Materials Chemistry and Physics 148 (2014) 798–802

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Study on superhydrophobic surfaces of octanol grafted electrospun silica nanofibers

Long-Yue Meng [a, b], Shunyu Han [b], Nanzhe Jiang [b], Wan Meng [b, *]

[a] *Key Laboratory of Natural Resources of Changbai Mountain and Functional Molecules, Yanbian University, Yanji 133002, China*
[b] *Department of Chemical Engineering, College of Engineering, Yanbian University, 977 Gongyuan Road, Yanji 133002, China*

HIGHLIGHTS

- Superhydrophobic surface was prepared from electrospinning SNFs and by grafting octanol on their surface.
- The surface of SNFs changed from superhydrophilic to superhydrophobic.
- The CA of MSNFs became 150.2° because of interactions between grafted octyl groups.

ARTICLE INFO

Article history:
Received 23 July 2013
Received in revised form
27 May 2014
Accepted 24 August 2014
Available online 16 September 2014

Keywords:
Polymers
Nanostructures
Glasses
Surface properties

ABSTRACT

In this work, superhydrophobic surfaces were successfully prepared by grafting of octanol on the surface of electrospun silica nanofibers (SNFs). The chemical compositions and microstructures of the prepared SNFs surfaces were investigated by using N_2 full isotherms, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and contact angle measurements. The results indicate that the surface of SNFs changed from being superhydrophilic to superhydrophobic by octanol surface grafting. The contact angle of the octanol-grafted SNFs was close to 150.2° because their surface was modified by $-(CH_2)_6-CH_3$ groups. The 3D network of SNFs networks and the low surface energy of the alkyl side chains played important roles in creating the superhydrophobic surface of the SNFs.

1. Introduction

The wettability of a solid surface is a subject of intense research nowadays because of a surfeit of its potential applications such as self-cleansing, corrosion and heat resistant, anti-fingerprint, and anti-contamination surface treatments, field-effect transistors, oil capture agents, anti-fogging applications, drag reduction, stain-resistant textiles, conductive products, and anti-bacterial paints [1–6]. Hydrophobicity and hydrophilicity are two principal wettablility conditions. According to Neinhuis and Barthlott, the surface is hydrophilic if the contact angle (θ) is in the range of $0° \leq \theta < 90°$, and is hydrophobic; if the contact angle is $90° < \theta \leq 180°$ [3]. Hydrophobicity is observed in nonpolar substances, which tend to aggregate in aqueous solutions to exclude water molecules [7,8].

Recently, biomimetic applications of surface treatments have been investigated with considerable attention being paid to subjects such as the lotus effect (self-cleaning), silver ragwort leaves, and strider's leg over the past few years [9–14]. The self-cleaning effect (superhydrophobicity or ultrahydrophobicity) is one of the best-known biomimetic effects, and was developed by the use of a superhydrophobic and water-repellent surface that exhibited a high water contact angle (CA) of around 150° and a small sliding angle of about 2° [14]. In general, the superhydrophobicity of many natural surfaces can be attributed to the combined effects of hydrophobic wax-like materials, a unique intrinsic roughness, and complex structures at the micro- and nanoscale [15–19].

Till now, many different methods have been employed for the production of superhydrophobic surfaces, such as atom transfer radical polymerization (ATPR), casting, chemical vapor deposition (CVD), dip coating, electro-spinning, etching, layer-by-layer self-assembly, polymerization, pyrolysis, sol–gel, solution-immersion, spray, and template methods [20]. Electro-spinning, especially, is an efficient approach to fabricate micro- and nanofibers with controllable compositions and structures. In recent years, this

---

* Corresponding author. Tel.: +86 (0)433 273 2340; fax: +86 (0)433 273 9626.
E-mail address: mengw@ybu.edu.cn (W. Meng).

http://dx.doi.org/10.1016/j.matchemphys.2014.08.051
0254-0584/

method has been used to fabricate various devices using hydrophobic polymers and inorganic materials in the form of fiber substrates with suitable morphologies for the construction of biomimetic and superhydrophobic surfaces [14].

Silica-based materials have a high potential for application in many areas including environmental applications, photonics, catalysis, sensing, and surperhydrophobic surfaces. Guo et al. fabricated highly heat-resistant and superhydrophobic mats by a (fluoroalkyl)silane (FAS) modification of electrospun pure silica nanofiber (SNF) mats for the first time [21]. The inorganic SNF mats were obtained via electro-spinning of a blend solution of poly(vinyl alcohol) (PVA) and silica gel, followed by calcination to remove the organic component. Zhao et al. reported on the fabrication of flexible fluorinated SNF membranes with biomimetic non-wettable surfaces, which are prepared by electro-spinning of a blend solution of PVA and silica gel in the presence of silica nanoparticles, followed by calcination and fluoroalkysilane modification [14].

