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PAPER

Tunable wettability *via* counterion exchange of polyelectrolyte brushes grafted on cotton fabric†

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Poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] (PMETAC) was grafted onto cotton fabric by surface-initiated atom transfer radical polymerization (SI-ATRP). The wettability of the as-prepared cotton fabric surface can reversibly switch between superhydrophobic (154°) and superhydrophilic ($< 5^\circ$) by exchanging the counterions between perfluorooctanoate anion (PFO) and SCN^- , respectively. The effect of solvent on the counterion exchange was investigated, and we found that water was a poor solvent for counterion exchange, while other solvent systems, such as water/methanol, methanol and acetone, were good solvents for counterion exchange in this study. Moreover, the effect of the anions on the wettability of the PMETAC films was also studied. The as-prepared cotton fabric with controllable wettability may find application in soft superhydrophobic materials and multifunctional textiles.

Introduction

Smart surfaces with dynamically controllable properties in response to various external stimuli have received great attention in recent years, due to their wide use in controllable adsorption and desorption of proteins and cells, drug delivery, biosensors, microfluidics, smart windows and so on.^{1–4} Controllable surface wettability by external stimuli is a very important aspect in the preparation and application of smart surfaces, because of their special use in biological applications and self-cleaning materials.⁵ Many kinds of external stimuli, such as temperature,^{6–8} pH,^{9–10} UV light,^{11–12} solvent,¹³ electrochemical potential,¹⁴ multistimuli combining two or more of the above stimuli and so on,^{15–17} can be used to adjust the wettability of the smart surface. Jiang *et al.*⁸ grafted poly(*N*-isopropylacrylamide) (PNIPAAm) onto a rough silicon substrate by ATRP, demonstrating that reversible switching between superhydrophobicity and superhydrophilicity can be achieved by controlling the temperature and the roughness of the substrate, which can enhance the stimuli-responsive wettability. Stratakis *et al.*¹⁰ prepared a pH-responsive polymer surface by “graft from” poly(2-(diisopropylamino)ethyl methacrylate) onto a rough surface. The pH-responsive polymer surface can reversibly switch from superhydrophilic at low pH to superhydrophobic at high pH.

Counterion exchange is a simple and versatile method for adjusting surface properties and has been intensively studied in

recent years.^{18–21} The layer-by-layer self-assembly (LbL) technique is often used in preparing surfaces with controllable wettability by counterion exchange. Wang *et al.*¹⁸ deposited poly(diallyldimethylammonium chloride) (PDDA) and poly(sodium 4-styrene sulfonate) (PSS) multilayers on a silicon surface by a LbL technique and the water contact angle (CA) of the obtained polyelectrolyte multilayer film can change from about 10° to 120° by replacing the Cl^- with PFO. Yang *et al.*²¹ prepared the (PDDA/PSS)_{*n*}PDDA multilayer on cotton fabric by a LbL method, which had reversible hydrophobic and oleophobic properties through counterion exchange. Through a LbL method, the wettability of the LbL films might be adjusted, but the changed range of the wettability is rather limited in most conditions.

SI-ATRP is a useful method for grafting polymer brushes onto a solid surface, by which polymer chains are attached through an anchor group to a surface. Recently, a few polyelectrolyte brushes with controllable wettability, by choosing the proper counterions, which were prepared by SI-ATRP, have been developed.^{22–24} However, most of the reports for surfaces with controllable wettability are also rather limited in the change of the CA. In this study, cotton fabric was chosen to “graft from” PMETAC by SI-ATRP, and the reversible switch between superhydrophilic and superhydrophobic can be realized by counterion exchange in proper solvent. The CA can change from 154° to almost 0° when the counterion changed from PFO to SCN^- . The effect of the solvent on the counterion exchange was studied and we found that the solvent system had a great effect on wettability modulation of the PMETAC brush film, which was little studied in the previous reports. Moreover, the influence of the counterions on the wettability of the PMETAC films was also studied.

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The cotton fabric is a soft and folding substrate, and the wettability of the surfaces can be adjusted by counterion exchange, which can broaden the application of superhydrophobic materials.

Experimental section

Materials

Cotton fabrics used in this experiment were purchased from a local fabric store. Before use, the cotton fabrics were immersed in 0.2 M NaOH aqueous solution for 30 min, cleaned by ultrasonic washing in acetone and water, and dried at 120 °C. METAC (Tokyo Chemical Industry Co., Ltd, 80%) was used as received. Cu^IBr (Sinopharm Chemical Reagent Factory, 98.5%) was washed with acetic acid several times until no green color and then washed with ethanol until the pH reached 7. Tetrahydrofuran was dried with Na for 24 h and freshly distilled before use. Cu^{II}Br₂, 2-bromoisobutyl bromide, ethyl 2-bromoisobutyrate and 4-dimethylaminopyridine (DMAP) were purchased from Alfa Aesar and used without further treatment. Other reagents used in this experiment were used as received.

