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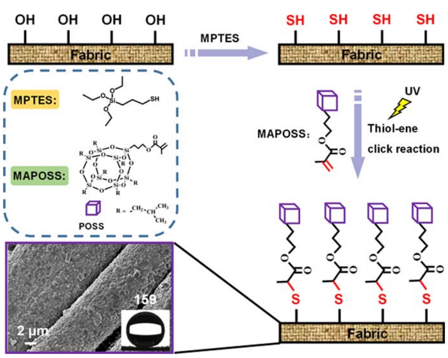
Facile generation of robust POSS-based superhydrophobic fabrics via thiol-ene click chemistry

Kun Hou, Yicheng Zeng, Cailong Zhou, Jiahui Chen, Xiufang Wen*, Shouping Xu, Jiang Cheng, Pihui Pi*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

GRAPHICAL ABSTRACT



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ABSTRACT

Robust polyhedral oligomeric silsesquioxane (POSS)-based superhydrophobic fabrics were successfully generated by surface modification of fibers with mercapto silanes followed by click coupling with methacryl-heptaisobutyl POSS (MAPOSS). MAPOSS grafted onto the fabric surfaces not only increased the surface roughness but also lowered the surface energy of fabric, resulting in superhydrophobicity with a water contact angle of 159° and a sliding angle of 7°. Importantly, the as-prepared superhydrophobic cotton fabric is tolerant to corrosive liquids, UV irradiation, high temperature environment, ultrasonic washing and mechanical abrasion. And the as-prepared superhydrophobic fabric could be used as an adsorbent material for removing oil from water. In addition, MAPOSS could be easily grafted onto other porous substrates (including but not limited to polyester fabrics, filter papers and melamine sponges) to endow these materials with high hydrophobicity. Therefore, this facile, environmentally friendly, low cost and versatile method offers great technological promise in the preparation of robust superhydrophobic coatings on a large scale.

1. Introduction

Superhydrophobic surface with a water contact angle (WCA) greater than 150° and a sliding angle (SA) lower than 10° has triggered more and more research interest due to its excellent water repellency and self-cleaning property [1–6]. Many previous efforts have proven that the wettability of a surface is governed by both the proper micro/nanoscale structures and low-surface-energy materials [7–10]. Based on this principle, numerous superhydrophobic surfaces were successfully fabricated through different methodologies on diverse substrates

* Corresponding authors.
E-mail addresses: xfwen@scut.edu.cn (X. Wen), phpi@scut.edu.cn (P. Pi).

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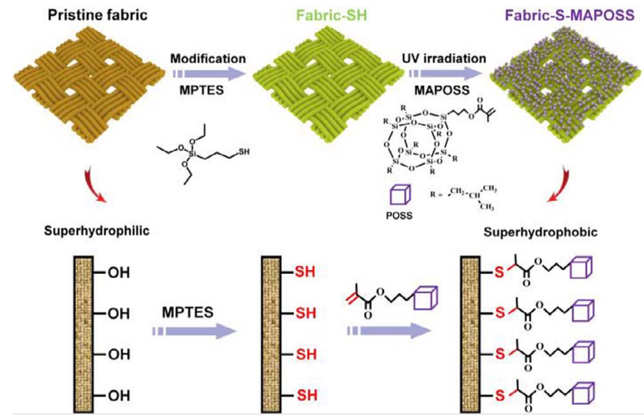
[11–16]. Unfortunately, most of the micro/nanoscale structures of the existing superhydrophobic surfaces are vulnerable to mechanical damage or detachment and then lose their superhydrophobicity. And the low-surface-energy materials for fabricating superhydrophobic surfaces could not generally withstand high temperature, UV irradiation and corrosive liquids. These above drawbacks significantly limit the practical application of superhydrophobic surfaces [3,17,18]. Recently, some studies have succeeded in developing robust superhydrophobic surfaces [16–22], but the fabrication process of these surfaces is expensive, time-consuming and requires harmful materials such as fluoride materials. These fatal weaknesses hinder their industrial fabrication and practical application. Therefore, the robust superhydrophobic surfaces fabricated by a facile and eco-friendly method are highly desired.

Polyhedral oligomeric silsesquioxane (POSS) possesses well-defined nano-scale organic/inorganic hybrid frameworks with a cage-like Si—O—Si core surrounded by eight organic functional groups [23,24]. The rigid silica core endows POSS with some unique physicochemical properties, such as good chemical resistance, mechanical toughness, thermal stability and hydrophobicity. And the organic groups surrounding the cubic silica core in POSS can serve as reaction sites for further chemical functionalization [25–31]. Over the past decades, POSS has been chosen as an important building block to modify nanomaterials [32–34] and polymers [35–37] in the preparation of superhydrophobic surfaces. For example, Xue et al. demonstrated that fluorinated POSS (FD-POSS)-modified Fe_3O_4 nanoparticles exhibited excellent superhydrophobic and magnetic properties [32]. Zhang et al. reported a superhydrophobic-superoleophilic microfibrous membrane comprised of polymer of intrinsic microporosity (PIM-1)/POSS polymer composites through electrospinning process. The addition of POSS particles was found to greatly increase the hydrophobicity and surface roughness of fibers [35]. Our group also prepared a robust superhydrophobic fabric using a crosslinkable POSS-containing fluorinated copolymer. In this copolymer coating, POSS segments self-assembled into many nano-scale protrusions on the surface, increasing roughness of the coating surface [37]. Therefore, POSS could be utilized to tune the surface energy and surface roughness. Inspired by the above studies, it is desired that POSS could be directly immobilized onto substrates to create stable superhydrophobic surfaces. Meantime, the process of such POSS-based superhydrophobic surfaces would also be simplified. However, to the best of our knowledge, rarely such attempt has been successfully done so far.

