A general route to transform normal hydrophilic cloths into superhydrophobic surfaces

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Herein, we describe a simple and inexpensive method for forming superhydrophobic cloths with the highest water contact angle of close to 180°, in which normal commercial cloths serving as pristine materials are modified with suitable gold micro/nanostructures.

The amazing water repellence of many biological surfaces, in particular plant leaves, has recently aroused great interest.[1] The ability of these surfaces to make rain droplets roll or bounce off and thereby remove dust and surface contaminants very effectively is often called the "Lotus Effect".[2] The surfaces of these leaves have micrometer-scale roughness, resulting in water contact angles up to 160°, because the trapping air minimizes the real contact area between the droplets and surfaces.[3] The wettability of solid surfaces is controlled by both the chemical composition and the geometrical structure.[4] Therefore, superhydrophobic surfaces that have water contact angles larger than 150° have been obtained mainly in two ways: one is to crease a rough surface and the other is to modify the surface with low-surface-energy materials.[5] The as-prepared superhydrophobic surfaces are not restricted to fundamental research but are extended potentially to practical application, such as self-cleaning traffic indicators, the reduction of frictional drag on ship hulls and satellite antenna.[6] Although many methods are very successful in mimicking the superhydrophobic surfaces, success is limited to the formation on rigid substrates because deforming the substrate will destroy the superhydrophobic property. However, in order to extend the application, it is necessary to prepare soft superhydrophobic materials, that can be folded. Herein, we describe an inexpensive and facile method similar to the traditional dyeing technology for transforming normal hydrophilic cloths into superhydrophobic surfaces, which will be convenient for mass production.

The method employed is described as follows: first, four kinds of commercial cloths (sample A is pure cotton; samples B–D contain about 80–90% cotton) were cleaned by ultrasonic washing in ethanol and water, respectively; second, the hydrophilic cloths were immersed into an aqueous solution of $HAuCl_4$ (12 mM) and trisodium citrate (17 mM) at room temperature for 2 min. In this process, the aqueous solution absorbed into the cloths and penetrated into the cloth fibers because of their hydrophilicity, similarly to blotting paper. Next, the solution with cloths was transferred quickly into an oven heating at 98 °C for 30 min. The color of cloths changes from white into the characteristic red color of nanoscale gold (Fig. 1), indicating the reduction of $HAuCl_4$. The as-prepared cloths were carefully washed in turn with water and ethanol to remove the excess reagents. After drying, the morphologies of the products were characterized by an XL30 ESEM FEG field emission scanning electron microscope (SEM, FEI Company with 20 kV operating voltage). XPS analysis shows that the product is in the Au^0 state (data not shown). The control experiment was done by a similar process, only increasing the concentration of the $HAuCl_4$ and trisodium citrate to 24 mM and 34 mM, respectively. The resultant products exhibit a gold color, suggesting that more gold is reduced in the cloths. Finally, the surface modification was carried out by immersing the as-prepared product in an ethanol solution of *n*-dodecanethiol (1×10^{-3} M) overnight. Contact angles were measured on a Drop Shape Analysis System G10/DSA10 (Kruess, Germany) contact-angle system at ambient temperature. A distilled water droplet (4 mg) was used as the indicator in the experiment to characterize the wetting property of the as-prepared surfaces.

The hydrophobicity of four kinds of cloth surfaces after modification by gold micro/nanostructures and *n*-dodecanethiol was studied by contact angle measurement. As shown in Fig. 2, all of them have water contact angles of larger than 150°. By contrast, the pristine materials are easily drenched by the water droplet, namely, our method can lead to forming superhydrophobic cloths. Usually, the deformation of substrates will destroy the superhydrophobic property of materials. However, the superhydrophobic cloths here can retain their superhydrophobicity after folding several times. In addition, it is surprising that the water droplet on sample D rests on the protrudent cloth fibers as a sphere with seemingly no contact to the cloth surface, in which the contact angle may be considered as approximating 180° (Fig. 2(D)).

