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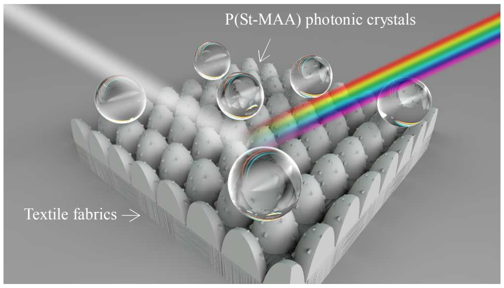
Highlighting the novelty of the work

The fabrics with P(St-MAA) photonic crystals possess high hydrophobicity and vivid structural colors. The possible mechanism of hydrophobicity and model of water droplets on the resultant fabric are investigated.



Study on the high hydrophobicity and its possible mechanism of textile fabric with structural colors of three-dimensional Poly (styrene-methacrylic acid) photonic crystals

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Abstract:

In our previous research, the structural color properties of Poly (styrene-methacrylic acid) (P(St-MAA)) photonic crystals fabricated on soft textile fabrics by colloidal self-assembly method had been investigated. However, the hydrophobicity property of the resultant textile fabrics was rarely reported. Through the applications of field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and wettability analyses, a possible mechanism of hydrophobicity of resultant textile fabrics was proposed. It was confirmed that the hydrophobic P(St-MAA) colloidal microspheres could almost completely fill in the most gaps of textile fabrics and form uniform photonic crystal film on textile fabrics in the end of the assemble process, which effectively prevent water droplets from infiltrating through the surface of fabrics. Moreover, the minute protrusions on each P(St-MAA) colloidal microsphere surface and as-prepared regular rough photonic crystal array were combined to form a double-rough structure similar to the morphology of lotus leaf, which could greatly enhance the hydrophobicity of the resultant textile fabrics.

Introduction

Nowadays, hydrophobicity is regarded as one of the important properties for most of materials in practical aspects, and how to construct hydrophobic surfaces have received more and more research attention.[1-4] In particular, in textile industry, the research about hydrophobic textiles has become a hot spot due to high demand for functional textile products.[5] Conventionally, hydrophobic textile is mostly produced by two steps in traditional dyeing and finishing process. The first step is to endow textile products with coloration by attaching colorants of dyes or pigments onto fibers, yarns and fabrics on dyeing and printing processes, a kind of chemical pigment coloration; the second step is to apply water repellent finishing agents on colored textile products to produce a hydrophobic surface, known as water repellent finishing. The most common water repellent finishing agents include long-chain alkane compound (typically 18 carbon atoms) and certain organic silicone polymer, such as pyridine quaternary ammonium salts, methylol melamine derivative, stearic acid chromium complex, fluorinated compound and organic silicone.[4,6,7] Obviously, the conventional methods to prepare hydrophobic textile products have some notorious disadvantages including long and cumbersome procedures and high equipment cost. Moreover, the water repellent finishing agent may easily affect the shade of colored textiles and cause pollution to environment due to the emission of water repellent finishing agents.

In the previous study, our reseach groups have successfully fabricated orderly three-dimensional (3D) Poly (styrene-methacrylic acid) (P(St-MAA)) photonic crystal structures on textiles by gravitational sedimentation and vertical deposition assembly and obtained gorgeous and tunable structural colors[8,9]. Furthermore, the optical property of the prepared photonic crystals and self-assembly behavior of P(St-MAA) colloidal microspheres on polyester fabrics by gravitational sedimentation had been investigated in detail[10,11]. As more research going on, our research group strove to develop more interesting features apart from the structural colors for those textile fabrics with photonic crystal structures. To our delight, it was found that the resultant textile fabrics showed high hydrophobicity after the photonic crystal structure was successfully fabricated on them. In some previous researches[12,13], it was reported that by some self-assembly process like electrostatic self-assembly, some nanoparticles like SiO_2 were used to improve the hydrophobicity of textile fabrics and even endow superhydrophobicity, however, those nanoparticles were dispersed in disorder on the prepared textile fabrics, which did not display structural colors. Therefore, it is significant to deeply study the high hydrophobicity of the textile fabric with photonic crystal structure, showing bright and vivid structural colors.

In this paper, based on the premise that three-dimensional P(St-MAA) photonic crystals with bright and tunable structural colors on textile fabrics had been fabricated through colloidal self-assembly, the possible mechanism of hydrophobicity of resultant textile fabrics was deeply investigated. It is convinced that the high hydrophobicity of 3D photonic crystals on textile with vivid structural colors will provide a new idea to prepare hydrophobic textile and revolutionize the fashion industries in view.

