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Fabrication of superhydrophobic fluorine-free films on cotton fabrics through plasma-induced grafting polymerization of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane

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ABSTRACT

A facile and cost-effective technique was designed to construct fluorine-free superhydrophobic films on cotton fabrics in the present paper. Superhydrophobic films were fabricated by immersing cotton fabrics in the monomer solution of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane ($D4^{Vi}$) and followed by the treatment of the air low temperature plasma with glow discharge at a pressure of 10 Pa. The cotton fabrics before and after the plasma treatment were characterized by field emission scanning electron microscopy (FESEM), infrared spectroscopic analysis (FTIR), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA). The wetting behavior of the cotton fabrics was evaluated by the water contact angle (WCA) measurement. The results showed that polymer films could be coated on the cotton fibers through the plasma induced grafting polymerization of $D4^{Vi}$. The glow discharge power and the treating time of low-temperature plasma were critical to the grafting polymerization of $D4^{Vi}$ to the cotton fabrics. Moreover, the treated cotton fabric demonstrated an extraordinary superhydrophobicity with a WCA more than 150° for a 5 μL water droplet and excellent thermal stability and durability of washing 30 cycles.

1. Introduction

The superhydrophobic phenomenon is widespread in nature, such as lotus leaf effect [1]. The excellent features of self-cleaning and anti-stain of superhydrophobic surfaces have drawn intensive attention in the past years [2]. Inspired by the microstructure of lotus leaves, construction of rough surfaces with a sophisticated micro/nanostructure and a low surface energy is the main strategy to fabricate superhydrophobic surfaces with a water contact angle larger than 150° [3].

Currently, superhydrophobic films are widely used in self-cleaning coatings, oil/water separation materials, and functional textiles with a special wettability [4]. Cotton fabric, as a principal and popular clothing material, has excellent comfort, softness and biodegradability [5]. However, the cotton fabric is easily soaked and stained by liquids due to the abundant hydroxyl groups on its surface [6]. Typically, many novel methods have been designed to prepare superhydrophobic cotton fabrics, such as sol–gel, chemical vapor deposition, and Layer-by-Layer assembly technique [7]. Recently, plasma technique has been proved to be a very promising approach to functionalize various substrates though taking advantage of the highly reactive plasma species. The surface chemistry and roughness may be tuned simultaneously, which makes it possible to fabricate superhydrophobic surfaces in a one-step process [8]. Low-pressure plasma and atmospheric plasma processing technologies have been commonly used for surface modification and graft

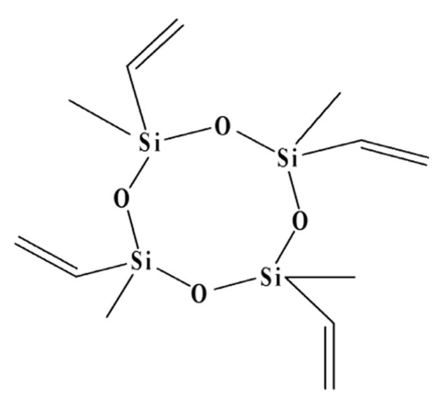

Fig. 1. Molecular structure of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane.

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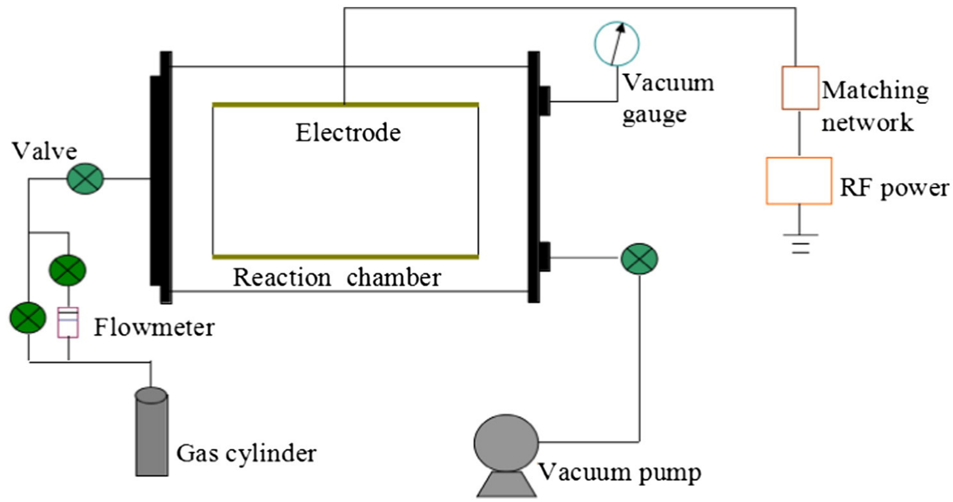

Fig. 2. Schematic representation of the structure of the plasma apparatus.

polymerization [9]. Active particles can be produced at low pressure through the generation of the glow discharge plasma. The active particles have a relatively strong capability to induce surface modification and graft polymerization on a substrate [10]. In comparison to conventional wet chemical modification techniques, plasma surface modification is a simple, efficient, and cost-effective dry technique without the use of a large amount of water and chemicals [11,12]. Therefore, this technique is benign to the environment. In addition, the films formed by the plasma induced grafting polymerization may display controllable thickness, composition uniformity, dense membrane, and less pinhole. Therefore, the plasma-induced grafting polymerization technique has been used to prepare a variety of films, like metals films, amorphous inorganic films, and organic films [13].

In the present paper, we reported a simple and fluoride-free method to prepare superhydrophobic cotton fabrics though constructing films with a sophisticated micro/nanostructure and a low surface energy via air glow discharge plasma grafting polymerization with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane ($D4^{Vi}$) at the low pressure. The superhydrophobic films were formed due to polymerization with the vinyl of $D4^{Vi}$ by the plasma. More importantly, even after 30 cycles of washing, the treated cotton fabrics can still keep excellent hydrophobicity.

2. Experimental section

2.1. Materials and devices

Desized, scoured, and bleached woven cotton fabrics (32 branch twill cotton fabric and 100% cotton) were supplied by Esquel Textile Industrial Co. Ltd (Guangdong, China). The fabrics were washed by absolute ethanol (99.7%) supplied by Hangzhou Gaojing Fine Chemical Co. Ltd (Zhejiang, China) and distilled water for 5 min and were dried in an oven at 80 °C prior to use. Air (99.5%) was supplied by Hangzhou Electrochemical Group Co. Ltd. Detergent 209 was purchased from Nanjing East Mu Fine Chemical Co. Ltd (Jiangsu, China). $D4^{Vi}$ (90%, CAS#27342-69-4) was purchased from Zhejiang Quzhou Jun Shun silicone Co. Ltd (Zhejiang, China). The molecular structure of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetr-asiloxane was showed in Fig. 1.

The low-temperature plasma was produced by a conventional radio frequency (RF) capacitance coupling plasma device (Model: HD-1A, Changzhou Changtai Plasma Technology Development Ltd.) with a frequency of 13.56 MHz and the RF power continuously adjusted from 0 W to 500 W. The reaction chamber was a hard glass cylinder withstanding high temperatures with a size of φ230 mm × 250 mm. A schematic representation of the plasma device is shown in Fig. 2.

Fig. 3. Fabrication process of superhydrophobic cotton fabric treated with air LT-plasma.