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# Acid and temperature dual-responsive cotton fabrics with polymer coating

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ABSTRACT

This paper reported the development of functional cotton fabrics (CFs) with polymer coating. Copolymer originated from isopropylacrylamide and acrylic acid was synthesized and coated onto CFs using a simple dip-coating process, aiming at enhancing the technical valve of CFs with rectified stability and sensitivity to the environmental factors. Various techniques were employed to study the morphology and properties of cotton textile before and after coating. The results showed that the introduction of copolymer coating significantly enhanced the thermal and chemical stability of cotton textiles. More interestingly, the prepared CFs exhibited active responses to acid and temperature with superhydrophilicity and underwater superoleophobicity. When employing the CFs as a membrane, the fabrics could selectively separate water from crude oil-water mixture with high efficiency, making the material a promising and highly energy-efficient candidate for various applications.

## 1. Introduction

Cotton fabrics (CFs) have been widely used in industry and daily life for centuries due to their softness, breathability, compatibility, non-toxicity as well as low cost [1–3]. The long aspect ratio of individual fiber and porous structure of fiber yarn endow CFs an excellent adsorbent for various applications, such as separation of oil from oil-water mixture [4], removal of metal ions in water [5]. Despite the excellent properties of CFs, some characters like the inherently hydrophobic property, marginal stability to chemicals and poor sensitivity to the environmental factors, confine their wide applications, especially in some high-end areas for personal and functional protection [4–6]. Therefore, effective conversion of CFs into renewable and multi-functional products with value addition has generated considerable academic and industrial attention, not only due to their potential use in thermal, biological and environmental applications, but also to meet the demand arising from the consumers for advanced materials.

Coating process is one of the typical methods to enhance the technical value of CFs, and different polymers have been applied using coating technique over the years to develop functional textiles [7–15]. For example, a Janus cotton fabric was elegantly generated for oil-water separation using a polymer containing poly(dimethyl siloxane) and poly(*N*, *N*-dimethylaminoethyl methacrylate) [11]. Among various polymers, poly(N-isopropylacrylamide) (PNIPAM) is a temperature-responsive material that can be synthesized via free radical polymerization [16]. The material undergoes a reversible volume phase transition at near-physiological temperature, exhibiting dramatic changes in particle size, surface charge density, and water content over a small temperature range [17]. This thermal sensitivity made PNIPAM-based material attractive in applications like tissue engineering [18], drug release [19]. In addition, the availability of isopropylacrylamide to be copolymerized with other monomers, like acrylic acid which exhibited chemical valve effect once polymerized [20], was expected to endow the developed copolymer multi-functionality. However, few reports were found in literatures for the application of such material with controlled wettability for environmental remediation.

Motivated by the above discussion, this paper reported the preparation of CFs with responses to environmental factors by applying a thin layer of copolymer originated from isopropylacrylamide and acrylic acid, aiming at enhancing the functionality of CFs with thermal and chemical valve effect. The responses of prepared CFs stimulated by pH and temperature were evaluated by studying the flux of solutions under different conditions. The mechanism behind the smart functionalities of CFs was discussed, and the application of developed textile for water-oil separation was demonstrated.

## 2. Experimental section

### 2.1. Materials

Commercial CFs were purchased from a local market. N-Isopropylacrylamide (NIPAM) and N, N-Methylenebisacrylamide

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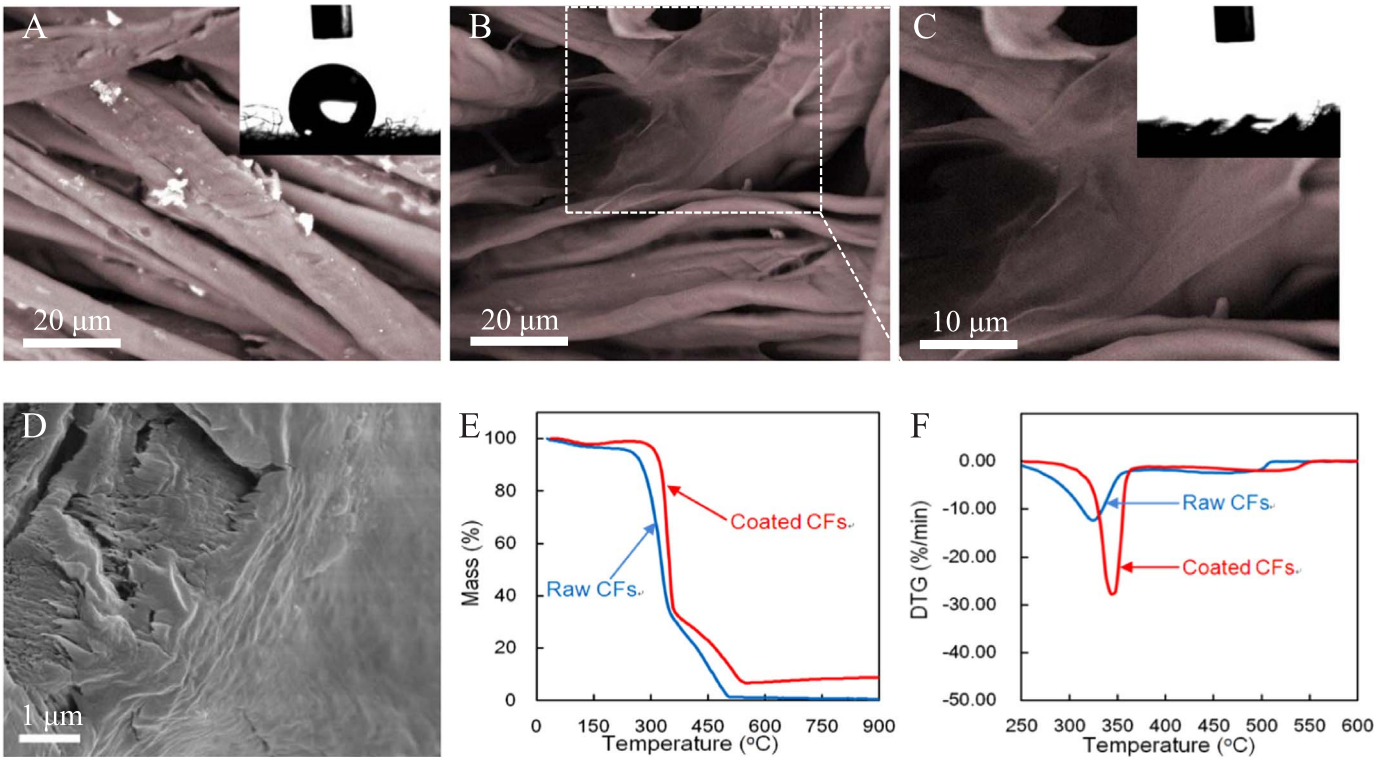


**Fig. 1.** Morphology and thermal stability of CFs before and after polymer coating (A-D: SEM images of Raw and Coated CFs, the insets are CA of Raw and Coated CFs against water; E and F: TGA and DTG curves of samples).

(MBA) were obtained from Sinopharm Chemical Reagent Company, China. Acrylic acid (AA), acetic acid ($CH_3COOH$), sodium dodecylsulfate (SDS) and TritonX-100 were obtained from Tianjin Zhiyuan Reagent Company, China. Sodium hydroxide (NaOH), ammonium persulfate (APS) and sulfuric acid ($H_2SO_4$) were purchased from Tianjin Baishi Chemical Company, China. All chemicals were analytical grade and used directly without further purification. Ultrapure water (Millipore, resistivity > 18.5 MΩ cm) was used in experiment.

### 2.2. Preparation of Coated CFs

Raw CFs were purified in an alkali solution to remove non-cellulosic compounds on fiber surface [21]. For the preparation of Coated CFs, NIPAM (1.40 g) and AA (0.057 g), MBA (0.10 g), SDS (0.050 g), which function as monomers, cross-linker and emulsifier, were dissolved in water (150.0 mL) and heated to 70.0 °C for 0.5 h under a nitrogen purge. Then APS solution (0.10 g, dissolved in 10.0 mL water), an initiator for the polymerization of NIPAM and AA, was added into the above mixture dropwise. This was followed by adding CFs (10.0 cm × 15.0 cm) into the solution and polymerization was carried out under magnetic stir (200.0 rpm) for 6 h. The final product was obtained by processing the sample in an oven at 70.0 °C for 1 h and following rinsing with water for three times. For comparison, copolymer micro-gels consisting of NIPAM and AA blocks were synthesized using the same procedure with absence of CFs.

### 2.3. Characterization

Various techniques were employed to characterize CFs before and after polymer coating. The morphology of sample was observed on a scanning electron microscope (SEM, Phenom XL, Phenom-World BV). The breaking force of sample was measured according to the ASTM Standard (D5035-95). Identical samples with 25.0 mm in width and 100.0 mm in length (gauge length 50.0 mm) were subjected to the tensile load on a universal testing machine (C43-104, MTS). Thermal stability of CFs was studied on a thermogravimetric analyzer (TGA, STA 449F3, Netzsch) with a heating rate of 10.0 °C/min from room temperature to 900 °C in air condition. The wetting behavior of sample against water and oil was evaluated by measuring the contact angle (CA) on a goniometer (XG-CAMA, Shanghai Xuanyichuangxi Industrial Equipment Co., Ltd.). During the measurement of underwater CA, the sample was first immersed in water and then oil droplet was gently deposited on the sample. The image of droplet was captured by a camera equipped on the goniometer. At least five measurements were conducted at different positions of sample, and the average value with standard deviation was reported. The particle size of copolymer micro-gel in water was evaluated by a Zetasizer Nano System (ZS90, Malvern Instruments).

### 2.4. Setups for oil-water separation

Solely gravity-driven filtration process was developed for oil-water separation. During the experiment, a piece of CFs (4 cm × 4 cm), serving as a membrane for oil-water separation, was fixed between two glass tubes (diameter 1.5 cm) using a clip. Solutions with different pH values (4.0–10.0) were prepared by dissolving sulfuric acid or sodium hydroxide in water, and the flux of liquid passing through the membrane was tested under each condition (pH value and temperature). For oil-water separation, the cotton sample was wetted by water at first, and then the mixture consisting of crude oil (collected from Karamay Oilfield, China) and water was poured into the upper glass tube. The efficiency for oil-water separation was defined by the weight ratio between the oil content in the filtrate and the one in the feeding mixture [22].

## 3. Results and discussion

### 3.1. Morphology and properties of Coated CFs

SEM images were acquired to compare the differences on surface morphology of CFs before and after polymer coating (Fig. 1). Small