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Wood-based microhaired superhydrophobic and underwater superoleophobic surfaces for oil/water separation

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Wood-based superhydrophobic and underwater superoleophobic surfaces are fabricated using a scalable replication technique. Lignin-based polymer is microstructured with a heated mold, resulting in a superhydrophobic/superoleophilic surface covered with microhairs. The microhaired surface is used to clean crude oil spills and to separate oil/water mixtures by absorbing oil. After treating the microhaired surface with argon plasma it acquires underwater superoleophobic property necessary for removing water from the oil/water mixtures.

Frequently occurring oil spills and their massive cleanup efforts both result in extensive damages to the environment, public health and enormous economic losses. Conventional methods used for oil spill cleanup are known to have low efficiency, poor recyclability, high operational costs and use toxic chemicals.[1,2] In recent years the focus in oil/water separation research has been on designing novel materials with special wetting behavior, which are also used for water collection, anti-bioadhesion, corrosion resistance and other applications.[3–5] Materials with superhydrophobic/superoleophilic surfaces are used to absorb or filtrate oil from oil/water mixtures, while superhydrophilic/underwater superoleophobic materials selectively remove water. Such materials are obtained by combining chemical composition with surface micro- and nanoroughness, and can be fabricated using polymers, ceramics, metals and other materials.[6–10] Electrochemical deposition, wet etching, chemical modification, growing nanoparticles and nanotubes are used to create special wetting surfaces.[11–19] Despite the promising properties, the existing methods have several disadvantages: organic chemicals used for surface modification (fluorine-based) are usually harmful and unstable in oily wastewater, and the conventional microstructuring methods are time-consuming, expensive and potentially toxic due to possible micro-/nanosized particulate release into water during separation.[20–22] Therefore, new effective and easily scalable methods based on environmentally friendly materials are required for fabricating materials with special wetting properties for oil/water separation.

Artificial special wetting materials are inspired by natural superhydrophobic surfaces of plants and insects, and underwater superoleophobic surface of fish scales.[23–25] Hence materials which are directly available in nature have a great potential to efficiently mimic such surfaces and make them environmentally friendly. Oliveira *et al.* used diatomaceous earth to fabricate superhydrophobic surface, superhydrophobic wood was produced by sol-gel process and fluorination, nanocellulose aerogels coated with titanium dioxide and octyltrichlorosilane, and calcium carbonate powder treated with fatty acid were used for oil removal.[1,26–29] In recent years biodegradable polymers from such renewable materials as cellulose, lignin and starch are used to replace petrochemical-based polymers in different fields.[30,31] Polymers based on wood components are especially attractive, as cellulose and lignin are the most abundant natural polymers.[32] Lignin is a by-product of the paper industry, and is usually burned or processed into animal feed and cement.[33]

In this work, we report scalable special wetting surfaces fabricated from a wood-based polymer known as ”liquid

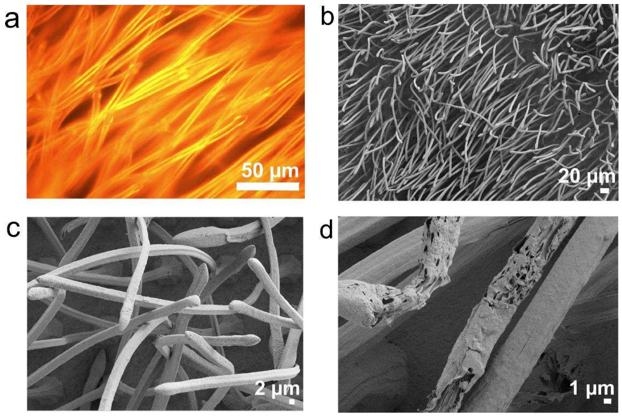

Fig. 1 Micrographs of wood-based microhairs fabricated by hot pulling. a) Optical microscopy image of the microhairs. b, c) SEM images of the microhairs. Their dimensions are: ∼5 μm in diameter, >200 μm in length, aspect ratios ∼40-50. d) Higher magnification SEM image reveals the submicron details of the microhairs. The fibrous structure possibly originates from the processed wood fibers contained in the ”liquid wood” polymer.