Experimental

Materials

Monodisperse P(St-MAA) colloidal microspheres with perfect sphericity and different diameters were made in laboratory via soap-free emulsion polymerization.[8] Black plain weave polyester fabrics and twill cotton fabrics were bought from the local market. Deionized water (>18

MΩ cm, Millipore Milli-Q) was used for the whole experiments. Note that when black textile fabric was used as substrate material, it had remarkable ability to absorb the transmitted light and scattered light outside the photonic band gap, and enhance the chroma of structural colors markedly from photonic crystals.

Fabrication of photonic crystals on textile fabrics

Gravitational sedimentation

The photonic crystals with structural color on polyester fabrics were fabricated by allowing a dilute colloidal suspension of P(St-MAA) to deposit on textile fabrics through gravitational sedimentation. Firstly, the colloidal microsphere suspension was diluted to 1 wt % with deionized water. Then, a piece of polyester fabric was placed in a lidless petri dish which was subsequently filled with the diluted microsphere suspension. Finally, the polyester fabric with the P(St-MAA) colloidal suspension was located in a vacuum drying oven at a constant temperature of 60 °C with a relative humidity of 40-60% for more than 24 hours dependent on various deposition rate of colloidal microspheres. After drying the sediment, water in the colloidal suspensions was evaporated and the structural color of P(St-MAA) photonic crystals on textile fabrics was obtained. Specifically, the schematic diagram of gravitational sedimentation method of P(St-MAA) colloidal microspheres on textile fabrics is shown in Fig. 1.

Vertical deposition

The photonic crystals with structural color were fabricated by a vertical deposition method on black cotton fabrics cleaned by ultrasonic in deionized water. Firstly, after an ultrasonic treatment for 10 min, the colloidal suspension of P(St-MAA) microspheres was diluted to 2 wt % with deionized water. Then, a piece of cotton fabric was vertically placed in a glass bottle which was subsequently filled with the diluted microsphere suspension. Finally, the cotton fabric with the diluted microsphere suspension was located in a vacuum drying oven at a constant temperature of 60 °C with a relative humidity of 40-60% for more than 72 hours dependent on various deposition rate of colloidal microspheres. After drying the sediment, water in the colloidal suspension was evaporated and a solid structure of well-ordered P(St-MAA) photonic crystals on cotton fabrics was obtained. Specifically, the schematic diagram of vertical deposition method of P(St-MAA) colloidal microspheres on textile fabrics is shown in Fig. 1 as well.

Padding process

In order to compare with the hydrophobicity of fabrics prepared by self-assembly process, a series of padding treatments on cotton fabrics were done in our study, in which the P(St-MAA) microspheres emulsion was applied as common finishing agent. The cotton fabric samples were immersed in P(St-MAA) microspheres emulsion of various concentrations, then padded with a pick-up ratio of 70-80% by electric padder (P-AO, Jingke, China), then dried at 80 °C for 5 minutes, and finally cured at 150 °C for 3 minutes by a curing machine.

Characterization

Structural color

The structural colors of P(St-MAA) photonic crystals on textile fabrics were observed by a three-dimensional video microscope (KH-7700, HIROX, Japan) and a digital camera (EOS600D, Canon, Japan). Note that the images of microscope were observed at normal incidence.

Surface morphology

The surface morphology of the original fabrics and P(St-MAA) photonic crystal structure on fabrics were observed by a field emission scanning electron microscopy (FESEM, ALTRA55, Germany) and an atomic force microscopy (AFM, XE-100E, Korea). All FESEM images were collected at an electron gun with accelerating voltage of 1 kV.

Wettability

Water contact angles (CAs) and wetting time of the original and resultant fabrics were measured on a contact-angle system (Easy Drop, Germany) at ambient temperature and saturated humidity. Deionized Water droplets (3.0 μL) were carefully dropped onto the fabric samples. The water contact angle (CA) value and wetting time were obtained by measuring three different positions of the same sample and then calculating a mean value. Specifically, for the wetting time, we referred to the AATCC Test Method 79-2000 and the video recording of a contact-angle system (Easy Drop, Germany) was used. A drop of water is allowed to fall from a fixed height onto the taut surface of a test specimen. The time required for the specular reflection of the water drop to disappear is measured and recorded as wetting time.

Results and discussion

The structural color and hydrophobicity of the resultant textile fabrics

Based on our previous study,[10] three-dimensional P(St-MAA) photonic crystals on polyester fabrics were successfully fabricated by gravitational sedimentation self-assembly and exhibited brilliant and variable structural colors by changing the diameters of colloidal microspheres or the viewing angles as shown in Fig. 2 and Fig. 3. Even more exciting, it was found that the as-prepared polyester fabrics not only had vivid structural colors, but also possessed better hydrophobic property than the original polyester fabrics.

