Article

Strongly Hydrophobic and Superoleophilic PMMA Based Nanocoated Cotton Fabrics

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Abstract: Oil–water separation is among the critical issues worldwide due to recent massive oil spills. Moreover, domestic and industrial water pollution due to oil discharge affects marine and aquatic life. Cotton is the most predominant fiber globally because of its use as a principal and popular clothing material. Cotton is also the leading raw material for technical and functional textile applications. In this study, the fabric was cured with poly (methyl methacrylate) (PMMA) nanoparticles to develop hydrophobic and oleophilic cotton fabrics. The dehydrating agents, *N,N'*-dicyclohexylcarbodiimide (DCC) and dimethyl aminopyridine (DMAP), were used to catalyze the esterification. The results proved that the excellent hydrophobicity of modified cotton fabric provides a water contact angle higher than 140°. In addition, Fourier transforms infrared (FTIR) spectroscopy, as well as X-ray photoelectron spectroscopy (XPS) analysis, confirmed the fabric surface modification. Surface morphological analysis by scanning electron microscope (SEM) revealed the uniform rough surface structure of the modified fabric with nano-coating. The modified fabric resulted in the high separation efficiency of oil and water, suggesting this strategy to be suitable for advanced oil–water separation.

Keywords: cotton fabrics; PMMA nanoparticles; oil–water separation; superoleophilicity; strongly hydrophobicity

1. Introduction

Many natural surfaces, especially lotus leaves, which are incredibly water repellent, have recently attracted great interest [1]. Due to the increasing amount of oil-containing wastewater from our daily life, oil spills, chemical leaks and industries discharges, which have caused a severe threat to the environmental and ecological system, oil–water separation has gained much attention around the globe [2–4]. Moreover, people will inevitably produce oily sewage in industries and routine life. If it is not treated well before discharge, it will impact on the environment. Directly discharging this oily sewage will further pollute water resources and even damage the ecological environment.

At present, strongly hydrophobic and superoleophilic surfaces are widely used in oil–water separation materials, self-cleaning coatings, and functional textiles with excellent wettability [5–7]. Lately, with the expansion of the leisure and outdoor sports textile market, the demand for hydrophobic fabrics is also expanding. The hydrophobicity of several fabrics was improved by nanostructures obtained by nanotechnology [8–11]. From a chemical point of view, cotton is a polysaccharide. The properties of these natural polymers can be easily modified with acrylic polymers to obtain useful materials with a

wide range of properties, e.g., hydrophobic, hydrophilic, flame retardant, swelling, heavy metal ions sorbing [12,13]. Cellulose-based materials are the main and popular clothing material with excellent comfort, softness, sustainability, enough tensile strength, and biodegradability; they also have wide applications, and are eco-friendly [14–16]. However, due to the abundant hydroxyl groups on the surface of cellulose materials, they are prone to be soaked and stained by liquids [9]. At present, new methods for preparing strongly hydrophobic cotton fabrics are the sol-gel method, chemical vapor deposition method, dip coating method, and layer by layer assembly method [17–19]. There are numerous types of inorganic nano-sized particles, such as SiO_2 , TiO_2 , and ZnO [20–24]. Surface-modifying chemicals of fluorinated silanes [25–27] or alkylated silanes [28–31]. Although strongly hydrophobic and superoleophilic surfaces have been prepared on the surface of cotton fabrics, there are still many problems. For example, high-cost reagents such as dopamine, graphene, or precious metals are used for surface modification to obtain rough structures [32,33]. In addition, fluorinated compounds and fluoropolymers have attracted much attention due to their shallow surface free energy; since roughening these polymers in a specific way leads to strongly hydrophobicity directly [34–37].