Substrate preparation and modification. Cotton fabrics were cut into 4 cm × 4 cm pieces. Two pieces of cotton fabric were immersed into a toluene solution with (3-aminopropyl) triethoxysilane (APS) 400 μL for 6 h. The cotton fabrics were washed with toluene for several times and dried at 60 °C overnight. The cotton fabrics modified with APS were immersed in the mixture of THF (20 mL), triethylamine (0.414 g), 2-bromoisobutyl bromide (0.915 g) and a catalytic amount of 4-dimethylaminopyridine. The reaction proceeded at room temperature for about 12 h. After the reaction completed, the cotton fabrics were washed with THF several times and dried at 60 °C. The cotton fabrics immobilized with 2-bromoisobutyl bromide were obtained.

SI-ATRP

The grafting of the PMETAC on cotton fabric by SI-ATRP followed the method reported previously.²⁴ METAC (10.37 g, 40 mmol), methanol (8 mL) and H₂O (2 mL) were added into a flask, and degassed with N₂. Cu^{II}Br₂ (0.0247 g, 0.11 mmol) and Cu^IBr (0.157 g, 1.1 mmol) were added to the flask, and the solution was bubbled with N₂ for 30 min. The initiator modified substrates (4 cm × 4 cm × 2) were immersed into the above mixture and degassed for another 10 min. The flask was sealed with a rubber septum and degassed by two freeze-pump-thaw cycles. 2,2'-dipyridyl (0.416 g, 2.7 mmol) was dissolved in 1 mL methanol and a certain amount of ethyl 2-bromoisobutyrate was added to the reaction mixture with a syringe when the reaction mixture was frozen in liquid nitrogen and back-filled with nitrogen. Then, the polymerization solution was degassed by another three freeze-pump-thaw cycles, and left at 20 °C for 20 h. After the polymerization completed, the cotton fabrics were washed with methanol for two times and H₂O for three times, and dried at 60 °C.

Counterions exchange

All the counterion anions were at a concentration of 0.1 M in this work, and different solvent systems (water, water/methanol

mixture, methanol and acetone) were selected. The PMETAC modified cotton fabric was immersed in NaPFO solution for 1 h and washed with water five times, and then dried at 60 °C. Then the PFO bearing films were dipped into the other anions, such as NaSCN, NaCl, NaPF₆, and LiClO₄ for 3 h, and rinsed with a large amount of water five times and then dried at 60 °C. The cycles of the counterions exchange were repeated several times by immersing the samples into different anion solutions.

Characterization

CAs of the cotton fabrics surfaces were measured by DSA 100 optical contact-angle meter (DSA 100, Kruss company, Ltd, Germany) at room temperature and the average CA values were obtained by measuring the same sample at five different positions with 5 μL water droplets. Because the protruding fibers of the cotton fabrics have some elasticity and can exhibit force on the water droplet, it is difficult to get accurate values for advancing and receding water contact angles.^{25–26} So only the static water contact angles are reported here. The microstructures of samples were observed by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Japan). The chemical composition of the prepared samples were confirmed by X-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron spectrometer (Perkin-Elmer, USA) using an AlKα line excitation source with the reference of C1s at 285.0 eV.

Results and discussion

Cotton fabric is widely used in our daily life and shows hydrophilic properties. Cotton fabric with superhydrophobic properties has attracted great attention in recent years because of its wide use in outdoor sporting textiles, multifunctional textiles, soft superhydrophobic materials and so on.^{25,27} In this work, cotton fabric was used as a substrate for grafting the polymer brushes, because there were a large number of hydroxyl groups and the surface of the cotton fabric was rough and soft. PMETAC brush was “grafted from” onto the cotton fabric by SI-ATRP. Fig. 1 showed the XPS spectra of the original cotton fabric and the cotton fabric grafted with PMETAC brush. The original cotton fabric only contained C and O elements, and the little Si2p peak at 102.4 eV was attributed to the impurity of the cotton fiber. As shown in Fig. 1b, the N1s peak at 402.2 eV and Cl2p at 197.8 eV demonstrated the presence of PMETAC, indicating that the PMETAC was successfully grafted onto the cotton fabric. From the SEM images of Fig. 2a and b, it can be seen that the original cotton fabric was tightly woven and had a fibrous structure, and nanogrooves can be observed on the fiber. The nanogrooves on the fiber disappeared after the modification of the PMETAC, and the fiber was relatively smooth due to the coverage of a polymer film layer on the surface, as shown in Fig. 2c. This further demonstrated the grafting of the PMETAC onto the cotton fabric.