Fig. 4 shows the shape of a water droplet on the original polyester fabric and the resultant fabric samples with P(St-MAA) microspheres of different diameters. As we know, the wettability of the liquid is quantified by the contact angle (θ), defined as the angle between the liquid/vapor interface and the solid surface.[14] In Fig. 4, the water contact angle (CA) of various resultant fabric samples are 122.0±0.4°, 123.7±0.9°, 126.3±0.5° and 128.6±0.4°, respectively, compared to that of the original polyester fabric of only 99.6±1.0°. It is clear that the resultant polyester fabrics had much higher water contact angles than the original sample, which signifies the better hydrophobicity.

In addition, the wetting time of the as-prepared fabrics is regarded as another important index to evaluate hydrophobicity in our study. Fig. 5 shows the wetting process of one of the resultant polyester fabric sample with 185 nm P(St-MAA) microspheres. As shown in Fig. 5, the wetting time of this sample is more than 1200 s, however, for original polyester fabric in our study, it is merely about 31 s. In other words, the resultant polyester fabric had markedly longer wetting time than the original polyester fabric.

In addition to polyester fabric, our group also has successfully constructed the three-dimensional P(St-MAA) photonic crystals on cotton fabric displaying bright structural colors, as shown in Fig. 6. It is known to all that different from polyester fabric, cotton fabric is made from natural cotton fibers, familiarly known for its high hydrophily. Fig. 7 shows the shape of a water droplet on the original and resultant cotton fabric. As shown in Fig. 7, it is hardly possible for us to capture the fleeting view of the water droplet staying on the original cotton fabric surface due to its rapid permeation, however, for the resultant cotton fabrics, an opposite phenomenon is observed in many different samples, that is to say, the water droplet can easily stay much longer on the surface of cotton fabric, indicating high hydrophobicity. Fig. 6 (f-h) shows the shape of a water droplet on the original cotton fabric and resultant fabric samples corresponding to Fig. 6 (a-d). The water contact angles (CAs) of variously resultant cotton fabric samples are 120.1 ±0.7°, 124.1±1.1° and 129.2±0.5°, respectively, compared to that of the original cotton fabric of just 57.8±1.5°. In addition, the wetting time of the resultant cotton fabric sample with P(St-MAA) microspheres of 185 nm is more than 290 s, much longer than the original cotton fabric of 441 ms in our study. Therefore, it is simply speculated that during the self-assembly process cotton fabric might experience some significant changes so that its inherent wetting ability has to be reversed.

The mechanism of high hydrophobicity of the resultant textile fabrics

In order to reveal the reasons for the high hydrophobicity of those resultant fabrics, a range of experiments were designed in our research. First of all, it is supposed that the prepared P(St-MAA) colloidal microspheres emulsion plays an important role in the high hydrophobicity of resultant fabrics by itself. To verify the point, a conventional padding process was used to treat cotton fabrics, in which P(St-MAA) colloidal microspheres emulsion was used as a common finishing agent. Table 1 shows the contact angles and wetting times of those finished cotton fabrics by P(St-MAA) colloidal microspheres emulsions of different concentrations. It can be observed that the finished cotton fabrics have higher contact angles and longer wetting times than original fabric, which proves that the as-prepared P(St-MAA) microspheres emulsion is actually a kind of hydrophobic material, endowing the finished fabrics with hydrophobicity to some extent. Moreover, it is also noticed that the higher concentrations of colloidal microspheres emulsion are, the larger and longer of contact angles and wetting times of those fabrics become, which can been easily explained by the FESEM images in Fig. 8. It is clearly found that the amount of P(St-MAA) colloidal microspheres deposited on the surface of the cotton fibers and filled in the gaps between the fibers is proportional to the concentrations of colloidal microspheres emulsion used in padding process. However, it is undeniable that the contact angles and wetting times of the finished cotton fabrics are far smaller and shorter than completely resultant samples. Therefore, it is considered that the inherent hydrophobicity of P(St-MAA) microspheres emulsion can't fully explain the remarkable hydrophobicity of those resultant fabrics.

It is very convinced that the morphology of the fabric plays a vital role in the wettability. Therefore, it is necessary to investigate the morphology changes of textile fabric substrates during the self-assembly process. Fig. 9 presents the gravitational sedimentation self-assembly process of P(St-MAA) colloidal microspheres on polyester fabric. Fig. 9(a) displays the FESEM images of original polyester fabric. It is noticed that there are many gaps among the fibers, and the warp yarns and filling yarns are arranged orderly. In Fig. 9(b-f), it can be seen that the P(St-MAA) colloidal microspheres are firstly deposited on the surface of polyester fibers and gradually fill voids between the fibers and yarns during the initial stage of self-assembly process. After most voids are adequately filled, with the progress of self-assembly, orderly P (St-MAA) photonic crystal film is fabricated on the surface of the polyester fabrics, which seems to be relatively flat and compact with the naked eye. Fig. 10 is just the magnification of Fig. 9, and the above process can be more clearly observed from Figure 10. Furthermore, Fig. 11 demonstrates the changes of water contact angles (CAs) of resultant polyester fabrics in gravity sedimentation process at different self-assembly time. From Fig. 11, it is found that the water CAs of the resultant fabrics substantially keep increase with the extended assembly time, which indicates that the hydrophobicity of the resultant fabrics are continually improved during self-assembly process.