Moreover, in the conventional polymerization of fluoropolymers, a large number of toxic volatile organic compounds are used as solvents, such as tetrahydrofuran (THF), isopropanol and N, N-dimethylformamide (DMF) [38–40]. By virtue of cost-viability and effectiveness for the evacuation and assortment of oil, the use of absorbent materials is considered to be the most appropriate wastewater treatment method. Some spongy materials with poor hydrophobicity retain both water and oil. Due to the absorption of water, they cannot absorb enough oil to reach the maximum capacity, making them unable to effectively remove or separate oil pollutants from water [41–45]. Therefore, strongly hydrophobic and superoleophilic materials, which selectively adsorb oil-based and oil-based organic pollutants and repel water, have attracted much attention due to their efficient and selective removal and separation of oil and water. Thus, the development of oil–water separation materials is of great impact. Moreover, diblock copolymers, poly[(methyl methacrylate)-*b*-(trifluoroethyl methacrylate)] (PMMA-*b*-PTFMA), and diblock copolymer of poly[(methyl methacrylate)-*b*-(lauryl methacrylate)] (PMMA-*b*-PLMA) have been grafted to the surface of cotton fabric to obtain superhydrophobic cotton fabric [46,47]. Recently, Yamashita et al. [48] have developed superhydrophobic and superoleophilic cotton fabrics by surface modification using fluoroalkylated oligomeric silica/triazine derivative, which is rather complex chemistry.

Although many methods have been very successful in simulating strongly hydrophobic surfaces, their success is limited to the formation of rigid substrates, because deformation of the substrate can destroy the hydrophobic properties. However, to expand the application range, it is necessary to prepare flexible hydrophobic and superoleophilic materials. In this work, a cost-effective and straightforward method of developing strongly hydrophobic and superoleophilic cotton fabric using PMMA nanoparticles is reported. More prominently, even after washing several times (~10 times) with water as well as with solvent, the modified cotton fabrics can still keep excellent hydrophobicity without losing tensile strength. Furthermore, the possibility of using strongly hydrophobic and superoleophilic fabric as a filter for the separation of oil from water was explored with high efficiency. The composition and surface morphology of the cotton fabrics treated with PMMA nanoparticles, DCC, and DMAP were characterized using electron microscopy, particle size analysis, X-ray photoelectron spectroscopy, and Fourier-transform infrared spectroscopy. The hydrophobicity of cotton fabrics was evaluated by measuring the contact angles of sessile water drops on the fabrics. Moreover, this method of making hydrophobic and superoleophilic PMMA-based nanocoated cotton fabrics is cheaper and less toxic, making it a promising approach for industrial applications.

2. Materials and Methods

2.1. Materials

Woven cotton fabric with warp and weft counts of 60 s, warp/inch 140, and weft/inch 110 was purchased from Qingdao Dongye Textile Co., Ltd. and used as a substrate. The analytical grade of Methyl methacrylate (MMA), Triethylamine (TEA), ethanol, acetonitrile toluene, and N-hexane were bought from Shanghai Reagent. The commercial-grade of Hydrophobic initiator 2,2'-azodiisobutyronitrile (AIBN) and cross-linker *N,N'*-methylene bisacrylamide (MBA) were purchased from Adamas Pharma, and they were purified by recrystallization in methanol. The analytical grade of Polyoxyethylene-20 (Tween 20) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich and were used as received. The analytical-grade of dehydrating agents, *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), and dimethyl aminopyridine (DMAP) were purchased from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). The dyes, Methylene blue and Oil Red O, were purchased from Damas-Beta. Nitric acid (HNO₃), H₂O₂, and dichloromethane (DCM) were bought from Shanghai Titan Technology Co. Ltd. (Shanghai, China). Vegetable and vacuum oils were purchased from the local market of Shanghai. Deionized distilled water was used in all experiments.

2.2. Synthesis of PMMA Nanoparticles

First, 55 mL of HNO₃ aqueous solution (pH 1.8) was placed in a three-necked round-bottomed flask (100 mL) equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet for 30 min. Later, 90 mg of SDS diluted in water, 80 mg of AIBN diluted in DMF, and the solution were stirred at a constant rate (300 rpm); after that, the temperature was increased to 70 °C. Then, 1 mL MMA was injected continuously in 20 min by ALC-IP 800 injection pump. After one hour, 0.22 mL of Tween 20 and 120 g of MBA were injected successively, with an interval of 10 min. After 5 min, 300 g of SDS was gradually inserted over a period of one hour. The reaction continued for 3 h.