It has been previously reported that through adjusting the counterions, the wettability of the polyelectrolyte brushes films can be controlled.^{22,23} The PMETAC brush film showed superhydrophilic properties, and the CA was about 152° after

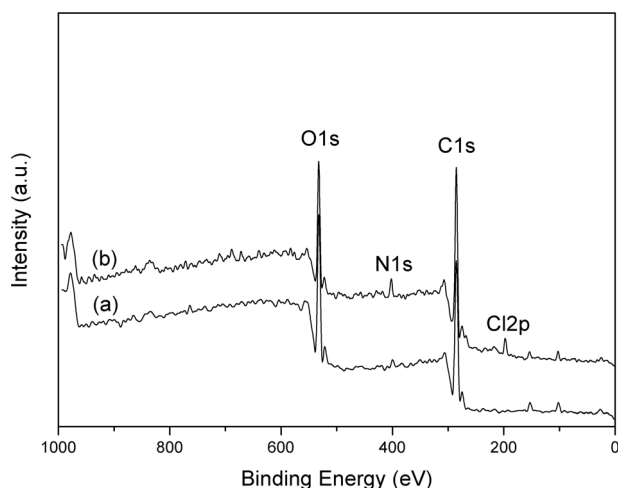


Fig. 1 XPS spectra of (a) the original cotton fabric and (b) the cotton fabric modified with PMETAC.

immersing in 0.1 M NaPFO aqueous solution for 1 h. The PMETAC film with PFO showed strong adhesion and a 5 μ L water drop could adhere to the cotton fabric even if the substrate was put upside down. However, the wettability of the PMETAC surface showed no change after exchange from PFO to SCN^- in water for 3 h. XPS spectra was used to confirm the counterion exchange, and the change of the atomic concentration on the surface of the sample was shown in Table 1. Before the XPS spectrum test, all the samples were washed with distilled water using the Soxhlet apparatus for more than 12 h in order to remove the absorbed free polymer and anions. The PFO-bearing film contained an atomic concentration of F of about 29.19%, and the atomic concentration of F decreased slightly to 22.22% after the exchange from PFO to SCN^- , as shown in Fig. 3, indicating that the counterion exchange was incomplete within 3 h in water. Using water as a solvent, due to the existence of the large amount of PFO on the surface, the CA of the PMETAC film showed superhydrophobic properties even after the exchange with SCN^- . When the PMETAC brush film bearing with PFO was immersed in SCN^- aqueous solution for 72 h, the CA of the surface remained above 150° , demonstrating that water was the poor solvent for counterion exchange. According to the study of Chi *et al.*,²⁸ the solvent system could affect the exchange rate of counterions on surfaces. So a series of solvents, including water/methanol mixture, methanol and acetone, were selected in this work. The PMETAC brush film can change from superhydrophobic to superhydrophilic after counterion exchange between PFO and SCN^- in the proper volume ratio of water/methanol mixture, methanol and acetone.

Table 1 The atomic concentration of the PMETAC brush film bearing with PFO and SCN^-

Solvent		Atomic concentration (%)				
		Counterions	C	O	F	N S
water	PFO		49.00	18.83	29.19	2.98 0
	SCN^-		51.29	23.09	22.22	2.23 0.16
water/methanol (1 : 1 v/v)	PFO		53.35	19.64	24.55	2.46 0
	SCN^-		64.72	28.57	2.85	3.43 0.43
methanol	PFO		48.57	19.68	29.34	2.41 0
	SCN^-		59.45	31.24	4.15	4.48 0.69
acetone	PFO		49.36	22.74	24.85	3.05 0
	SCN^-		66.16	28.69	1.45	3.25 0.45