The surperhydrophobicities are believed to be due to the presence of cooperative binary structures at micro- and nanometer scales, which reduce the energies of the surfaces.[7] The morphology of the four superhydrophobic cloths was observed with SEM, and the gold micro/nanostructures on the various cloth fibers were quite similar. From Fig. 3, the surfaces show the structures on four different length scales. One is given by the fibers weaving the

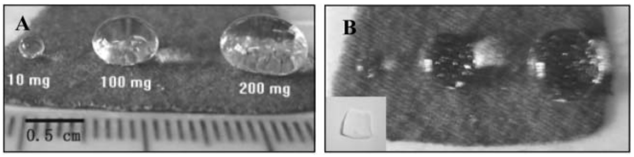

Fig. 1 Optical microscope images of water droplets with different sizes on a superhydrophobic cloth: (A) side view; (B) top-down view. The inset of image (B) is for pristine materials.

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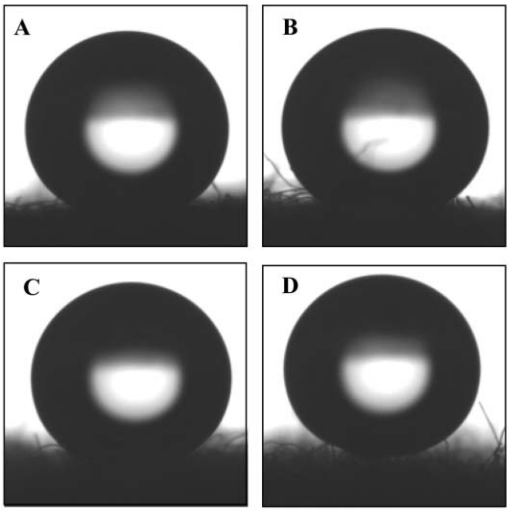

Fig. 2 The profile of water droplets on different superhydrophobic cloths (corresponding contact angles): (A) sample A (162.4 ± 1.6°), (B) sample B (152.1 ± 2.8°), (C) sample C (158.6 ± 2.2°), (D) sample D (close to 180°).

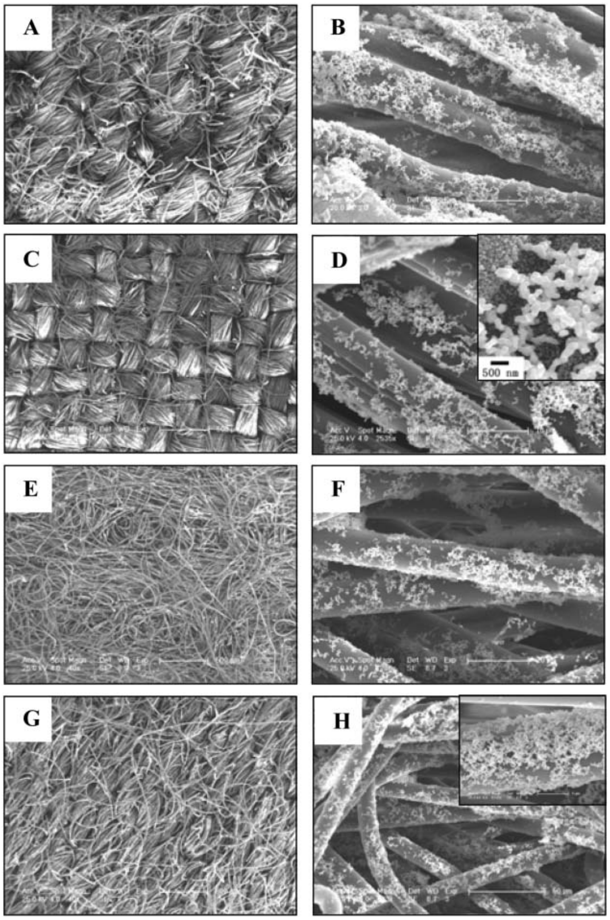

Fig. 3 SEM images of gold micro/nanostructures formed on the four cloth fibers at low (left) and high (right) magnification.: (A) and (B) sample A, (C) and (D) sample B, (E) and (F) sample C, and (G) and (H) sample D. The inset in (D) and (H) is the high-magnification SEM image of sample B and D, respectively.

