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One-pot fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via sol-gel reaction

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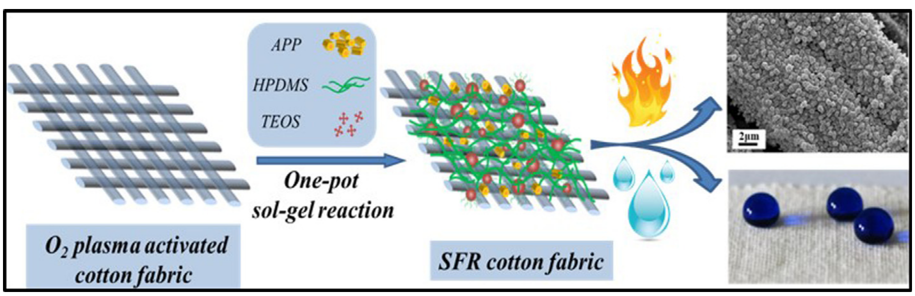
GRAPHICAL ABSTRACT



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ABSTRACT

Waterproof and flame-retardant fabrics are widely utilized in many fields, such as automotive interiors, indoor decorations, outdoor clothing and tents. Herein, a facile one-pot sol-gel approach was developed to construct superhydrophobic and flame-retardant (SFR) coatings on cotton fabrics. The cotton fabric was activated by O_2 plasma and then immersed into the ethanol suspension containing tetraethoxysilane (TEOS), hydroxyl-terminated polydimethylsiloxane (HPDMS) and ammonium polyphosphate (APP). The hydrogen bonding interaction between APP and cellulose motivated the APP to attach to the cotton fibers during the initial stirring process. After the addition of ammonia, the *in situ* sol-gel reaction of TEOS and HPDMS was initiated to generate polydimethylsiloxane-silica hybrid (PDMS-silica). The micro-nano structured composite coating on cotton fabric was successfully fabricated by the PDMS-silica and APP. The SFR cotton fabric showed outstanding durability and self-cleaning ability with a water contact angle (WCA) above 160°. When exposed to fire, the SFR cotton fabric quickly charred to extinguish the fire by generating a dense intumescent char layer under the physical barrier effect of PDMS-silica and the intumescent flame-retardant effect of APP. This one-pot approach for fabricating SFR cotton fabric is simple, cost-effective and timesaving, demonstrating significant advantages in practical production.

1. Introduction

The flammability of combustible fabrics has caused lots of fire disasters, which brings not only massive damage to human properties and lives worldwide but also severe destruction to our surrounding environment. Flame-retardant modification of these fabrics is necessary to prevent fire from spreading. Among plenty of the flame-retardant treatments of fabrics, surface modification is one of the most convenient and effective strategies, such as impregnation [1], chemical grafting [2,3], layer-by-layer assembly [4–7] and sol-gel reaction [8,9]. However, most of the flame-retardant ingredients used in these methods are hydrophilic, which are vulnerable to fouling and water. This may result in not

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only the destruction of flame retardancy but also the decreased mechanical properties of substrates after repeated laundering processes.

Nowadays, there are two common approaches to improve the water-resistance of fabrics and meanwhile reduce the loss of flame retardants. One method is using adhesives such as polyurethane and epoxy resin to improve the adhesion of flame retardants [10]. However, these adhesives with no flame retardancy will probably bring about the decrease of flame-retardant properties. The other more promising method is endowing the flame-retardant coatings with hydrophobicity [11–14]. Superhydrophobic surfaces are defined as those with a water contact angle (WCA) above 150° and a sliding angle (SA) below 10°. Until now, various approaches were developed to fabricate superhydrophobic materials, including sol-gel reaction [15–17], vapor deposition [18–20], electrospinning technique [21], templating method [22], and phase separation [23]. Guo et al. proposed a facile and cost-effective one-pot method to construct a superhydrophobic polydopamine@SiO_2 coating on cotton fabric via the hydrolysis-condensation reaction of silanes and the copolymerization of dopamine at room temperature. The prepared superhydrophobic cotton fabric showed excellent durability, and exhibited great potential applications for oil-water separation and scald-protection clothes [16]. Silicone with low-surface-energy and high thermal stability is not only employed as a flame retardant in polymer for fire prevention and heat insulation, but also widely used to prepare superhydrophobic coatings, performing eco-friendlier and more economical than fluorine-containing materials [24–27]. In addition, some previous works reported that silica or silicone were usually utilized as flame retardants with phosphorus- and nitrogen-containing compounds to achieve some synergetic effects, and flame-retardant properties could be further improved [9,12,28]. Until now, there were very few studies about the fabrication of synergistically silicone-, phosphorus- and nitrogen-containing coatings with superhydrophobicity and flame retardancy. It was illustrated that layer-by-layer assembly and pad-dry-cure techniques were applied to fabricating superhydrophobic and flame-retardant coatings on cotton fabrics, and the fabricated fabrics showed excellent superhydrophobicity and flame retardancy [11,13]. However, there are still some disadvantages of these approaches for large-scale production, such as the use of expensive and toxic fluorine-containing compounds, the requirement of specific equipment and time-consuming operations. Zhang et al. also proposed a facile and cost-effective approach to fabricate hydrophobic and flame-retardant coatings on cotton fabrics through self-assembly techniques and sol-gel reaction [8]. However, this prepared fabric showed a WCA of about 120°, and could not reach to superhydrophobicity for the absence of enough low-surface-energy and micro-nano structures on its surface.

