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Preparation of a robust cellulose nanocrystal superhydrophobic coating for self-cleaning and oil-water separation only by spraying

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ABSTRACT

Cellulose nanocrystal (CNC) is usually prepared by acid hydrolyzation of cellulose mainly coming from wood and crops such as cotton, flax, and hemp. A robust superhydrophobic coating was successfully created by two-step spraying method, in which a commercial spray paint is used as adhesive and first sprayed onto the substrates, followed by spraying modified CNC onto the adhesive. The resulting coatings on the wood and glass slide show excellent superhydrophobicity with a water contact angle (WCA) of 163°, outstanding self-cleaning, and high mechanical strength. In addition, the stainless steel mesh coated with adhesive and hydrophobic CNC is efficient and reusable for oil-water separation and shows high resistance to chemical corrosion and UV radiation. This CNC superhydrophobic coating can be applied on unlimited substrate surfaces only by spraying and is beneficial to promote industrial use value of wood and crops.

1. Introduction

Wettability of solid materials surfaces is an important factor that influences their use. In particular, a superhydrophobic surface attracts scholars' attention because of its powerful functions such as self-cleaning, waterproof, anticorrosion, and antifogging (Sheng et al., 2017; Wang et al., 2015; Xiao et al., 2015; Huang et al., 2016). An artificial superhydrophobic coating could be prepared by various methods such as electrostatic spinning (Hardman et al., 2011), etching (Kim et al., 2011), chemical vapor deposition (CVD) (Huang et al., 2017a, 2017b), and layer-by-layer assembly (Peng et al., 2016). However, some of these methods often require complex equipment. Sometimes, the process is not suitable for large-scale preparation of superhydrophobic coatings. For example, the CVD requires a sealed space and high reaction temperatures (Vilaró et al., 2016; Zhang et al., 2015), while etching requires a laser (Cheng et al., 2015a, b; Huang et al., 2015). However, spraying is a simple method and can be used on all kinds of substrates surfaces (Li et al., 2014, Li et al., 2015a, b; Ge et al., 2014). Therefore, spraying has been rapidly developed for superhydrophobic coatings. In addition, most of the materials used in superhydrophobic coatings are non-biodegradable inorganic materials such as TiO_2, SiO_2, and $CaCO_3$, (Zhao et al., 2015; Yang et al., 2016; Lim and Lee, 2017; Li et al., 2015a,b; Patowary et al., 2015; Gurav et al., 2014) or a combination of inorganic and organic materials (Lin et al., 2016). However, in recent times, because of the increasing awareness of saving environment from the harmful effects of inorganic materials, biodegradable materials are attracting interest (Rani et al., 2015; Arrieta et al., 2016; Huang et al., 2017a, b). Therefore, in this study, we proposed that cellulose nanocrystal (CNC) is used as the main material to prepare a superhydrophobic coating.

CNC is a kind of biopolymer that could be prepared by acid hydrolyzation of cellulose which mainly comes from wood and crops, such as cotton, flax, and Hemp (Mariano et al., 2014; Angelova et al., 2004). Because of its high crystallinity, CNC has excellent mechanical properties and is usually used as a reinforcing material (Bettaieb et al., 2015; Feng et al., 2017). Moreover, nanofibrillated cellulose (NFC) is widely used as superhydrophobic gels, superhydrophobic papers, etc. (Zhou et al., 2016; Balu et al., 2008). However, the use of CNC is rarely reported in the superhydrophobic field, and it is helpful for promoting use value of crops to fabricate superhydrophobic coatings.

Because of a large number of hydroxyl groups on its surface, CNC shows high hydrophilicity. As CNC-water suspension is directly sprayed onto a substrate surface, a smooth CNC film would be formed after drying. However, this is not something required for a superhydrophobic coating. Therefore, to prepare hydrophobic CNC paints, hydroxyl groups on the CNC surface must be replaced with some suitable hydrophobic groups (Kaboorani and Riedl, 2015; Zhang et al., 2016). Traditionally, modification methods for CNC are divided into two types: liquid phase method and gas phase method. Both of them need to be conducted under anhydrous conditions. Therefore, removing water is a

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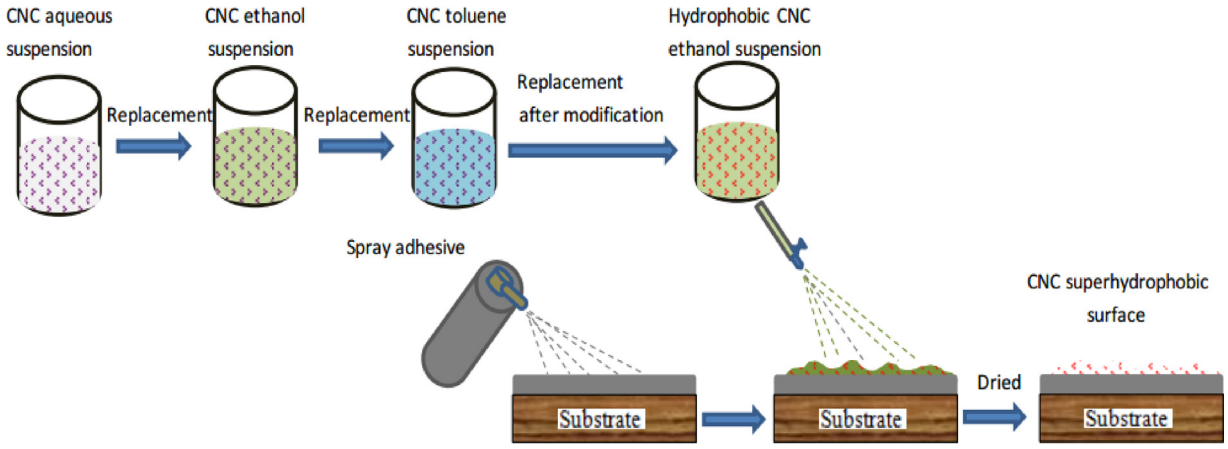

Fig. 1. Schematic of the fabrication process for CNC superhydrophobic coating.

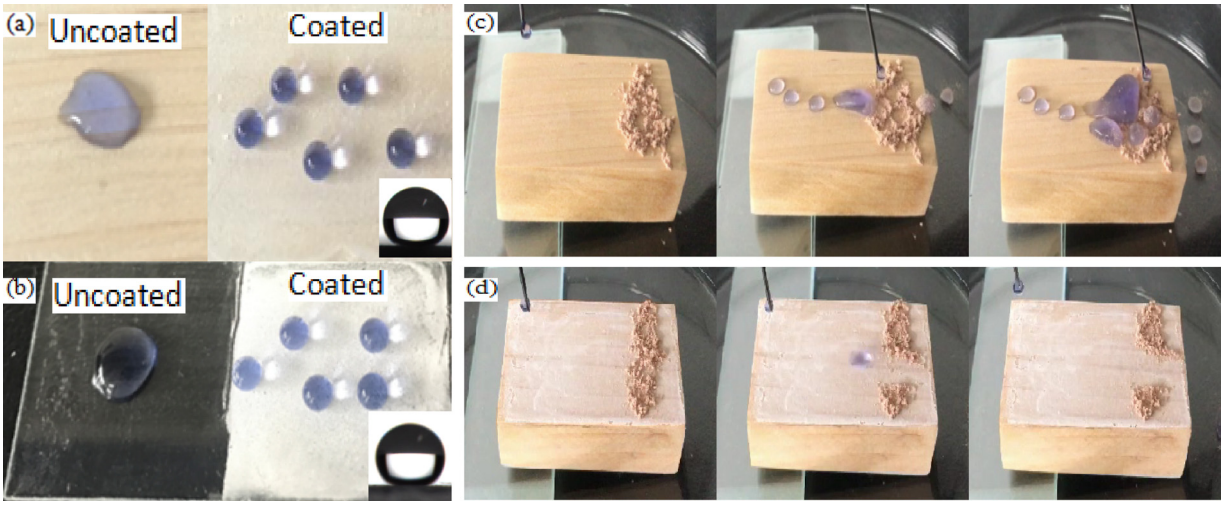

Fig. 2. Status of water droplets on uncoated and coated (a) wood and (b) glass slide; the self-cleaning test of the (c) uncoated and (d) coated wood.

key step for the modification of CNC. Traditionally, dialysis is the main method for removing water. However, it takes a long time. Here, some dialysis processes were replaced only by a simple centrifugation process, which saved much time.

Almost all superhydrophobic coatings suffer from poor mechanical strength, which is the main factor restricting their future application (Yun et al., 2014). Here, in order to improve mechanical strength of superhydrophobic coatings, a commercial spray adhesive was used as a binder to supply the adhesion between CNC and substrates. Our research group has successfully used CNF and lignin-coated CNC (L-CNC) particles to prepare superhydrophobic coatings by CVD, which requires a confined space and an eighty of high temperature (Huang et al., 2016, 2017a, b). Here, a simple spray method is used to prepare a self-cleaning surface on glass slides and wood.

In addition to self-cleaning, oil-water separation which could solve the problem of oil leakage is also an important application of superhydrophobic materials such as superhydrophobic aerogels and superhydrophobic membranes (Si et al., 2015; Tang et al., 2013). However, these materials are of weak strength and not durable. Therefore, to improve their strength, many studies have shown the preparation of superhydrophobic materials for oil-water separation (Li et al., 2016; Cheng et al., 2015a, 2015b Some studies have used etching to prepare a superhydrophobic mesh (Ganne et al., 2016); however, they are not as convenient as spraying. Herein, we showed that a durable superhydrophobic mesh could be prepared simply by a spraying method.

Compared with the traditional methods, superhydrophobic coatings prepared in this study afford the following advantages: 1) CNC is an eco-friendly and resourceful material; 2) the preparation method is simple and can be easily scaled up; and 3) the coating possesses excellent mechanical strength.

2. Experiment

2.1. Materials

Cellulose nanocrystals (CNCs, solids ~12%) and were purchased from the University of Maine, Process Development Center (Orono, ME, USA). A commercial quick drying transparent topcoat as an adhesive was purchased from Jushifu Appliance Co., Ltd, Shenzhen, China. Toluene, 1H,1H,2H,2H-perfluorooctyltrichlorosilane (FOTS, $CF_3(CF_2)_5(CH_2)_2SiCl_3$, 97%), and anhydrous ethanol (> 99.5%) were was purchased from Alfa Aesar. All chemicals were used as received without further purification. Small pieces of glass slides were first cleaned using deionized water and then rinsed with ethanol. Small pieces of wood (dimensions 4.5 cm × 2.5 cm × 1.5 cm), the glass slide, and the stainless steel mesh (0.08 mm diameter) with a pore diameter of 175 μm were used as substrates.

2.2. Preparation of CNC superhydrophobic coating

2.2.1. Ethanol exchange

To prepare a CNC-ethanol suspension, a 4 wt% of CNC-water