Similarly, for the resultant cotton fabrics obtained at different assembly time, their hydrophobic performances present the same variation tendency as well. Therefore, based on the analysis of Fig. 9 to Fig. 11, it is not hard to understand that the pinning of P(St-MAA) microspheres to voids of fabric fibers and the formation of compact photonic crystal film on fabric substrate effectively prevent water droplets through the surface of fabrics, which is convinced to partly account for the high hydrophobicity of the resultant textile fabrics.

Although the above analysis can partially explain the hydrophobicity changes of the fabric in the process of assembly, it is believed that there are some other profound reasons for the high hydrophobicity of the resultant fabrics. Fig. 12 presents the microstructure P(St-MAA) photonic crystals on polyester fabrics. Fig. 12(a) and (b) are the top surface images of the P(St-MAA) photonic crystals on polyester fabric at high magnification taken by FESEM and AFM, respectively. It is shown an ordered {111} crystal plane of three-dimensional P(St-MAA) photonic crystals on the basis of our previous research.[8,9] Apparently, such a three-dimensionally ordered structure can endow the resultant fabric surface with a certain degree of roughness, which is supposed to have great influences on its wettability referred from many previous studies.[15-19] Furthermore, from Fig. 12(c), it can be clearly seen that in fact the surface of the well-ordered P(St-MAA) photonic crystal array on polyester fabric is not flat and has a lot of orderly embossments similar to egg tray, which directly produces a highly rough surface on polyester fabrics and traps a large proportion of air in the residual space available for each arranged microspheres. Due to the trapped air, when the water droplet falls to the surface of the resultant fabrics, it tends to stay on the top of neighboring microspheres, minimizing the corresponding contact area between the water droplet and photonic crystals, thus the residence time of the droplet on fabric surface increases and the high hydrophobicity is endowed to the fabrics.[20] In addition, much to our excitement, in Fig. 12(c), it must be noticed that there are lots of irregular nano-protuberances on each P(St-MAA) microsphere's surface, which is regarded to extra strengthen the roughness of P(St-MAA) photonic crystals. Therefore, it is not difficult to image that when the water droplets fall into the surface of resultant fabrics, they contact first with those irregular nano-protuberances without doubt, which is effective to prevent their infiltration into the fabrics.

On the basis of previous researches, hydrophobic character originated from the rough microstructure of a surface was thus like the “lotus effect”.[5,21-23] As we all know, the epidermis of the lotus plant possesses papillae with 10 to 20 μm in height and 10 to 15 μm in width, on which the so-called epicuticular waxes are imposed. These rough papillae structure and hydrophobic waxes can endow lotus high hydrophobicity. According to the above analysis, if the surface of the resultant polyester fabric can be seen as a lotus leaf surface, the microsphere particles of bumped P(St-MAA) photonic crystal array are equivalent to the mastoid micro-structure on lotus leaf surface, and lots of minute protrusions on the surface of each P(St-MAA) microsphere are similar to the villus of the mastoid micro-structure on lotus leaf surface. Such analogy is considered to ingeniously explain the high hydrophobicity of the resultant polyester fabrics in supplement. However, it should be noted that under our experimental conditions, the contact angles of all fabric samples are less than 150°, that is, the related fabric samples don’t have superhydrophobicity, which might be attributed to the much ordered photonic crystal structure on fabric substrates, limiting their hydrophobic properties to some extent. Therefore, it is thought that the as-prepared photonic crystals on fabrics are just similar to the lotus, and the related hydrophobicity is not completely ascribed to lotus effect.

In summary, it is assumed that the high hydrophobicity of those resultant fabric samples could be mainly attributed to three key points: firstly, the P(St-MAA) microspheres emulsion itself is a hydrophobic material, which can endow the fabric with a certain degree of hydrophobicity. However, this is not the main reason for its high hydrophobicity; secondly, during the assembly process, most of gaps among the fibers and yarns are filled with hydrophobic P(St-MAA) microspheres and the surface of the fabrics is evenly covered with photonic crystal film, which can effectively prevent water droplets through the surface of the fabrics; thirdly, the special protrusions on each P(St-MAA) colloidal microsphere surface and as-prepared regular rough photonic crystal array are cooperated to form a similar morphology of the lotus leaf with double-rough structure, which can greatly enhance the hydrophobicity of the resultant fabrics. An appropriate model can be used to describe the shape of water droplets on the those resultant fabrics with an three-dimensional P(St-MAA) photonic crystals, just as shown in Fig. 13.

Conclusions

In this paper, the prepared textile fabrics with P(St-MAA) photonic crystals exhibit high hydrophobicity except for vivid structural colors via different colloidal self-assembly processes. On one hand, during the self-assembly process, the hydrophobic P(St-MAA) colloidal microspheres can completely fill in the gaps of textile fabrics and form ordered photonic crystal film on textile fabrics, which effectively prevent water droplets through the surface of fabrics. On the other hand, the minute protrusions on each P(St-MAA) colloidal microsphere surface and as-prepared regular rough photonic crystal array are combined to form a double-rough structure at the nanoscale similar to the morphology of lotus leaf, which greatly enhances the hydrophobicity of the resultant textile fabrics. It is believed that the three-dimensional P(St-MAA) photonic crystals not only provide the textile fabrics bright and variable structural colors, but also bestow outstanding hydrophobicity without any extra chemical additives, which certainly exerts significant impacts on textiles and fashion industries.

Acknowledgments

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Table Legends

Table 1. The contact angles and wetting times of cotton fabrics treated by P(St-MAA) colloidal microspheres emulsions with different concentrations after a padding process.

Table 1

	Original fabric	Concentrations of P(St-MAA) microspheres emulsion			
		10%	20%	50%	100%
Contact angles (°)	57.8±1.5	61.1±1.6	97.9±0.9	114.6±1.0	119.1±0.5
Wetting time (ms)	441	617	1373	8525	55000

Figure Legends

Fig.1. The schematic diagrams of gravitational sedimentation method and vertical deposition method of P(St-MAA) colloidal microspheres on textile fabrics. Where, the left one is gravitational sedimentation, the right is vertical deposition.

Fig.2. The morphologies of original black polyester fabrics (a) and the resultant polyester fabrics (b-h) taken by a three-dimensional video microscope. Where, diameters of the assembled P(St-MAA) microspheres of (b-h) are 304 nm, 286 nm, 265 nm, 255 nm, 222 nm, 206 nm and 185 nm, respectively. The scale bar is 1000 um.

Fig.3. The iridescence of polyester fabrics fabricated with the P(St-MAA) colloidal microspheres with the same diameter of 286 nm taken by a digital camera. The scale bar is 0.5 cm.

Fig. 4. The shape of a water droplet on the original polyester fabric (a) and the resultant polyester fabric samples (b-e). Where, diameters of the assembled P(St-MAA) microspheres of (b-e) are 286 nm, 275 nm, 255 nm and 185 nm, respectively.

Fig. 5. The wetting process of the resultant polyester fabric samples with P(St-MAA) microspheres of 185 nm.

Fig. 6. The structural colors and the shape of a water droplet on original cotton fabric (a, e) and the resultant fabric samples with P(St-MAA) microspheres of different diameters:(b, f) 292 nm; (c, g) 255 nm; (d, h)185 nm. The scale bar is 1000 um.

Fig. 7. The shape of a water droplet on the original cotton fabric (a) and the resultant cotton fabric samples with different sizes (b-d). Where, diameters of the assembled P(St-MAA) microspheres of (b-d) are 282 nm, 255 nm and 185 nm, respectively.

Fig. 8. FESEM images of original cotton fabrics (a, b) and the resultant cotton fabrics treated by P(St-MAA) colloidal microspheres emulsion with different concentrations (c-f). Where, concentrations of (c-f) are 10%, 20%, 50% and 100%, respectively. (a) is magnified to 100 times, the scale bar is 200 um; while the others (b-f) are 2000 times, the scale bar is 10 um.

Fig. 9. FESEM images of the resultant polyester fabrics in gravity sedimentation self-assembly process at different times of (a) 0 h, (b) 1 h, (c) 3 h, (d) 7 h, (e) 13 h and (f) 24 h, respectively, where, the images are magnified to 100 times, the scale bar is 200 um.

Fig. 10. FESEM images of the resultant polyester fabrics in gravity sedimentation self-assembly process at different times of (a) 0 h, (b) 1 h, (c) 3 h, (d) 5 h, (e) 7 h and (f) 24 h, respectively, where, the images correspond to the (a-f) of Figure 9 and are magnified to 1000 times， the scale bar is 10 um.

Fig. 11. The contact angles of resultant polyester fabrics in gravity sedimentation self-assembly process at different times.

Fig. 12. The microstructure P(St-MAA) photonic crystal on polyester fabrics from microsphere diameter of 265 nm. Where, (a) is the top-view (×20000) taken by FESEM; (b) is the top-view (2 μm×2 μm) taken by AFM; (c) is the cross-section of (b).

Fig. 13. The model of the shape of water droplets on the resultant fabric with P(St-MAA) photonic crystals.

Figure 1

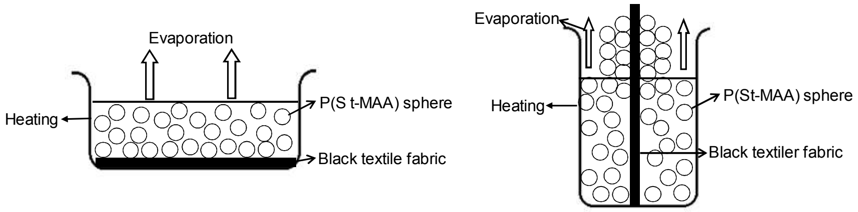


Figure 2

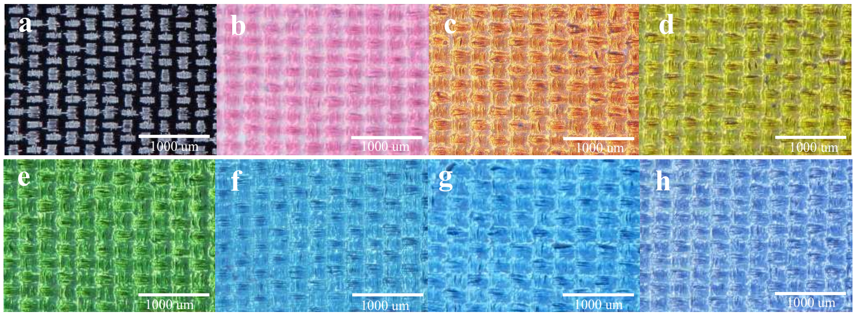
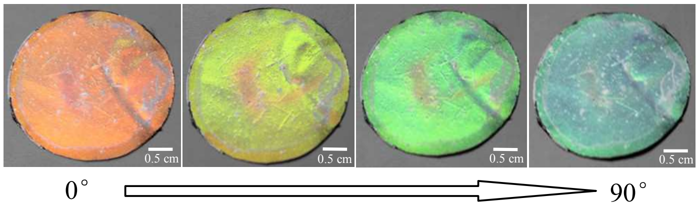


Figure 3



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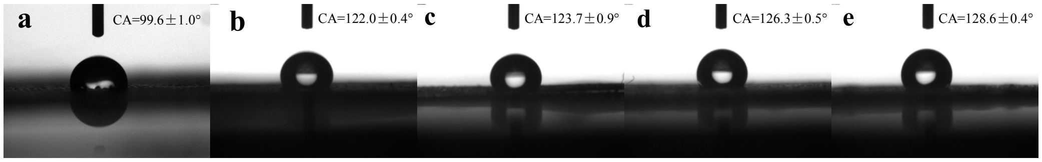

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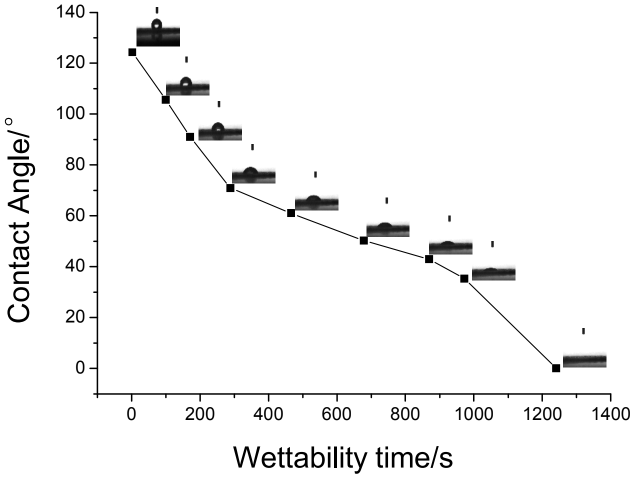

Figure 6

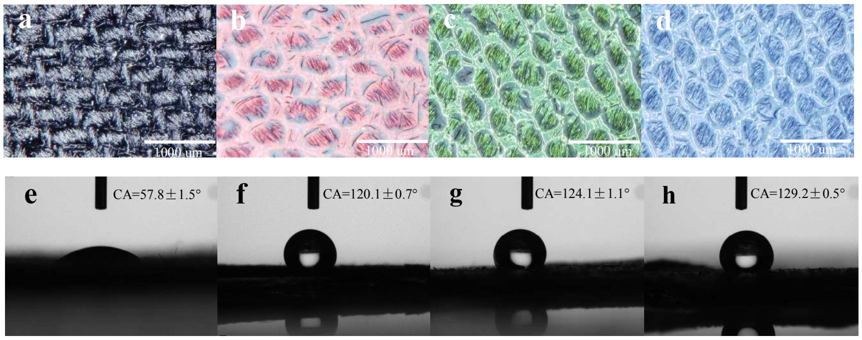

Figure 7

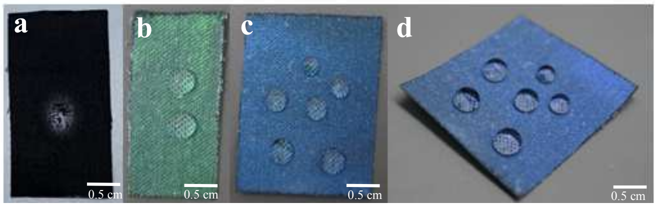

Figure 8

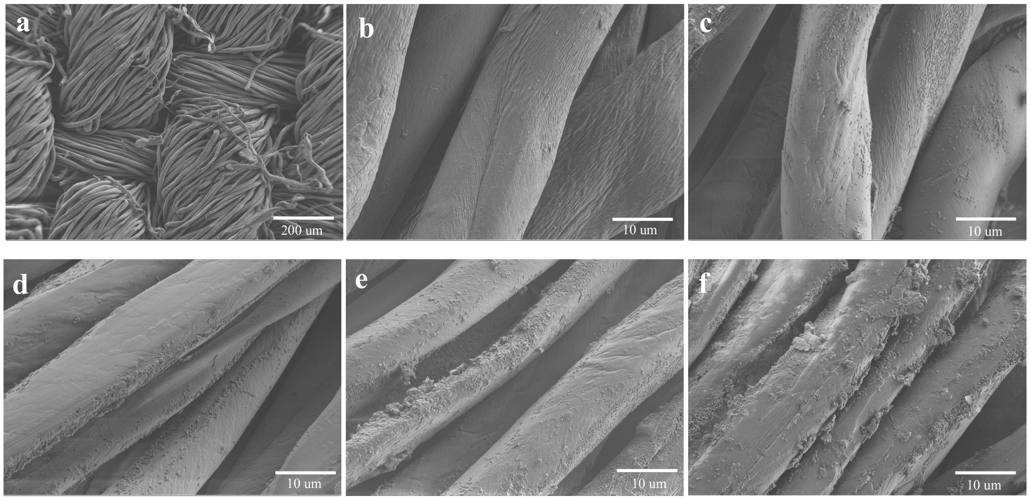

Figure 9

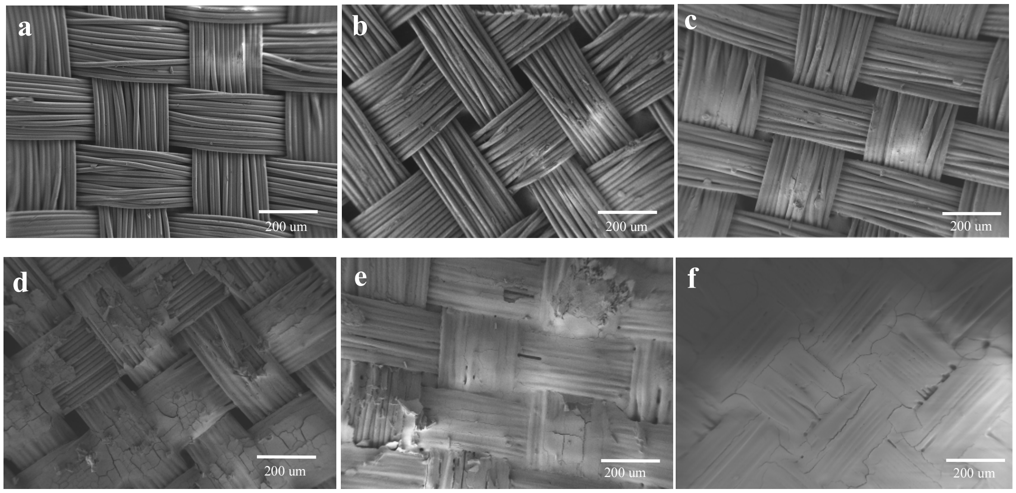

Figure 10