2.3. Pre-Treatment of Cotton Fabric

The desired, scoured and bleached fabric was washed and rinsed with detergent and deionized water to remove the surface impurities. Then the washed fabric was soaked into acetone for 10 min and gently rinsed with deionized water, followed by drying at 80 °C for 20 min. The pre-treated cotton fabric was cut into 5 × 5 cm² small squares.

2.4. Fabrication of Hydrophobic Cotton Fabric

The fabrication process of strongly hydrophobic and superoleophilic cotton fabric is illustrated in Figure 1. The dried fabric was soaked into a dispersion of synthesized PMMA nanoparticles at room temperature for 5 min and dried for 1 h at 50 °C in a laboratory oven. After that, the fabric was put into a closed vessel containing DCC/DMAP in ethanol solution at 50 °C for 32 h, later on dried for 1 h, and then rinsed successively with ethanol and water to remove an excessive amount of DCC and physically-absorbed nanoparticles. Finally, the fabric was dried at 50 °C for another 1 h.

Figure 1. Flow diagram of the fabrication process of strongly hydrophobic and superoleophilic cotton fabric.

2.5. Characterization

The size and distribution of PMMA nanoparticles were measured by a Zeta Potential and Particle Size Analyzer (DTS1060, Malvern, UK). The surface morphology of cotton fabric before and after applying the PMMA nanoparticles on the cotton fabric was analyzed by field emission scanning electron microscopy (FESEM SU8010 Hitachi) to observe the changes of the fabric surface. The wettability of the cotton surface was determined by the water contact angle using a fully automated video contact angle measuring instrument (OCA40Micro); the water contact angle was determined at different positions, and then the average value was taken. The infrared absorption spectra from 4000 cm^{-1} to 650 cm^{-1} of the pristine and modified cotton fabric were measured by a Fourier transform infrared spectrometer (Nicolet 6700) using an attenuated total reflection (ATR) mode. The surface elements of pristine fabric and modified cotton fabric were also measured by X-ray photoelectron spectra (Escalab 250Xi). The tensile properties of both fabrics were tested on Materials Testing, Machine Tinius Olsen according to ASTM Standard test method [49], where the specimens 100 mm width and 150 mm length were mounted in clamps jaws with speed for the measurement of tensile strength was 300 mm/min, and the distance between clamps was 75 mm. Oil absorption capacity, the test process of the total oil absorption by using the ASTM Standard test method [50], that can be calculated by formula $N = W - W_0$ where N is final weight, W is weight absorbed by the fabric and W_0 initial weight of the fabric.

3. Results and Discussion

3.1. Effect of Reaction Time and Size of PMMA Nanoparticles

PMMA nanoparticle dispersions were optimized for contact angle by varying reaction time and concentrations to achieve the change in particle size of as-prepared nanoparticles. It can be noticed in Figure 2A that as the reaction time increased from 23 to 32 h, the contact angle increased, and it reached a maximum at 142° . However, as the reaction time increased from 32 to 38 h, the contact angle decreased slightly to 137° . Moreover, the concentration of nanoparticles was changed with a constant reaction time of 32 h; it was found that as the particle size decreased, the contact angle of the modified cotton increased. This is obvious with higher surface area as well as higher surface irregularity for smaller particle sizes. The maximum contact angle was 142.5° ; thus, 32 h reaction time and 159.9 (d.nm) particle size were selected for all further experiments.

Figure 2. Effect of the reaction time (A) and the size of PMMA nanoparticles (B) on the contact angle of the modified fabric cotton.

3.2. Surface Morphology

The surface morphologies of pristine and modified fabrics at different magnifications were observed using FESEM (refer, Figure 3). Before the surface modification, the surface of the fabric was relatively smoother; however, after modification, nano-sized roughness could be observed on the fabric

surface. On further magnification, the PMMA nanoparticles were seen on the surface of the fibers that resulted in nano-sized roughness, which is responsible for the hydrophobicity of the fabric.

Figure 3. FESEM images of (A–C) pristine (D–F) modified cotton fabric.

