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Research Article

Hemp-Based Sustainable Slippery Surfaces: Icephobic and Antithrombotic Properties

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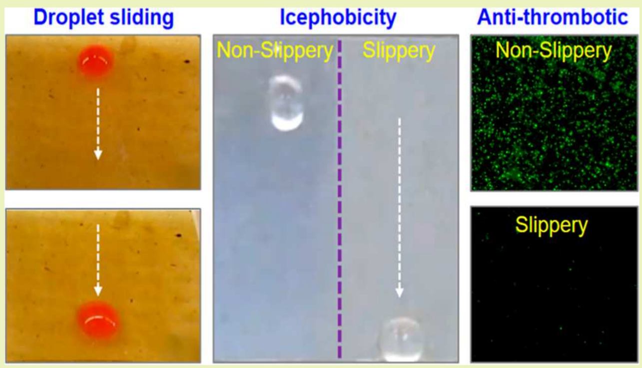
ABSTRACT: With the passage of the 2018 Farm Bill that removed hemp from the Controlled Substances Act altogether, production of hemp is experiencing a renaissance. Building on this revival and re-emergence of hemp, we designed and fabricated hemp-based sustainable and robust slippery surfaces by coating hemp paper with beeswax and subsequently infusing it with hemp oil. A wide variety of aqueous liquids and beverages easily slide on our hemp-based sustainable slippery surfaces, without leaving a trace. We also fabricated hemp-based sustainable slippery surfaces using different textured metals. Our hemp-based sustainable slippery metal surfaces display good icephobic and antithrombotic properties. With these attributes, we envision that our hemp-based sustainable slippery surfaces will pave the path to more safe, non-toxic, and biodegradable or recyclable slippery surfaces for applications in food packaging, anti-icing or de-icing coatings, and antithrombotic medical devices.



KEYWORDS: *hemp-based sustainable slippery surface, icephobicity, antithrombotic property*

■ INTRODUCTION

The demand for sustainable materials is evolving speedily, and their prevalence is increasing in recent times.[1−3] Sustainable materials are safe, non-toxic, and biodegradable or recyclable, thereby limiting waste.[4,5] Hemp (*Cannabis sativa*) is one such sustainable material that is considered as a strong alternative for numerous plant products.[6−8] The cultivation of hemp initiated around 2700 BC, when its properties as a medicinal plant were discovered for the first time.[9,10] However, domestic hemp's dominance in the United States took a significant downturn in 1937, when the United States federal government began to criminalize all cannabis.[11,12] Relatively recently, the passage of the 2018 Farm Bill removed hemp from the Controlled Substances Act altogether and made it legal for United States farmers to grow, process, and sell hemp commercially.[13] Over 40 states have now passed legislation allowing hemp cultivation, and the hemp market in the United States has increased tremendously.[14,15] Hemp-based materials have many applications in the global market,[16,17] and production of hemp is experiencing a renaissance.[18,19]

In this work, we developed hemp-based sustainable slippery surfaces (i.e., surfaces enabling high mobility of liquids), which are low-cost and ecological. We fabricated hemp-based sustainable slippery surfaces by first coating hemp paper with beeswax and subsequently infusing it with hemp oil. Our hemp-based sustainable slippery surfaces displayed slipperiness to a variety of edible liquid food products having different surface tensions. Furthermore, we fabricated hemp-based slippery sustainable metallic surfaces, which display good icephobic and antithrombotic properties. With these attributes, we envision that our hemp-based slippery surfaces will pave the path to more sustainable slippery surfaces.

■ MATERIALS AND METHODS

Hemp paper and hemp oil were purchased from Hemp Traders. Beeswax was purchased from Stakich Inc. Aluminum, copper, steel, and titanium sheets were purchased from McMaster. Hydrochloric acid (HCl), acetone, ethanol, sodium hydroxide, sodium carbonate, iron(III) chloride, toluene, propylene glycol, diethylene glycol (DEG), and hydrofluoric acid (HF) were purchased from Sigma Aldrich. Different aqueous beverage products including milk, Coca-Cola, Gatorade, agave syrup, and honey, as well as food color dyes, were obtained from local grocery stores.

Fabrication of Hemp-Based Sustainable Slippery Surfaces. First, beeswax (150 mg/mL) was dissolved in hexane at 50 °C for 1 h. Next, hemp paper (50 mm × 50 mm) was immersed into the beeswax

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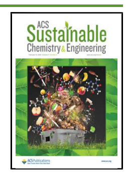

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solution for 10 min and was subsequently dried under ambient conditions. Then, beeswax-coated hemp paper was immersed in hemp oil, and subsequently, the excess hemp oil was allowed to drain away from the surface for 10 min to obtain the hemp-based slippery surface.

Fabrication of Hemp-Based Sustainable Slippery Metal Surfaces. The metal sheets were first etched *via* different protocols to obtain textured metal surfaces.

Copper: First, copper sheets (3 cm × 1 cm) were washed with acetone and ethanol and dried under ambient conditions. Next, copper plates were immersed in 5% sulfuric acid solution for 1 min to remove copper oxides, subsequently rinsed with deionized (DI) water, and dried with nitrogen gas. Next, the copper plates were etched in a solution of 1 g/mL concentration of $FeCl_3$ in DI water for 4 h and were subsequently washed with water and dried with nitrogen gas.

Steel: First, steel sheets (3 cm × 1 cm) were washed with acetone and ethanol and dried under ambient conditions. Next, the steel sheets were etched in 2.5 M HCl solution at 100 °C for 5 min and were subsequently washed with water and dried with nitrogen gas.

Aluminum: First, aluminum sheets (3 cm × 1 cm) were cleaned using acetone and ethanol and dried under ambient conditions. Next, the aluminum sheets were etched in 2 M HCl solution for 10 min and were subsequently washed with water and dried with nitrogen gas.

Titanium: First, titanium sheets (1 cm × 1 cm) were washed with acetone and ethanol and dried under ambient conditions. Titania nanotubes were fabricated by electrochemical anodization using a titanium anode and a platinum cathode in the 95:2:3 DEG/HF/H_2O (by volume) electrolyte solution at 60 V for 24 h, followed by annealing in air at 530 °C for 6 h. After anodization, titania nanotube surfaces were rinsed thoroughly with DI water and dried with nitrogen gas under ambient conditions.

After etching, each of the textured metal substrates was immersed in hemp oil at 100 °C for 1 h to obtain hydrophobic surfaces. The excess hemp oil was washed with acetone and ethanol and subsequently cured at ambient conditions for 1 h. Finally, hydrophobic textured metal substrates were immersed in hemp oil, and subsequently, the excess hemp oil was allowed to drain away from the surface for 10 min to obtain the hemp-based sustainable slippery metal surfaces.

Sliding Angle and Surface Tension Measurements. Sliding angles of different liquids and surface tensions of different liquids were measured using a goniometer (Ramé-Hart 260-F4). All results are the average of three individual measurements.

Morphology Characterization. Scanning electron microscopy (SEM) images of the hemp paper were obtained using a JEOL-6500F scanning electron microscope at 15 kV. The samples were coated with a thin film of gold prior to imaging.

Ice Adhesion Strength Measurements. Ice adhesion strength was measured using a custom-built apparatus.[20] Our apparatus consisted of a Peltier plate with a temperature controller, a force gage equipped with a probe and connected to a data acquisition system, and a linear translation stage on which the force gage was mounted. In a typical ice adhesion strength measurement, the hemp-based sustainable slippery metal surface was placed on the Peltier plate, and 0.5 mL of water in a cuvette was placed in direct contact with the surface. The Peltier plate was maintained at a temperature of −20 °C for 1 h. During this time, water in the cuvette froze to form ice that adhered to the surface. Subsequently, the linear translation stage was moved at a rate of 0.8 mm/s such that the probe applied a shear force on the entire width of the cuvette until ice detached from the surface. The peak force applied by the probe was measured using the force gage and the data acquisition system. Ice adhesion strength was determined as the peak force divided by the nominal ice surface interfacial area. The reported ice adhesion strength values are an average of eight trials conducted at three different locations of the hemp-based sustainable slippery metal surface.

Platelet Adhesion. Human blood was drawn from a healthy individual with care to avoid locally activated platelets. All practices were approved by the Colorado State University Institutional Review Board, which agrees with the National Institutes of Health's "Guiding Principles for Ethical Research". Next, blood was centrifuged at 150 *g* for 15 min to separate the human blood plasma. Then, the sterilized (irradiated under UV for at least 30 min) hemp-based sustainable slippery titania surfaces were incubated in 1 mL of the plasma in a 24-well plate at 37 °C in the presence of 5% CO_2 on a horizontal shaker plate at 100 rpm for 2 h[21] After incubation, the plasma was aspirated, and the unadhered platelets were removed by gently rinsing twice with phosphate-buffered saline (PBS). The hemp-based sustainable slippery titania surfaces were then incubated in 2 μM calcein-AM solution in PBS for 30 min in a dark environment. Subsequently, surfaces were rinsed with PBS and imaged using a fluorescence microscope (Zeiss). The total number of adhered platelets was obtained using ImageJ software. The as-received titanium and titania nanotube (without hemp oil) samples were studied used for comparison.

Cytotoxicity. