Materials and Design 140 (2018) 30–36

Contents lists available at ScienceDirect

Materials and Design

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

Facile preparation of mechanically durable, self-healing and multifunctional superhydrophobic surfaces on solid wood

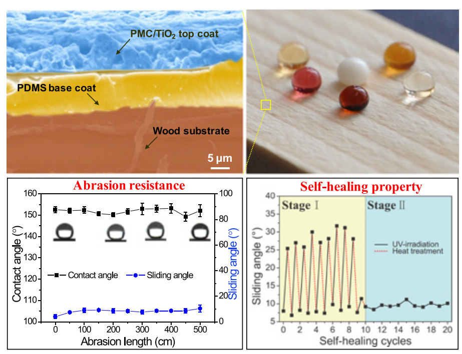
Kunkun Tu, Xiaoqing Wang *, Lizhuo Kong, Hao Guan

Department of Wood Modification, Research Institute of Wood Industry, Chinese Academy of Forestry, Xiangshan Road, Haidian District, Beijing 100091, China

HIGHLIGHTS

- Superhydrophobic wood surfaces were prepared by spray coating of PMC/TiO_2 nanocomposites onto the PDMS pre-coated substrate.
- The coated wood surface was durable enough to withstand repeated abrasion damages while retaining its superhydrophobicity.
- The coated wood surface exhibited desirable photocatalytic activity and enhanced photostability during UV exposure.
- Superhydrophobicity of the surface damaged by UV irradiation could be restored by a simple heat treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form 13 November 2017
Accepted 15 November 2017
Available online 23 November 2017

Keywords:
Superhydrophobic
Durability
Self-healing
Photocatalytic
Wood

ABSTRACT

Maintaining the hierarchically roughened structures and non-wetting properties are critically essential for a superhydrophobic surface upon sunlight irradiation, physical rubbing or organic contamination in practical applications but remain extremely challenging. Herein, by simply spraying a waterborne perfluoroalkyl methacrylic copolymer (PMC) emulsion mixed with TiO_2 nanoparticles onto polydimethylsiloxane (PDMS) pre-coated substrates, mechanically durable, self-healing superhydrophobic surfaces were fabricated on solid wood. The coated surfaces exhibited exceptional repellency toward water as well as organic liquids with low surface tensions including ethylene glycol. The as-prepared coatings on the rigid wood substrate showed excellent durability against mechanical abrasion while retaining the rough surface textures due to the hydrophobic binder PMC anchoring the nanoparticles tightly on the surface, thus sustaining the superhydrophobicity of the surface. Moreover, the non-wetting properties of the surface damaged by ultraviolet (UV) irradiation can be automatically restored by a simple heat treatment, which facilitates the migration of the underlying hydrophobic PDMS onto the surface replenishing the necessary low-surface-energy materials. Besides, the TiO_2-containing coatings exhibited photocatalytic activity in degrading organic contaminants and can also preserve the underlying wood substrate from photodegradation during UV exposure. The developed method herein features environment-friendly raw materials, facile processing and large-scale fabrication. Such superhydrophobic wood surfaces with multi-functionalities may open new avenues in the field of novel wood-based materials.

* Corresponding author.
E-mail address: wangxq@caf.ac.cn (X. Wang).

https://doi.org/10.1016/j.matdes.2017.11.029

1. Introduction

Wood has been widely used in our daily life in various applications (e.g. furniture, indoor decoration, building and construction) owing to its appealing features such as affordability, recyclability, renewability and mechanical strength. However, wood is naturally hydrophilic and hygroscopic materials because of the abundant hydroxyl groups (−OH) present and their highly porous structure, enabling rapid absorption of water and moisture. This affinity to water renders wood susceptible to staining, fouling, dimensional instability, fungal and bacterial infections [1], which dramatically shortens its service life and results in an undesirable waste of valuable resources. Hydrophobization treatments are thus needed to increase the durability of this hydrophilic material. One of the promising approaches for enhancing water-repellency of wood is to fabricate superhydrophobic surfaces on the substrate mimicking the lotus effect in nature, in which water drops can easily roll off the surface taking away the contaminants on it. Such a superhydrophobic surface can minimize wood-water interactions thereby avoiding damages associated with water absorption. Moreover, the superhydrophobic surfaces are expected to endow wood with new functionalities such as self-cleaning, anti-fouling, and anti-corrosive properties, which should further widen its exploitation potential in new application areas.

It is well established that two general rules have to be fulfilled to accomplish superhydrophobic surfaces with water contact angles >150° and sliding angles lower than 10°: the coating must have suitable roughness patterns that are superimposed with low surface energy materials [2–5]. Fabrication of superhydrophobic surfaces on the wood substrate, however, is rather challenging owing to its complex, heterogeneous surface structure as well as limited thermal and chemical resistance. So far, only limited methods such as sol-gel processes [6,7], hydrothermal treatments [8,9], dip-coating [10,11], spray-coating [12], polymer grafting [13], and plasma etching [14] have been developed to fabricate superhydrophobic wood surfaces. Despite considerable progress in the development of superhydrophobic wood surfaces, some challenges still remain that seriously restrict their practical applications. One of the major challenges with superhydrophobic surfaces is the wear resistance and long-term durability [15]. Mechanical wear such as sandpaper abrasion and even simple finger wiping could damage the fragile surface roughness features that are essential for superhydrophobicity, leading to loss of non-wettability. Besides, environment factors such as sunlight irradiation, high temperature and moisture could impair the hydrophobic surface layers causing undesired pining of water droplets. Another important challenge is the poor repellency of the superhydrophobic surface toward low surface tension liquids, leading to organic contamination and loss of water-repellent function. Therefore, development of long-lasting, oil-repellent superhydrophobic wood surfaces is needed for their practical applications.