3.3. FTIR Spectra

The FTIR spectra of pristine and modified cotton fabric are shown in Figure 4. In the spectrum of pristine cotton fabric, the stretching vibrations of -OH , $\text{-CH}_2\text{-}$, and C-O-C appeared at 3337 cm^{-1} , 2998 cm^{-1} , 1162 cm^{-1} , 1110 cm^{-1} , and 1054 cm^{-1} , respectively. In the spectrum of modified cotton fabric, new peaks appeared at 1786 cm^{-1} , 1803 cm^{-1} , 1858 cm^{-1} , and 2949 cm^{-1} . They are the stretching vibrations of anhydride carbonyl, ester carbonyl, carboxy carbonyl, and methyl. Furthermore, it can be seen that the hydroxyl peak in the modified FTIR has become shallower for the modified fabric showing the relative lesser hydroxyl groups available on the treated surface.

Figure 4. FTIR spectra of the pristine and modified cotton fabric.

3.4. Tensile Strength

The force–elongation curve of pristine and treated fabric, and the breaking force and elongation data were assembled in Table 1. It can be seen that after modification, the breaking force of the fabric decreased slightly, while the breaking elongation of the fabric increased somewhat, indicating that the treatment had little influence on the mechanical property of the cotton fabric.

Table 1. Breaking force and elongation of pristine fabric and modified fabric.

Sample	Breaking Force (N)	Breaking Elongation (%)
Pristine Fabric	562 ± 20	16 ± 2
Modified Fabric	546 ± 18	19 ± 1

3.5. Hydrophobicity

When the original and modified cotton fabrics were placed onto the water surface, from Figure 5, it was seen that the pristine one quickly drowned to the bottom, while the modified one floated on the water surface. The static water contact angles of the pristine and modified cotton fabrics were determined by dropping 5 μ L water droplets on the surface of the fabrics at a different position. The droplet readily permeates into the pristine fabric to a full extent, indicating the excellent hydrophilicity of the pristine cotton fabric. In contrast, the water droplet could stay on the surface of the modified fabric for a long time (12–15 min at least) with the contacting angle more than 140°, indicating the excellent hydrophobicity of the modified cotton fabric. The PMMA-coated cotton fabrics can float on the surface of the water for a very long time (more than a day), while pristine settle down in the water.

Figure 5. (A) Water droplet (dyed with methylene blue) and oil droplet (DCM dyed with Oil Red O) on the (a) pristine and (b) modified cotton fabric after ten washes (B) The modified fabric floating on the surface whereas pristine sunk.

3.6. XPS Analysis

The chemical compositions of the original and PMMA coated cotton fabrics were characterized by XPS measurement. The XPS were utilized to investigate the chemical constituent elements of the carbon, oxygen and nitrogen. Figure 5 and Table 2 shows the XPS spectra of the pristine cotton fabric and the cotton fabric modified with PMMA nanoparticles. Compared with the pristine cotton fabric, modified fabrics have higher carbon content (74.76%) and lesser oxygen content (22.24%). This is due to less hydroxyl group being left after the surface modification. In addition, nitrogen-related bands at 401.4 eV in modified fabric arise from C=N in the carboimide from DCC [51]. The convolutions (in O1s peak) are due to surface modification of cotton fabric, refer Figure 6B. The above XPS results endorse the formation of the PMMA coated layer on the cotton fabric surface.

Table 2. Atomic percentage and binding energy (BE) of elements O, C, and N of pristine and modified fabrics.

Element	Atomic (%)		BE(eV)	
	Pristine	Modified	Pristine	Modified
O _{1s}	59.61	22.24	533.15	532.26
C _{1s}	38.82	74.76	286.66	284.98
N _{1s}	1.57	3.00	401.6	399.29

Figure 6. XPS results of (A) pristine and (B) modified cotton fabric.

3.7. Oil–Water Separation and Absorption Property

The properties of hydrophobicity and underwater oleophilicity are essential for oil–water separation. The modified cotton fabric with exclusive wetting property can be used for the selective absorption of oil from oil–water mixtures efficiently under various conditions (e.g., floating oil layer or underwater oil droplet or even oil–water mixtures). The modified cotton fabric was used for the selective absorption of the n-hexane layer floating on the water (see Figure 7 and Supplementary video: Video S1). The results showed that the n-hexane floating layer on the water could be completely removed by contact with a small piece of modified cotton fabric.