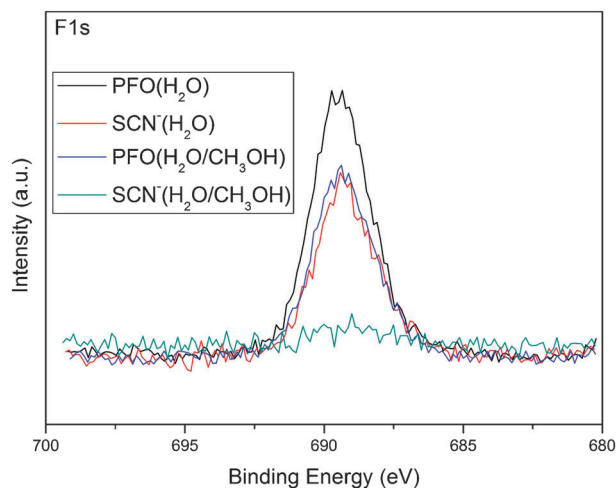


Fig. 3 XPS spectra in the F1s region of the PMETAC brush films bearing PFO and SCN^- in different solvents (water, water and methanol mixture (1 : 1 v/v)).

From Table 1, it can be seen that the atomic concentration of F decreased to 2.85% and the S increased to 0.43% after replacing the PFO with SCN^- , suggesting the exchange from PFO to SCN^- was almost complete in 3 h in water/methanol mixture (1 : 1 v/v). Due to the low surface content of N and S on the as-prepared cotton fabric, the atomic concentration of N and S may be not accurate. The PMETAC films can switch from superhydrophobic (154°) to superhydrophilic ($<5^\circ$) by counterion exchange in a water/methanol mixture (1 : 1 v/v). Different volume ratios of H_2O and CH_3OH were selected to study the wettability change of PMETAC films bearing PFO and SCN^- . When the volume ratio of H_2O and CH_3OH was 3 : 1, the wettability of the PMETAC films after exchange from PFO to SCN^- showed almost no change (seen the supporting information†). However, the wettability switch can be realized

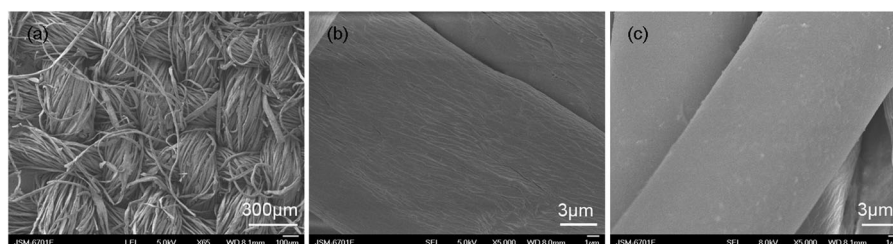


Fig. 2 FE-SEM images: (a) original cotton fabric, (b) high magnification of (a), (c) cotton fabric modified with PMETAC.

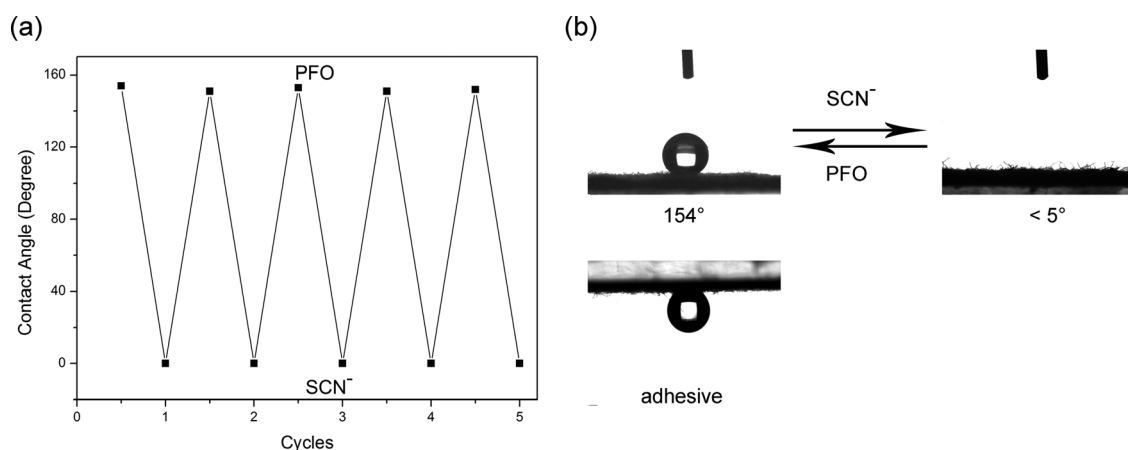


Fig. 4 (a) Reversible wettability change of the PMETAC films by repeated counterion exchange between PFO and SCN^- ; (b) the photographs of water drops on PMETAC brush films bearing PFO and SCN^- respectively, and the adhesive properties of PMETAC brush film bearing PFO.

when the volume ratio of CH_3OH further increased (1 : 1 v/v). These results further showed that water was a poor solvent for counterion exchange. Using methanol and acetone as solvents, the counterion exchange between PFO and SCN^- can be complete, as shown in Table 1. The CAs of the as-prepared surfaces bearing PFO were 154° in methanol and 151° in acetone, and the as-prepared surfaces both showed superhydrophilic properties after exchange from PFO to SCN^- . The results so far have shown that the solvent system had a great effect on wettability modulation of the PMETAC film on cotton fabric.