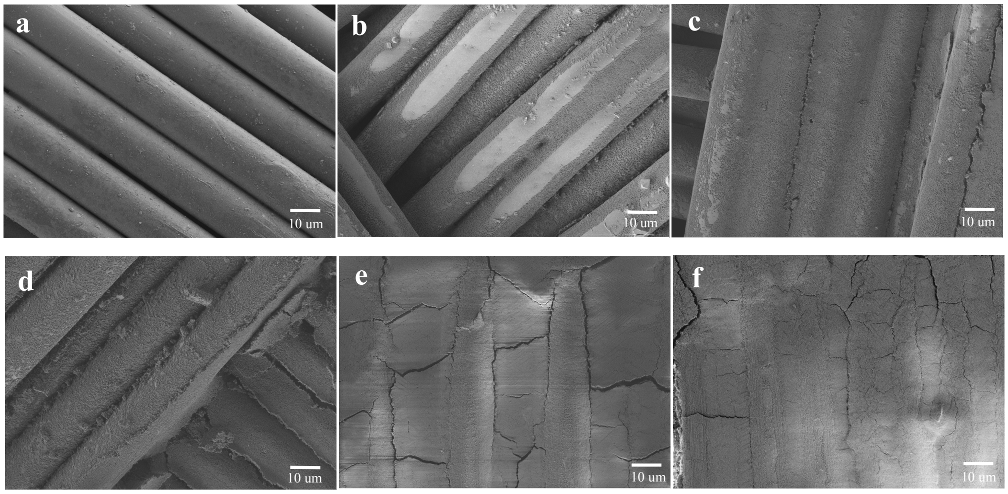

Figure 11

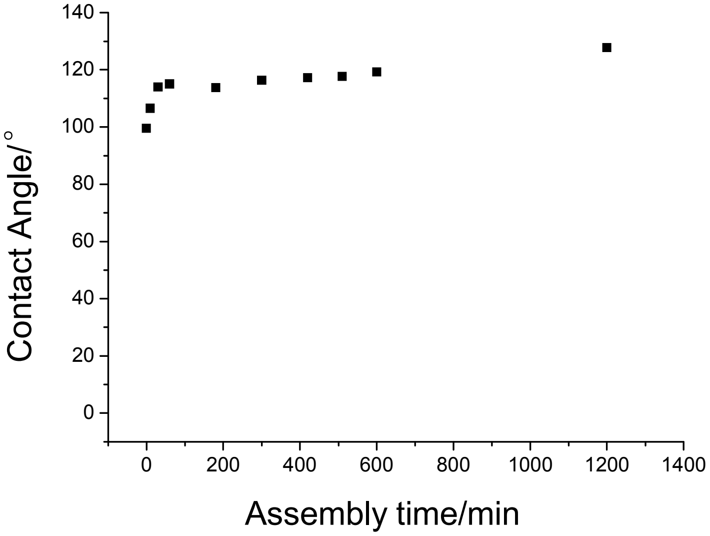
Contact Angle/°
140
120
100
80
60
40
20
0
0
200
400
600
800
1000
1200
1400
Assembly time/min

Figure 12

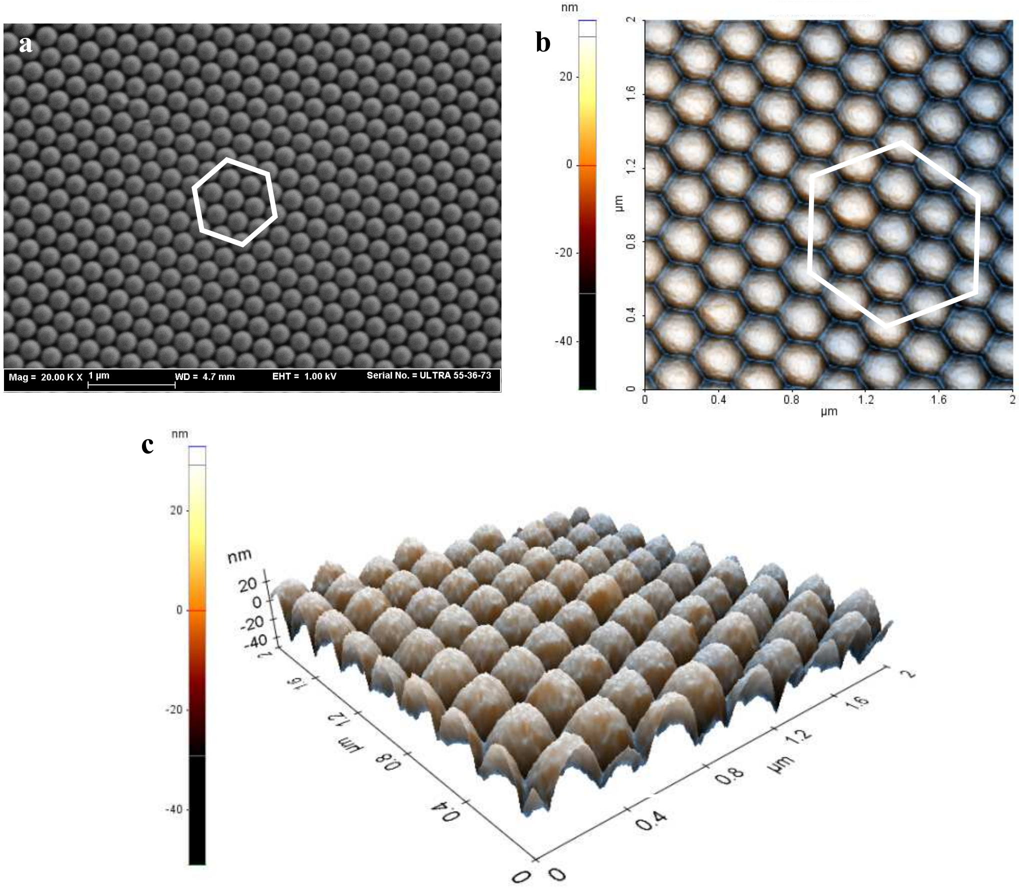

Figure13