The technology currently considered mature is the modification of polymers using long alkyl chain thiols, alkyl or fluorinated organic silanes, perfluorinated alkyl agents, long alkyl chain fatty acids, polydimethylsiloxane-based polymers, and their combinations. The most commonly selected fluorine-based chemicals for hydrophobicity improvement are fluoroalkylsilanes. These materials (e.g., fluorinated polymers) are chosen because of their extremely low surface free energy and the simple reaction of silane groups with hydroxyl groups on coating surfaces [22]. However, this technology is expensive and a smooth material surface is not easily obtained. Currently, non-fluorinated surface modifiers have been strongly sought after by the industry for many years. For this reason, experiments have been conducted on alternative materials, such as stearic acid-based modifiers and nanoparticles. As revealed by many works, the surface chemical composition plays an important role in determining the wetting behavior of solid surfaces.

In the present work, we prepared mesoporous SNF surfaces by electro-spinning, calcinations, and surface modification techniques. Subsequently, superhydrophobic surfaces were prepared from electrospun SNFs by grafting of octanol. The surface wettability and morphology of pristine and modified SNFs were studied. Also, the surface energy of the modified SNFs was investigated with regard to their morphologies and various testing liquids.

2. Materials and methods

2.1. Sample preparation

The precursor was prepared in polyvinylpyrrolidone (PVP)–ethanol solution using P123 (Triblock copolymer, Pluronic P123) as a structure-directing agent. First, 1.18 g PVP was dissolved in 7 ml ethanol under magnetic stirring at room temperature in order to obtain a homogenous solution. Likewise, 1.8 g tetraethyl orthosilicate (TEOS) and 0.08 g P123 were dissolved in 2 ml ethanol, again under magnetic stirring. After half an hour, the two solutions were mixed together for 20 min. Then, as catalyst for the hydrolyzation of TEOS, 1.2 ml 1 M HCl was added dropwise and the solution was stirred for 10 min. The precursor solutions were electrospun under an electric field of 25 kV at a tip-to-collector distance of 20 cm. A copper rod, used as an anode, was inserted in the spinning solutions in a syringe with a diameter of 1 mm. Aluminum foil was used as collector attached to the cathode. The as-electrospun silica/PVP fibers were calcined in a muffle furnace, which was heated from room temperature to 550 °C in air at a rate of 10 °C min^{-1} and stabilized at 550 °C for 2 h. Then, after the temperature decreased back to room temperature, the SNFs were finally obtained. Subsequently, 0.06 g SNFs, 0.5 ml octanol and 0.02 g p-toluene sulfonic acid were dissolved in 50 ml toluene at 120 °C in an oil bath overnight. The obtained products were filtered, washed with ethanol, and finally dried at 80 °C in vacuum (Fig. 1). The modified SNFs are denoted as MSNFs.

2.2. Characterization

N_2 adsorption–desorption isotherms were measured with Beckman Coulter SA3100 equipment at 77 K. Before the analysis,

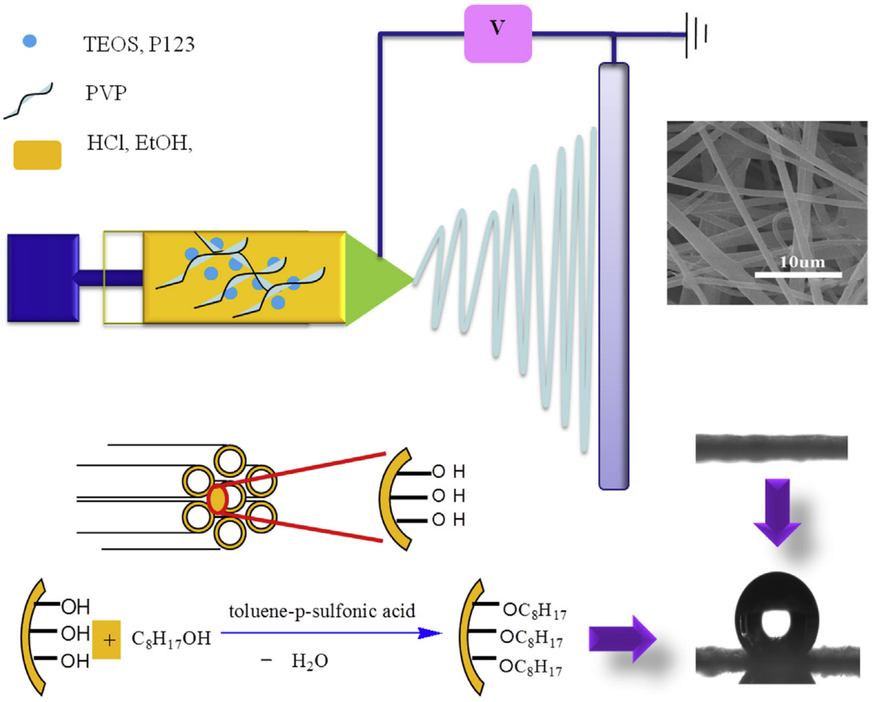

Fig. 1. Preparation procedure of octanol modified SNFs (MSNFs).