In a previous study, Lee *et al.*²⁰ demonstrated that water was the most appropriate solvent for direct counterion exchange on the surface of imidazolium ion-terminated self-assembled monolayers on Au. However, in this experiment, water was the poorest solvent for counterion exchange, and water/methanol mixture, methanol and acetone were the appropriate solvents. As we known, the nonaqueous solvents and mixed solvents have a profound effect on the selectivity of both anion and cation exchange and have been studied for many years.²⁹ The difference between the counterion exchange in water and organic solvent (water/methanol mixture, methanol and acetone) may be due to the reason that the hydrophobic PFO ion in water rejected the surrounding water molecules and was poorly solvated. So the large hydrophobic ions are usually unstable in water. Using water as a solvent, large and poorly hydrated ions (PFO) were absorbed by the PMETAC films better than small and well-hydrated ions (SCN^-), so the exchange from PFO to SCN^- was incomplete.³⁰ While, in organic solvent, *e.g.* water/methanol mixture, methanol and acetone, the PFO ions were more stable, so the situation was completely different, and the exchange between PFO and SCN^- was reversible in a certain time.

The influence of the counterions on the wettability of the PMETAC films was studied using a water and methanol mixture (1 : 1 v/v) as solvent. The CAs of the PMETAC films bearing Cl^- , PF_6^- , ClO_4^- and SCN^- were all smaller than 5° , indicating the superhydrophilic properties of the prepared PMETAC films. This may be due to the hydration capability of the anions combined with the capillary effect of the cotton fabric substrate.^{18,31}

The PMETAC films can reversibly switch between superhydrophobic to superhydrophilic by consecutive counterions exchange between PFO and SCN^- , and the CA showed almost no difference, even after five cycles, indicating the reversible switch of the wettability. As shown in Fig. 4, using water/methanol mixture (1 : 1 v/v) as solvent, the PMETAC films bearing PFO showed a CA about 154° , indicating the superhydrophobic property of the films. The CA of the PMETAC film bearing PFO showed an excellent stability with time, and the CA remained above 150° after 20 min (seen Fig. S1 in the supporting information†). A 5 μL water drop could adhere to the as-prepared cotton fabric even if the substrate was put upside down, indicating the strong adhesion between the water droplet and the PMETAC films bearing PFO. After exchange from PFO to SCN^- , the PMETAC film showed superhydrophilic properties. The strong adhesion of the PMETAC film bearing PFO is mainly governed by two factors: the chemical composition and the roughness of the surface. The hydrophilic groups in the PMETAC molecule may generate polar interactions with water, which contributes part of the adhesion.³² The surface roughness of the prepared cotton fabric is another reason for strong adhesion to the cotton fabric. When a liquid droplet wets a rough surface, there are typically two states: the Wenzel states and the Cassie state. In the Wenzel state, the liquid pins on the surface in a wet-contact mode, and is difficult to slide off the surface.³³ In the Cassie state, the liquid adopts a non-wet-contact mode, and can roll off easily. As can be seen from Fig. 2, the cotton fabric grafting with PMETAC presented a macro and micro structure, but the single fiber is relatively smooth. The water droplet lying on the prepared cotton fabric fully penetrated into the surface micro structures, which led to the high adhesion of the prepared cotton fabric and exhibited the Wenzel state.

Conclusion

In conclusion, PMETAC brushes were grafted onto cotton fabric by SI-ATRP. The PMETAC films can switch between superhydrophobic and superhydrophilic reversibly by counterion exchange from PFO to SCN^- , respectively. During the counterion exchange process, the solvent affected the rate of anions exchange,

and it was found that organic solvents, such as water/methanol, methanol and acetone, were good solvents for anion exchange. The PMETAC films bearing Cl^- , ClO_4^- , SCN^- , and PF_6^- all showed superhydrophilic properties. The cotton fabric substrate is abundant in nature, commonly available and environmentally friendly. The as-prepared cotton fabric with tunable wettability by counterion exchange may be used in soft and folding superhydrophobic materials, multifunctional textiles, which could broaden the application of superhydrophobic materials.

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