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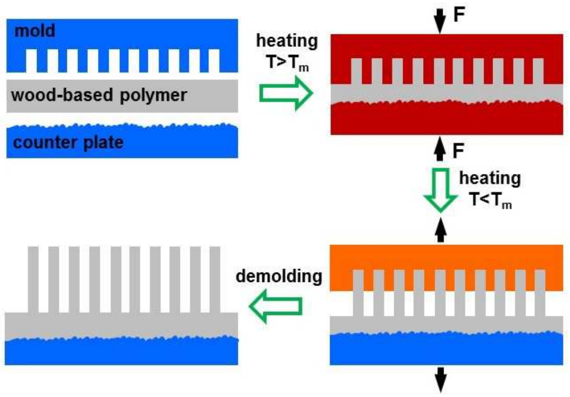

Fig. 2 Fabrication of the microhaired surface by hot pulling technique. Wood-based polymer heated above the melting temperature T_m is pressed into the mold. During the demolding step the mold is cooled and retracted, and the softened microstructures are elongated due to adhesion to the mold cavities, resulting in long microhairs.

wood". Recently developed "liquid wood" polymers are based on lignin and wood fibers, and are robust, recyclable, fully or partially biodegradable and nontoxic.[34,35] The special wetting surfaces are fabricated by microstructuring the polymer using a hot pulling technique. The resulting surfaces are covered with dense high aspect ratio microhairs, and are superhydrophobic and superoleophilic. The as-prepared microhaired material absorbs crude oil out of the water and separates oil/water mixtures. Importantly, the surface properties of the as-prepared material can be changed to hydrophilic and underwater superoleophobic by a short argon plasma treatment cycle, making the microhaired wood-based material capable of both "oil-removing" and "water-removing" oil/water separation methods.

Microhaired surfaces shown in Fig. 1 were fabricated using wood-based polymer Arbofill® Spruce (Tecnaro GmbH, Germany), which is made from lignin, wood fibers and plastics with bio-based content 80%, and is partially biodegradable.[34] The microstructures on the surface of the wood-based polymer were fabricated by hot pulling technique schematically illustrated in Fig. 2. Hot pulling is a modified hot embossing or nanoimprint process.[36,37] In standard hot embossing high demolding forces occur during the polymer and mold separation.[38] These forces are utilized on purpose by the hot pulling technique to increase the aspect ratios of the produced micro- and nanostructures.[39] The material is heated above the softening temperature during the demolding step, resulting in elongation of softened polymer microstructures due to adhesion to the inner sidewalls of the cavities in the microstructured mold insert. A hot embossing machine (Jenoptik, Germany) was used for hot pulling. Flattened wood-based polymer sheets were positioned between a counter plate and an opposing microstructured mold fabricated with LIGA technique.[40] In the vacuum chamber the plates were heated above the melting temperature of the material (T_m=146 °C) and the viscous polymer was pressed into the mold using the following parameters: T=155 °C, applied force 10 kN, velocity 0.5 mm/min, 3 min. During demolding step, the mold was cooled down to T=100 °C ($T_s < T < T_m$, T_s=36 °C) and was retracted by 1.2 mm with 0.8 mm/min velocity. After cooling and separating the plates, the resulting microhaired polymer was removed from the machine.

By using the described hot pulling method, high aspect ratio microhairs were fabricated on the "liquid wood" polymer surface. Optical and scanning electron microscopy (SEM) images of the fabricated wood-based microhairs are shown in Fig. 1. The microhairs are approximately 5 μm in diameter and over 200 μm in length. The mold insert used for fabricating microhairs consists of conically shaped holes with diameters of 12 μm and aspect ratios of approximately 1. Therefore, the aspect ratios of the resulting microhairs (~40-50) significantly exceed the aspect ratios of the mold cavities and previously fabricated structures using hot pulling technique.[36,39] The thicker tips of the microhairs replicate the conical shape of the mold insert openings (Fig. 1c). The difference between diameters of the microstructures in the mold and resulting microhairs is a result of pulling off the softened polymer during the demolding step. The higher resolution SEM image in Fig. 1d reveals the submicron details of the microhairs, which have porous fibrous structure possibly originating from the processed wood fibers contained in the "liquid wood".

The wetting behavior of the surface covered with wood-based microhairs is characterized by water and oil contact angle measurements (OCA 40, DataPhysics Instruments GmbH, Germany), and is shown in Fig. 3. For these measurements, 4.5 μl droplets of deionized water and oil (hydraulic oil Total Azolla ZS 10) were dispensed on the sample surfaces. The measured static water contact angle θ on the microhaired surface is 153.8 ± 2.1° (N=6 measurements) (Fig. 3a), whereas on the unstructured flattened surface the contact angles range from 95° to 115°, depending on the surface roughness. The high water contact angle indicates that the microstructured surface is superhydrophobic (θ>150°). The sliding angle of water droplets on the microhaired surface is 17.5.8 ± 5.4° (N=7) (Fig. 3b). It was measured using deionized water (7 μl) and a tilting stage. Moreover, the measured oil contact angle is 0°, as the oil droplet immediately spreads after touching the surface (Fig. 3c). Therefore, microstructuring by hot pulling induces both superhydrophobic and superoleophilic properties to the surface of the lignin-based polymer.

To modify the wetting characteristics of the microhaired wood-based surface from superhydrophobic to hydrophilic, we exposed as-prepared material to argon plasma. Argon plasma treatment was previously used to increase the hy-

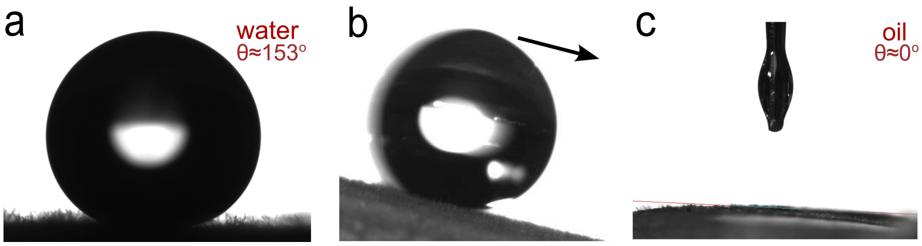

Fig. 3 The microhaired wood-based surface exhibits special wetting behavior with superhydrophobic and superoleophilic characteristics. Photographs of water droplets on the microhaired surface with a water contact angle of $\theta = 153^\circ$ (a), and a sliding angle of 13.5° (b). Oil droplet quickly spreads on the surface, and the oil contact angle is nearly 0° (c).

drophilicity of the superhydrophobic polymeric surfaces.[26,41] Argon plasma treatment (0.2 mbar, 30 W, 120 s) was carried out using reactive ion etching system (Sentech GmbH, Germany). The water contact angle changed from $153.8 \pm 2.1^\circ$ (N=6) on unmodified microhaired surface to $65.0 \pm 5.2^\circ$ (N=2) on plasma-treated surface. The surface topography of the as-prepared superhydrophobic and plasma-treated hydrophilic samples was studied using SEM and no distinguishable differences were observed.

The underwater oil wettability of the plasma-treated microhaired surface is characterized by measuring the oil contact angles under water using a setup illustrated in Fig. 4a. The oil droplet ($7\ \mu l$, Total Azolla ZS 10) was dispensed on the plasma-treated microhaired material placed upside down in the container filled with deionized water. As shown in Fig. 4b, the microhaired surface treated with argon plasma is underwater superoleophobic with an oil contact angle of $156.4 \pm 1.6^\circ$ (N=3). Underwater superoleophobicity is attributed to the rough structure and the hydrophilic nature of the dense microhairs. Underwater superoleophobic materials rely on water trapped on the micro-/nanostructured hydrophilic surface underwater to limit the contact between oil and solid. Similarly, the air on the superhydrophobic surface limits the contact between water and solid. These results indicate the multifunctionality of the microhaired wood-based surfaces, which can be used for ”water-removing” oil/water separations after plasma treatment due to their underwater superoleophobicity, additionally to ”oil-removing” separation by the superoleophilic/superhydrophobic as-prepared surfaces.

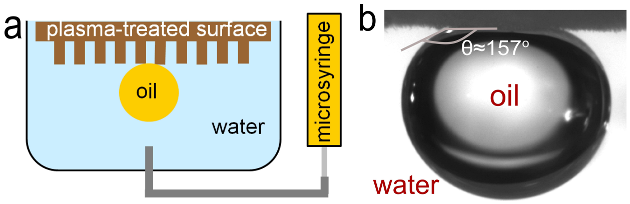

Fig. 4 Underwater superoleophobicity of the microhaired wood-based surface treated with Ar plasma. a) Schematic of the underwater contact angle measurement. Water trapped between microhairs limits the contact between oil and solid. b) Photograph of a $7\ \mu l$ oil droplet deposited under water on the plasma-treated microhaired surface with the oil contact angle of 157°.

The observed special wetting properties of the microhaired wood-based polymer make it a promising material for cleaning oil spills. To test the applicability of the superhydrophobic/superoleophilic as-prepared microhaired surface for oil removal out of water, we imitated a crude oil spill in a petri dish filled with water. Crude oil was received from the oil refinery MiRO, Germany. First, a droplet of oil (Total Azolla ZS 10) was dispensed into water to create a thin transparent oil layer. This oil layer reduces the spreading of the crude oil, which is added next, and hence improves the crude oil spill visibility during the experiment (Fig. 5a). The microhaired polymer was submerged into contaminated water, and was retracted after oil absorption. As it can be seen in Fig. 5a, most of the dispensed crude oil is absorbed by the microstructured polymer, and is locked within its surface after it is removed from water. Furthermore, we quantified the maximum crude oil uptake by the microhaired surface to be $114\ \mathrm{g/m^2}$, compared to $45\ \mathrm{g/m^2}$ for the flattened surface.