commercial cloths employed in this experiment as a support and corresponds to several micrometers.[8] A second length scale is roughly defined by the distance between the fused gold particles (100 nm to tens of micrometers in size). The size of fused gold particles forming the interconnected framework on the cloth fibers determines a third length scale of around 200 nm in diameter. The fourth scale is the roughness of the gold nanoparticles (approximately 13 nm), which can be observed among the fused gold nanoparticles as shown in the inset of Fig. 3(D). Such micro/nanostructures are favorable to trap a large amount of air, inducing contact angles of more than 150°.[9] The presence of air can be directly observed by looking through a drop of water onto the superhydrophobic cloths with an overhead view. Some silvery shiny spots in some of the fields are due to total reflection of light at some air trapped underneath the water drop (Fig. 1(B)).

Roughness makes a significant influence on the wetting behavior of a given surface.[10] In the case of a composite interface, the contact angle is an average between the value on air (180°) and on the solid (θ), which can be expressed by eqn (1).[11]

$$\cos \theta_r = f_1 \cos \theta - f_2 \tag{1}$$

Here θ_r and θ (95°) are the contact angles on the superhydrophobic cloths and on a smooth Au surface with a self-assembled monolayer of *n*-dodecanethiol, respectively; f_1 and f_2 are the fractional interfacial areas of the solid surface and the air in contact with the water droplet, respectively ($f_1 + f_2 = 1$). Consequently, it is easily calculated from this equation that the f_2 values of samples A, B and C are 0.946, 0.872 and 0.920, respectively, which indicates that air trapped beneath the water can dramatically increase the hydrophobicity, *i.e.*, the surface morphology plays very important role in preparing a superhydrophobic surface.[12] Although, from SEM observation, the gold micro/nanostructures on the four types of cloth fibers have approximately the same roughness, the contact angles on various superhydrophobic cloths show obvious differences and the contact angle on sample D is larger than that of the others. Therefore, it still needs to be explained why the largest contact angle, close to 180°, is found on sample D, from which the f_2 value is near to 1.000. In addition, it should be noted that the Cassie–Baxter equation applies to flat chemically inhomogeneous surfaces. The cloth surface considered is rough, therefore the values for the fractional water–air areas are just rough estimates.

According to the above calculation, the contact angle increases with increasing surface coverage and roughness of the micro/nanostructures,[13] accompanying with the increasing f_2 value. Although the roughness of gold micro/nanostructures on the cloth fibers was obviously increased by increasing the concentration of $HAuCl_4$ and trisodium citrate (Fig. 4), in the case of samples A, B and C, we still did not observe approximately-spherical water droplets (contact angle of above 170°) similar to that of sample D. According to the report of Otten *et al.*, the hair-covered leaf of Lady's Mantle (*Alchemilla vulgaris* L.) shows a water contact angle close to 180°.[14] They attributed the effective superhydrophobicity to the bundle of hairs stuck into a liquid-air interface and the elasticity of the hairs that can lift the water droplet from the leaf cuticula. In our work, a large number of cloth fibers extend outside the cloth surface, which can be observed from Fig. 2. The effect of the protrudent cloth fibers on the superhydrophobicity must be