Recently, serving as a surface chemical modification approach, photoinduced thiol-ene click chemistry has been successfully utilized to functionalize surfaces via chemical grafting strategy [38–41]. Enes could be covalently grafted onto thiol-terminated surfaces through modification of thiol silanes. As this method could conjugate a variety of components easily under mild reaction conditions and has short reaction time, we explore in this study to apply such photoinduced thiol-ene click chemistry to directly graft POSS with ene moiety onto thiol-modified substrates for creating robust superhydrophobic surfaces.

In this study, commercially available methacryl-heptaisobutyl POSS with ene moiety (MAPOSS, structure shown in Scheme 1) was covalently grafted onto sulfhydryl cotton fabrics via a facile photoinduced thiol-ene click chemistry method. After reaction, MAPOSS segments anchored on the fabric self-aggregated into submicronmeter protrusions on the surfaces, resulting in the hierarchical structures. A combination of such hierarchical structures with the inherent low surface energy of MAPOSS (due to hydrophobic Si—O—Si skeleton and corner alkyls) offers the as-prepared POSS-based fabric excellent superhydrophobicity. Moreover, the structural nature of POSS enables the as-prepared superhydrophobic surfaces to be excellent in some chemical and physical resistance challenges that commonly bother similar technologies in practice, namely tolerance for acidic or alkaline liquids, UV irradiation, high temperature, ultrasonic washing and severe abrasion. And the as-prepared superhydrophobic fabrics could be used as an adsorbent material for removing oil from water. In addition, MAPOSS could be easily grafted onto other porous substrates.



Scheme 1. Schematic illustration of the procedure for POSS-based superhydrophobic fabric via photoinduced thiol-ene click chemistry.

2. Experimental

2.1. Materials

Methacryl-heptaisobutyl polyhedral oligomeric silsesquioxane (MAPOSS, $C_{35}H_{74}O_{14}Si_8$) was obtained from Hybrid Plastics Inc (USA). Anhydrous ethanol, hydrochloric acid, sodium hydroxide, sodium chloride and dichloromethane were purchased from Damao Chemical Reagent Co., Ltd (Tianjin, China). All reagents are of analytical grade. 2-hydroxy-2-methylpropiophenone (HMPF) was purchased from Bayer and used as a photoinitiator. Methyl orange (MO), oil red O, methylene blue and 3-mercaptopropyltriethoxysilane (MPTES) were obtained from Aladdin. All chemicals were used without any further purification. Cotton fabric, polyester fabric, paper filter and melamine sponge were obtained commercially. These substrates were further purified by ultrasonic washing with a 2 wt% NaOH solution for 20 min, followed by washing several times with distilled water until reaching neutral. The cleaned substrates were then dried completely in an oven at 60 °C.

2.2. Fabrication of the POSS-based superhydrophobic fabrics

The procedure of generating the POSS-based superhydrophobic fabrics was shown in scheme 1. A piece of cleaned cotton fabric (3 × 3 cm) was first immersed in 20 mL of 0.15 mol/L MPTES/ethanol solution for 2 h at room temperature. The fabric was then washed with ethanol and dried at 80 °C for 1 h to obtain mercapto silane modified fabric (designated as fabric-SH). Finally, the fabric-SH was immersed in dichloromethane (30 mL) with MAPOSS and HMPF (accounted for 10% of MAPOSS mass), and then irradiated under 360 nm UV lamp (40 W) for 1 h. After reaction, the fabric was washed with ethanol and dried at 60 °C to obtain the target sample (designated as fabric-S-MAPOSS). POSS-based polyester fabric, filter paper and melamine sponge were prepared using the same method.

2.3. Durability evaluation of the POSS-based superhydrophobic fabric

The water contact angle (WCA) of the fabric was recorded using a contact angle analyzer. Water droplets with different pH values ranging from 1 to 14 were used to investigate the chemical stability of the POSS-based superhydrophobic fabric. The chemical resistance performance of the as-prepared superhydrophobic fabric was further studied by immersing the fabric into strong acidic (pH = 2) or alkaline (pH = 12) media for different time and then the WCAs were also measured. The superhydrophobic fabric was irradiated under a UV lamp (40 W) at a