To investigate the ability of the superhydrophobic/superoleophilic wood-based surface to separate oil and water from the oil/water mixture, we dispensed a droplet of mixture on a tilted microhaired ”liquid wood” surface, as shown in Fig. 5b. Both oil (Total Azolla ZS 10) and water used in this experiment were colored, accordingly, with red and blue paint. In the images shown in Fig. 5b, the oil/water mixture applied to the microstructured ”liquid wood” surface segregates into oil and water, and the oil is absorbed and locked by the microhaired surface, while the water stays on the surface of the material. The separation is observed by the color change from brown oil/water mixture to red oil and blue water. Therefore, these results suggest that microhaired wood-based surfaces enable effective separation of oil and water from the oil/water mixtures, and also help to reduce the environmental impacts of oil/water separations by utilizing natural materials for their fabrication.

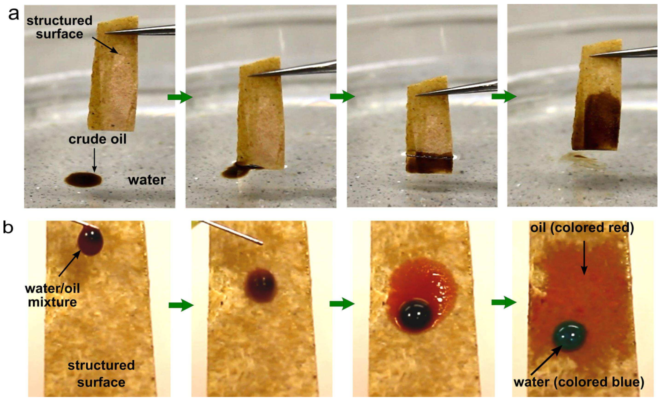

Fig. 5 Oil/water separation by microhaired wood-based surface. a) Crude oil spill cleanup in a petri dish. After dipping the sample into oil spill most of the crude oil is absorbed by the microhaired surface within few seconds. b) Colored oil/water mixture applied to the microhaired surface segregates into oil and water. The oil (colored red) is quickly absorbed and locked by the microhaired surface, while the water (colored blue) stays on the surface.

Conclusions

In summary, we fabricated superhydrophobic/superoleophilic and underwater superoleophobic wood-based surfaces capable of oil/water separation. The special wetting behavior is a result of the microhairs covering the surface. The microhairs are fabricated by scalable replication technique in which polymer microstructures are elongated with a heated mold. The superhydrophobic/superoleophilic microhaired surface is used to successfully clean simulated crude oil spill and to separate the oil/water mixture by absorbing oil. After treating the microhaired surface with argon plasma it acquires underwater superoleophobic characteristics. As a result, the microhaired wood-based surfaces can be used for both ”water-removing” and ”oil-removing” oil/water separations. Comparable to natural materials as sawdust, cotton and wool fibers traditionally used for oil spill cleanup, the microhaired wood-based material can help to reduce the environmental impacts of both oil spills and industrial oil/water separations, while improving the separation efficiency due to its multifunctional special wetting properties.

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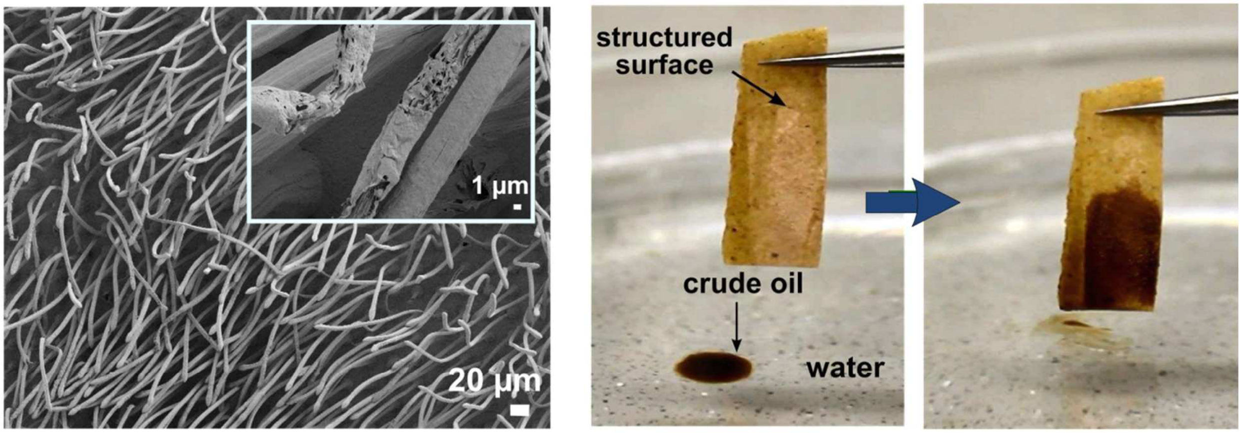

Wood-based microhaired superhydrophobic and underwater superoleophobic surfaces capable of effective oil/water mixtures separation are fabricated using a scalable replication technique.