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Wang, Hongxia, Ding, Jie, Dai, Liming, Wang, Xungai and Lin, Tong 2010, Directional water-transfer through fabrics induced by asymmetric wettability, *Journal of materials chemistry*, vol. 20, no. 37, pp. 7938-7940.

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Directional water-transfer through fabrics induced by asymmetric wettability†

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Received 22nd July 2010, Accepted 26th July 2010

DOI: 10.1039/c0jm02364g

Fabrics having an interesting unidirectional water-transfer effect have been prepared by a special coating technique to create a wettability gradient across the fabric thickness, and the treated fabrics also show considerably different breakthrough pressures on the two fabric sides.

Directional fluid transport is imperative to many important physiological functions and physical processes. Examples include sweating, fluid transport across cell membranes,¹ water transport from soil to air through plants,² desalination of seawater,³ flow management in fuel cells⁴ and microfluidic systems.^{5,6} While the fluid delivery in all of the directional fluid transport systems appears alike, the driving force for propelling the fluid motion in each of the systems could be very different. In biological systems, *aquaporins* (water channel proteins) play a critical role in transferring water across biological membranes⁷ by electrostatically flipping water molecules through the channel,⁸ while the gradients in mechanical pressure involves in many other directional fluid transport systems.

Surface tension heterogeneity has been known as a driving force to guide water motion on flat surfaces for decades. The imbalanced surface tension can be formed spatially in fluid due to the induced changes in local fluid properties⁹ (the motion is also called “Marangoni flow”), or facially by modification of solid surface,¹⁰ which shows great potential in droplet microfluidics.^{6,11} A natural example can be found in *Stenocara* beetle, an insect in the Namib Desert having a hydrophobic surface with a random array of hydrophilic bumps on the wings.¹² Such an asymmetric surface tension endows the *Stenocara* with an incredible ability to collect water for its survival in the dry desert environment, thus very useful for development of water-harvest devices.¹³ Nevertheless, all these works are based on flat surfaces. Little is known about using imbalanced surface tension to drive directional fluid motion through the thickness of porous materials.

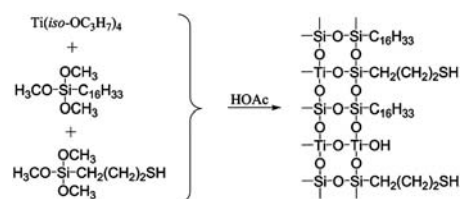
In this study, we have developed a simple, but very effective and versatile, method to produce an imbalanced surface tension across the thickness of fabrics, and demonstrated that the fabrics have the ability to spontaneously transfer water unidirectionally through the

fibrous architecture. A plain weave polyester fabric (thickness 520 μm) has been used as a sample porous membrane.

Our method is based on a solution coating technology to form a superhydrophobic layer containing TiO_2 and hybrid silica on a polyester fabric, and subsequent exposure of the one side of the superhydrophobic fabric to a multi-wavelength ultra-violet (UV) beam to make the irradiated fabric side hydrophilic, leading to the formation of asymmetric wettability through the fabric thickness.

The coating solution was prepared by a sol–gel route similar to the synthesis of TiO_2 - SiO_2 hybrid materials from titanium tetraisopropoxide and tetraethylorthosilicate,¹⁴ but different in that two organic silanes (hexadecyltrimethoxysilane and 3-trimethoxysilylpropane thiol-1) (Scheme 1) were used to leave non-hydrolysable groups in the product. Through a dip-coating process, a thin layer of conformal coating composed of TiO_2 and hybrid silica having hydrophobic hexadecyl and 3-thiol propyl groups was readily formed through the polyester fabric. Fig. 1 (Right panel) shows the scanning electron microscopic energy-dispersive X-ray (SEM-EDX) mapping images (see the ESI† for the cross-section view and TEM), indicating the formation of a uniform coating layer. The surface water contact angle increased to 170° on both sides of the fabric after the coating formation (Left panel of Fig. 1).

Subsequent UV irradiation from one side of the fabric led to a series of chemical reactions catalysed by TiO_2 within the irradiated portion of the membrane,^{14,15} converting those pre-formed hydrophobic surface groups in the coating layer into hydrophilic oxygen-containing groups, including the highly water-absorptive sulfonic acid and carboxylic acid (see the ESI†). The up-shift in the S2p binding energy from 161 eV and 163 eV to 167 eV seen in the high resolution X-ray photoelectron spectroscopy (XPS) spectra after the UV irradiation (Fig. 2a) indicates the occurrence of chemical changes from -S-H and -S-S- to $-\text{SO}_3\text{H}$, respectively. The corresponding XPS C1s spectra shown in Fig. 2b further confirm the presence of $-\text{COOH}$ groups in the irradiated surface. As a consequence, the surface water contact angle changed from 170° , characteristic of the superhydrophobic TiO_2 -silica coating (Left bottom panel of Fig. 1), to about 30° after the UV irradiation. Thus, the initially hydrophobic coating was converted into a hydrophilic surface through the photochemical reactions.



Scheme 1 The superhydrophobic coating formation.

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† Electronic supplementary information (ESI) available: Experimental section, FTIR, SEM, TEM, contact angles, XPS, XRD, UV transmittance and videos of directional water transfer through the fabric. See DOI: 10.1039/c0jm02364g

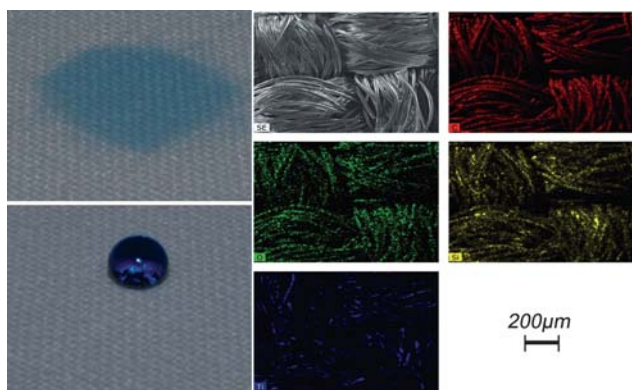


Fig. 1 Digital photographic images of water spreading in the plain-weave polyester fabric (*Top left*) and forming a water droplet on the TiO₂-silica coated polyester fabric (*Bottom left*), and SEM-EDX mapping of element C, O, Si, S and Ti on the coated fabric (*Right panel*).

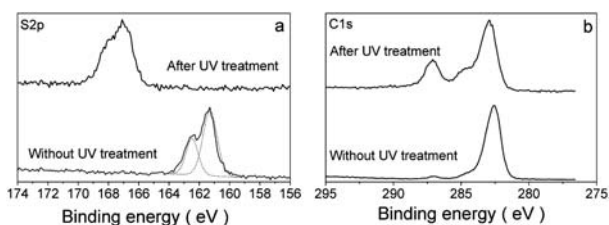


Fig. 2 High-resolution XPS spectra of a) S2p and b) C1s for the coated fabric before and after the UV irradiation.

Due to the UV-irradiation, the directly irradiated fabric side turned hydrophilicity. Water droplets can readily spread over the UV-irradiated fabric surface, but cannot transfer across the fabric through its thickness (Fig. 3, 1~6). Similar results were observed by repeatedly dropping water droplets onto the UV-irradiated side of the TiO₂-silica pre-coated fabric. When water was dropped onto the un-irradiated, superhydrophobic backside of the same fabric membrane, however, a very fast through-thickness water transfer was observed (Fig. 3, 1'~6'). Movies in the Supplementary Information shows such a water transfer phenomenon in real-time. These observations clearly show a through-thickness directional water transfer from the TiO₂-silica coated (hydrophobic) to the UV-irradiated (hydrophilic) side of the fabric.

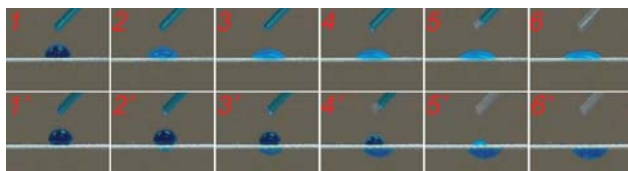


Fig. 3 Still frames from digital videos of a blue-coloured water droplet ($\sim 40 \mu\text{L}$, in which 50 mg/L of *Reactive blue 2* was used to guide the eye, but the presence of the dye showed no influence on contact angles of the water drop on the fabrics) on the TiO₂-silica-coated and UV-irradiated polyester fabric: (*Top*) dropped on the UV-irradiated fabric surface (image 1~6, time interval is 0.12 s), and (*Bottom*) dropped on the back side (image 1'~6', time interval is 0.28 s).

To confirm the through-thickness asymmetric UV treatment, we applied the same UV treatment to a double-layered fabric consisting of two TiO₂-silica-coated polyester fabrics. We found that the water contact angle of the front surface of the second layer fabric, which was in contact with the fabric layer receiving the UV irradiation, remained almost unchanged ($\sim 160^\circ$) after the UV treatment. The small reduction in the surface superhydrophobicity with respect to the pristine TiO₂-silica-coated polyester fabric (*i.e.* 170°) suggests that the UV beam has been substantially weakened after passing through the first layer fabric.

The surface water contact angle measurements on the top side for each of the constituent layers in the UV-irradiated double-layered polyester fabrics clearly show the presence of a surface tension gradient across the fabric thickness and the feasibility to adjust the hydrophobicity and hydrophilicity by changing the UV irradiation period (Note that the surface contact angle measurement for the un-irradiated side of a single-layered TiO₂-silica-coated fabric after the UV irradiation is difficult due to the fast water transfer through the fabric).

The wetting depth of the single layer TiO₂-silica-coated polyester fabric after the UV irradiation was measured by X-ray microtomograph (*micro-CT*). As shown in Fig. 4, the sliced 3D images at different fabric depth show different degrees of wetting. One side of the fabric was totally wetted by water, while the opposite side was dry. The degree of water wetting gradually decreased with increasing distance from the UV-irradiated hydrophilic surface, and no wetting was evident at a depth larger than 246 μm , which is less than the half of the fabric thickness.

To further characterise the directional water transfer across the asymmetrically modified fabric, we measured the initial pressure required to allow water to break through the fabric (critical break-through pressure, P_c). To facilitate understanding, the pressure unit cmH_2O is used. As shown in Fig. 5a, at least 18 cmH_2O of pressure was needed to transfer water from the hydrophilic to the hydrophobic side through the TiO₂-silica-coated polyester fabric after the UV irradiation for about 60 min, whereas the corresponding P_c was only

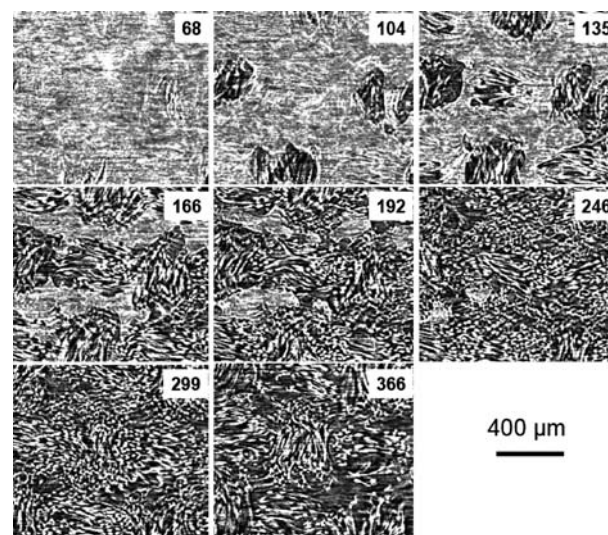


Fig. 4 Sliced *micro-CT* images of the UV-irradiated fabric. The inset numbers are the distance from the UV-irradiated hydrophilic fabric surface to the slice.

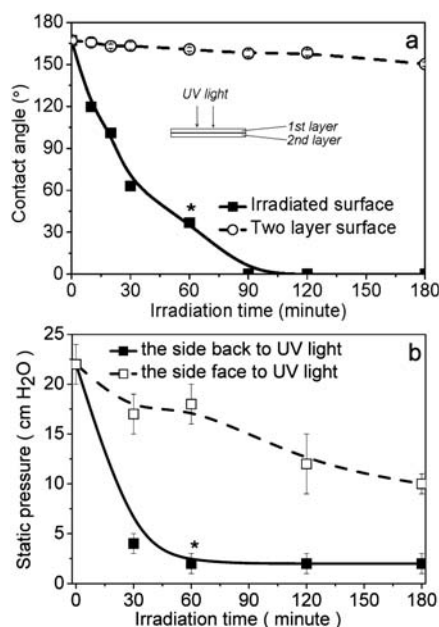


Fig. 5 a) The surface water contact angles of the polyester fabrics after different irradiation periods. b) The minimum pressure required for water to break through the polyester fabrics. The contact angles on the UV-irradiated surface and the breakthrough pressure for the sample shown in (Fig. 3 & 4) have been marked by * in the figures.

2 cmH₂O for water transport through the same fabric from the hydrophobic to the hydrophilic side (*i.e.*, the opposite direction). This clearly indicates a strong propensity for unidirectional water transfer through the TiO₂-silica-coated and UV-treated polyester fabric. For comparison, P_c for the uncoated pristine polyester fabric was also measured about 2 cmH₂O, and there is no fabric side-dependence or directional effect. For the TiO₂-silica-coated polyester fabric without the UV treatment, P_c was about 22 cmH₂O and no directional effect was observed either (Fig. 5b).

Due to the difficulty in directly observing water transfer through fabric materials, the actual directional water-transfer mechanism of the treated fabrics has not been clear, but warrant further research. Two possible mechanisms are proposed here. One is based on dragging of water from hydrophobic layer towards hydrophilic pore section. When the dragged droplet attaches to the hydrophilic pore surface, the hydrophilic pore will draw the droplet towards the hydrophilic section, resulting in directional water transfer. It is also possible for water to evaporate from a droplet on hydrophobic pore surface and condense on the hydrophilic pore section. Induced by the hydrophilic pores, the evaporation and condensation could be

accelerated. When the high concentration of moisture bridges the water droplet on hydrophobic side and the wetted hydrophilic pore section, directional water transfer is triggered.

While a polyester fabric was used as the model sample in this study, the solution coating and photochemical treatment may be a general approach towards the development of various fabrics with such a novel water-transfer capability. The directional water-transfer fabrics should be able to remove sweat effectively from the body side, which is very useful for sportswear, soldier's clothing, and daily life applications.

Funding support from Australia government through DSTO, Australian Academy of Science and Deakin University is acknowledged.

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