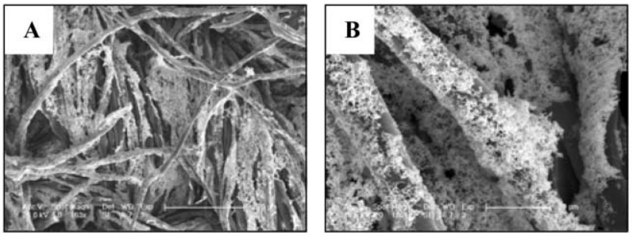

Fig. 4 SEM images of gold micro/nanostructures prepared from a high concentration of $HAuCl_4$ and trisodium citrate on sample A at different magnifications.

taken into account, which may be similar to the hairs on the leaves of Lady's Mantle. Fig. 5(A) shows a simple idealized model of the water droplet on the modified cloth. When a small water droplet is dropped on the cloth, it forces the protrudent cloth fibers into bundles, most of them will have to bend because of the weight of water droplet, which costs elastic energy, according to the elastic modulus of the cloth fibers. The elasticity of the cloth fibers results in a repulsive interaction between the cloth and the water/air interface. If the elastic modulus of the cloth fibers is large enough, the water droplet will be kept away from the cloth, as is observed on sample D. The relationship of elastic modulus (K) of cloth fibers, the distance (h) between the cloth and protrudent cloth fibers, and the elastic energy (Γ) can be described by eqn (2).[14]

$$\Gamma \propto \sqrt{\frac{K}{h}} \tag{2}$$

Based on compression experiments, the elastic modulus of samples A, B, C, D are 0.53, 0.22, 0.36, 0.90 Pa, respectively. The change of the contact angles for the various superhydrophobic cloths is consistent with the different elastic modulus of cloth fibers. The contact angles increase with the increasing elastic modulus, as a result, the droplet shape becomes more spherical. Therefore, we reasonably attribute the approximately spherical water droplet to that the higher elastic energy of the cloth fibers of sample D are enough to support the weight of water droplet away from cloth (Fig. 2(D)). When the elastic modulus of cloth fibers decreases, the water droplet on the samples will force the protrudent cloth fibers to bend more intensely, and then anchor onto the cloth, or even integrate with the cloth ($h = 0$). As a result, non-spherical water droplets were observed (Fig. 2(A)–(C)). In addition, if we increase the weight of water droplet on sample D, the elasticity of the protrudent cloth fibers can not support water droplets, as a result of decrease in contact angle (Fig. 5(B)).

Our studies also demonstrated that, besides the above-mentioned four cloths, superhydrophobic surfaces were also obtained from other commercial cloths. In our further exploration, we observed that the contact angle depends upon the type of cloth fibers. Poorly hydrophilic cloth fibers, such as silk, usually have contact angles of 120–140° whereas good hydrophilic cloth fibers, such as cotton, usually lead to superhydrophobic surfaces. This can be attributed to that the stable and rough gold micro/nanostructures prefer to be constructed on good hydrophilic cloth fibers during the chemical reduction from our SEM analysis.

In conclusion, we have successfully created superhydrophobic cloth by modifying surfaces with gold micro/nanostructures on different kinds of cloths. We observe that the contact angles not only relate to the surface roughness, but also will increase with the increasing elastic modulus of cloth fibers. The highest contact angle is close to 180°. For commercial application, superhydrophobic cloths with large-scale production, perhaps even superhydrophobic clothing, will be obtained possibly by industrialized techniques.

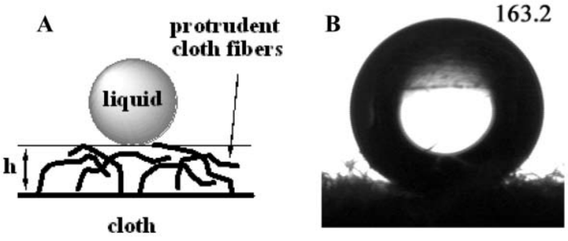

Fig. 5 (A) Model structure of the elastic deformation of the protrudent cloth fibers due to forming bundles at the water/air interfaces. (B) Shape of water droplet and corresponding contact angle on sample D (droplet weight 6 mg).

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