Figure 7. Modified cotton fabric absorbing floating oil layer (A) n-hexane in the water, (B) placing and immersing of modified cotton fabric on the surface of the water, (C) modified cotton fabric absorbing the n-hexane from water, and (D) n-hexane absorbed by the modified cotton fabric.

The modified cotton fabric was also used for the selective absorption of underwater (DCM) droplets, presented in Figure 8 and Supplementary video: Video S2. The modified cotton fabric completely absorbed dichloromethane leaving behind the clean water. The modified cotton fabric was further used for the separation of DCM/water mixture. After dyeing the DCM with Oil Red O, it was mixed with methylene blue-stained water in an equal volume. Then, the oil–water mixture was poured into a water–oil separation device, shown in Figure 9 and Supplementary video: Video S3, using modified cotton fabric as a separation material and subjected to an oil–water separation test. It was observed that the red DCM passed through the modified cotton fabric to the lower side of the separation device, and the blue water remained on the cotton fabric. Thus, the modified cotton fabric can be successfully applied to an oil–water separation.

Figure 8. The modified cotton fabric absorbed underwater dichloromethane (DCM) droplets (A) DCM drops in the bottom of the water (B) modified fabric dipped into the solution (C) absorbing the DCM from the water bottom (D) DCM absorbed by the modified cotton fabric.

Figure 9. The separation of oil from oil–water mixture by the modified fabric (A) mixture of DCM red oil and blue water, (B) pour into the oil–water separation device, (C) amount of water, and (D) amount of purifying DCM.

3.8. The Oil Sorption Capacity of Pristine and Modified Cotton Fabric for Various Oils

The hydrophobic modification of cotton fabric enables it to repel water and absorb oil. The sorption trial was taken out in pure oil without water to study and relate the maximum oil sorption capacity of pristine and modified cotton fabric for different oils. As presented in Figure 10, the oil sorption capacity of pristine cotton fabric for n-hexane, toluene, dichloromethane, vegetable oil, and vacuum oil is 7.14, 12.79, 13.04, 17.89, and 23.93 g/g, correspondingly. The corresponding oil sorption capacity of modified cotton fabric mentioned oil reaches about 12.59, 15.83, 18.26, 22.75, and 25.24 g/g. Thus, there is a significant improvement in the oil absorbency of modified fabric, and this strategy is beneficial for preparing oil sorbent with better oil sorption performance.

Figure 10. Sorption capacities of pristine and modified cotton fabric for different oils.

3.9. The Separation Efficiency of Modified Cotton Fabric

The result specifies that the modified cotton fabric presented admirable oil–water separation efficiency from 95.5% to 99.0% for selecting oil–water mixtures with diverse viscosities and densities, as shown in Figure 11. The high viscosity of vegetable oil led to relatively low separation efficiency. Overall, the modified cotton fabric showed high selectivity for oil and water, proving its potential to be used as a separation substrate for various water–oil separations.

Figure 11. The separation efficiency of modified cotton fabric.

4. Conclusions

In summary, a practical top-down approach to fabricate strongly hydrophobic and superoleophilic cotton fabric with PMMA nanoparticles using a simple coating method is demonstrated. Through oil absorption and oil–water separation experiments, DCC/DMAP catalytically modified cotton fabric can be successfully applied to oil–water separation when ethanol is used as a solvent, which provides a new choice for oil–water separation materials. This modified fabric can be used to remove floating oil layers and underwater oil droplets, as well as for water–oil separation without affecting the mechanical properties. As a result, the modified fabric shows excellent hydrophobicity even after numerous water and solvent washes. This worthwhile nano-coating offers excellent separation efficiency to prepare functional cotton fabrics.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/10/10/943/s1>, Video S1: Absorption of n-hexane droplet from the water with modified cotton fabric, Video S2: Absorption of underwater dichloromethane droplet from the water with modified cotton fabric, Video S3: Oil–water separation process through the modified cotton fabric.

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