Various strategies have been recently proposed to address these challenges with artificial superhydrophobic surfaces. One approach for improving the mechanical durability of man-made non-wetting surfaces is to use roughness at two length scale where nanoscale roughness is protected to some extent by microscale features [16–18]. In this way, a stable superhydrophobic state maintains even after some surface features are worn away. Alternatively, organic-inorganic nanocomposites with hydrophobic polymers as film-forming agents and nanoparticles for creating roughness have also been attempted to construct durable superhydrophobic surfaces, in which the polymers act as a binder to anchor the nanoparticles and their aggregates strongly on the substrate [5,10,19,20]. With a similar idea, mechanically resilient superhydrophobic surfaces was developed by combining a paint consisting of perfluorinated nanoparticles and commercial adhesives, which can be used on various substrates including cotton, paper, glass and steel [21]. Another novel concept in designing damage-tolerant superhydrophobic surfaces is to endow the coating with roughness-regenerating ability [17,22–24]. Due to the coating's self-similarity, a removal of the top layer of the coating materials upon mechanical abrasion will expose a new hydrophobic rough surface, ensuring continued superhydrophobicity.

Unlike artificial non-wetting surfaces, natural superhydrophobic plant leaves can withstand damages and sustain their non-wettability based on continuous renewal of the surface by regenerating the hydrophobic epicuticular wax layer as a result of biological growth processes [25,26]. Mimicking this self-healing ability to restore the non-wetting function in artificial superhydrophobic surfaces provides an interesting strategy to realize their long-term durability and has received increasing attention in recent years [27–32]. In a typical process, the hydrophobic substances were stored beforehand in the interior of the surface coating. Once the hydrophobic top layer was decomposed, the preserved healing agents could migrate to the surface to regenerate the superhydrophobicity by external stimuli such as temperature, moisture or UV-irradiation. Alternatively, inspired by *Nepenthes* pitcher plants, self-healing, slippery liquid infused porous surfaces (SLIPS) were created by using nano/microstructured substrates to lock in place the infused perfluorinated lubricant, which exhibited excellent repellency to various liquids and can quickly restore liquid-repellency upon physical damage [33]. Based on this concept, various bio-inspired SLIPS with different functions have been developed on a broad range of substrates [34–36].

Herein, we report a facile method to fabricate mechanically durable, self-healing and multifunctional superhydrophobic surfaces on solid wood by spraying coating of perfluoroalkyl methacrylic copolymer (PMC)/TiO_2 nanocomposites onto polydimethylsiloxane (PDMS) pre-coated substrates, as illustrated in Fig. 1. In this coating system, TiO_2 nanoparticles function as surface roughening materials, and the low surface energy PMC acts as a film-forming agent and polymer binder to anchor the nanoparticles strongly on the surface, which ensures good mechanical durability of the constructed superhydrophobic coatings. Besides, the PDMS base coat serves as a reservoir of the hydrophobe, which could migrate to the surface by a simple heat treatment to restore its superhydrophobicity once the surface hydrophobic PMC is damaged by ultraviolet (UV) irradiation. Furthermore, owing to the incorporated TiO_2, the superhydrophobic coatings endowed the wood substrate with enhanced UV stability preserving its original color and also exhibited photocatalytic activity in degrading organic pollutants. The method demonstrated herein involves only environmentally friendly coating materials without using harsh chemicals, which can be readily applied on wood and other cellulose-based materials including filter paper, textile and cotton by simple spray coating while maintaining their intrinsic appearances. The resulting multifunctional superhydrophobic surfaces could broaden the applications of wood and other cellulose-based materials.

2. Experimental section

2.1. Materials

Perfluoroalkyl methacrylic copolymer (PMC, Zonyl 8740) was supplied by DuPont Co. (Delaware, USA). Polydimethylsiloxane (PDMS, Sylgard 184) and the corresponding curing agent were provided by Dow Corning Co., Ltd. (Michigan, USA). TiO_2 nanoparticles (anatase, nominal particle diameter of 25 nm) and rhodamine B (RhB) were purchased from Aladdin Co., Ltd. (Shanghai, China). Butyl acetate (BA) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification. Wood blocks of 45 mm × 25 mm × 5 mm (longitudinal × tangential × radial) were obtained from the sapwood of Chinese fir (*Cunninghamia lanceolata*).

2.2. Preparation of superhydrophobic surfaces

Durable superhydrophobic coatings were prepared on solid wood based on a two-step process consisting of formation of a PDMS base