Herein, an innovative one-pot approach was proposed to fabricate a micro-nano coating via sol-gel reaction, which was applied on the cotton fabric to endow it with flame retardancy and superhydrophobicity simultaneously. The cotton fabric was activated by O_2 plasma and then immersed into the ethanol suspension containing tetraethoxysilane (TEOS), hydroxyl-terminated polydimethylsiloxane (HPDMS), ammonium polyphosphate (APP). APP was firstly attached on the cotton fibers via the hydrogen bonding interaction. The *in situ* sol-gel reaction of TEOS and HPDMS was then initiated under the catalysis of ammonia to generate the PDMS-silica hybrid (PDMS-silica). A composite coating with micro-nano roughness was constructed on cotton fabrics by PDMS-silica and APP particles, which simultaneously conferred the fabric with excellent superhydrophobicity and flame retardancy. The hydrophobicity of the fabricated fabrics was systematically evaluated, and the synergistic effect of PDMS-silica and APP on the flame-retardant properties was also comprehensively analyzed. This facile one-pot approach is timesaving, cost-effective and low-toxic. Our discoveries illustrated a new idea to efficiently fabricate bifunctional SFR coatings for practical applications

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, 98%) was bought from Aladdin Industrial Co., Ltd. (China). Hydroxyl-terminated polydimethylsiloxane (HPDMS, Mn = 560) was provided by Wuxi Quanli Chemical Co., Ltd. (China). Ammonium polyphosphate (APP, EPFR-APP222H) was provided by Guangdong Jushi Chemical Co., Ltd. (China). Cotton fabrics (plain weave, 260 g/m^2) were obtained from Guangdong Demei Fine Chemical Co., Ltd. (China). Ammonia (25–28 wt %) was purchased from Guangzhou Chemical Reagent Factory (China). All reagents were used as received directly.

2.2. Fabrication process of SFR coating on the cotton fabric

The one-pot fabrication process was illustrated by a schematic diagram which is shown in Fig. 1. At first, deionized water and ethanol were separately utilized to clean the pristine cotton fabric under ultrasonication. After dried at 60 °C, the cleaned fabric was then activated by oxygen plasma for 2 min to increase the content of oxygen-containing groups (hydroxyl and carboxyl, etc.) on its surface. Subsequently, anhydrous ethanol (100 mL), APP (4.00 g), TEOS (4.00 g) and HPDMS (2.00 g) were mixed adequately into a beaker equipped with a magnetic stirrer. Then, the plasma activated cotton fabric was immersed into the above mixture. After magnetic stirring for 30 min, APP particles were attached to cotton fibers. It was mainly ascribed to the hydrogen bonding between the oxygen-containing groups and —NH in APP and oxygen-containing groups in cellulose. Afterwards, ammonia was added dropwise in the suspension to adjust the pH of about 9 under constant stirring at 25 °C. Under the catalysis of ammonia, the hydrolysis and condensation reaction of HPDMS and TEOS was initiated, and the polydimethylsiloxane-silica hybrid (PDMS-silica) was gradually generated *in situ* on cotton fibers. The schematic of reaction process is illustrated in Fig. S1. The PDMS-silica was composed of crosslinked polydimethylsiloxane (PDMS) and numerous tiny organic silica particles. A micro-nano structured composite coating was gradually constructed on the cotton fabric surface by PDMS-silica and APP particles. After reaction in the beaker for 1 h, the cotton fabric was taken out and then rinsed twice by ethanol to remove the loosely attached substances. Finally, the SFR cotton fabric was obtained after drying at 60 °C, and the deposited coatings weighted about 26.5 g/m^2 in average.

2.3. Flame-retardant properties

Microscale combustion calorimetry (MCC) and vertical flame test were carried out to measure the flame-retardant properties according to our previous work [12]. MCC was conducted in line with the Method A of ASTM D7309, and 10–12 mg of sample was pyrolyzed under nitrogen atmosphere. The temperature increased from 150 °C to 750 °C at a heating rate of 60 °C/min. Then, the pyrolysis volatiles were oxidized at 900 °C in the combustor. The vertical flame test was carried out according to the test standard ASTM D6413. The samples were exposed to a vertical flame for 12 s, and the dimension of sample was 78 mm × 300 mm.