Ajax Finechem, Australia); hexamethylenetetramine (hexamine, $(CH_2)_6N_4$) (Aldrich, Germany) were used as precursor materials for the hydrothermal route of ZnO synthesis. ZnO nanoparticles with diameter in the range 5–7 nm were used as the seed stock (nucleation sites) for growing ZnO micro/nanorods. Synthesis of zinc oxide nanoparticles was carried out by following protocol. Zinc acetate dihydrate (4 mM) was dissolved in ethanol (EtOH) solution and 4 mM NaOH was also prepared in EtOH solution under rigorous stirring at 60 °C. The volume of EtOH solution for each complex was 20 ml. Then, as-prepared zinc acetate in EtOH solution was mixed with 20 ml of pure EtOH at 70 °C for 30 min. Subsequently, as-prepared NaOH solution was added and then the mixture was hydrolyzed in pre-heated water bath at 60 °C for 2 h.

Fabrics (rough and smooth) were purchased at commercial markets and used without prior surface treatment. The clothes were initially designated as 'rough or smooth' quality by feel and appearance. Both the fabrics smooth and rough were dipped in soap solution at room temperature for 24 h in order to remove any water soluble coating on the surface. Then cleaned cotton fabrics were washed with absolute ethanol for 30 min and care was taken to maintain the original microstructure of the fabric. Following washing, fabrics were dried under ambient conditions and stored in a desiccator.

The two clothes were dipped into the same colloidal ZnO seeding bath for 30 min at room temperature [24,32]. The seeded sample clothes were then dried in an oven at 90 °C for 1 h and kept in the desiccator for further use. ZnO micro/nanorods were grown by the hydrothermal route [33]. In brief, the ZnO crystal growth bath was made by adding equimolar concentrations of zinc nitrate and hexamine dissolved in deionized water at room temperature. Next, the seeded cotton fabric samples were placed in the same bath in a vertical position. The hydrothermal process was then carried out in an oven set at 95 °C for 5 h. As previously reported by our group, the growth of ZnO nanorods at this temperature is fast and high quality (lower defects) nanorods are formed [32–34]. Following the hydrothermal process, samples were thoroughly rinsed with deionized water and then annealed at 150 °C for 1 h.

Images of ZnO micro/nanorods on the fabrics were acquired by scanning electron microscopy (JEOL JSM 6301) operating at 20 kV. Several areas of each sample were imaged to provide an accurate representation. IR spectra were obtained by FTIR spectrometer (PerkinElmer Frontier) attached with universal ATR sampling accessory. Static water contact angle (WCA) and contact angle hysteresis (CAH = $_A$ (advancing) − $_R$ (receding)) measurements were performed by a customized contact angle instrument equipped with a DinoLite digital microscope (AM413T). Deionized water with droplet size of 5 μL (d = 2.12 mm) was used in static WCA and CAH measurements. Five WCA measurements were carried out on different areas of fabric surfaces and average values were recorded. The analysis of WCA was carried out using ImageJ 1.42j (National Institutes of Health, USA) with an additional plug-in developed by Stalder et al. [35].

Water droplet roll-off measurements (sliding angle) were performed only on the smooth cloth by using the customized contact angle instrument. Water droplet size was kept at 40 μL in all experiments. Dynamic water droplet impact studies conducted only on smooth cloth and pendant water drop tests conducted only on rough fabric were accomplished with an ultra-fast digital camera (Photron Ultima APX-RS with a frame capture rate of 5000 fps (frames per second). For dynamic impact studies, an inclined plane with the tilt angle was varied from 1° to 15° ± 2°. For the pendant drop test, samples of rough clothes were placed horizontally and rotated 180° (upside down). The water pendant drop behavior was compared to that a natural rose petal surface. Water droplets ranging in size from 5 to 20 μL were applied until detachment of the droplet from the experimental surface was observed.

3. Results

In Fig. 1a and b, diameter of the rough cloth yarn (fiber bundles) was ca. 500 μm (Fig. 1a). In the case of the smooth cloth, the diameter of the yarn was ca. 190 μm (Fig. 1b). The yarn consists of cotton and polyester fibers that are woven to form the cloth (Supplementary information V).

Higher magnification images obtained by scanning electron microscope (SEM) of cloth are shown in Fig. 2a–d. Fiber diameter in the rough cloth was ca. 16 ± 4 μm while that of the smooth cloth fiber was smaller at ca. 14 ± 3 μm. In terms of fiber orientation in rough cloth, the majority of fibers conformed to the orientation of the weave however a great number of fibers appeared to be randomly oriented (Fig. 2a and b). On the other hand, the fibers in the smooth cloth were all well behaved with uniform order (Fig. 2c and d). FTIR analysis shows that the smooth cloth is mixture of cotton and polyester while the rough fabric was pure cotton (see Supplementary information V).

ZnO structures and distribution are depicted in SEM images of rough cloth fibers in Fig. 3a–d. ZnO crystal structure established by X-ray diffraction (XRD) is described in a previous report [36]. Diversity in terms of distribution patterns and ZnO parameters (height, diameter and orientation) was enormous on rough cloth surfaces. Two prominent features characterized the distribution of ZnO rods: (1) Clustered centers of ZnO micro/nanorods and in complement, (2) Extended regions devoid of ZnO. The dimensions of regions devoid of any ZnO ranged from tens of microns to 100 μm or more (when measured along the longitudinal axes of fibers). Dimensions of ZnO rods varied from cluster to cluster in the range of 0.3–4 μm in diameter with mean value 1.7 ± 1.1 μm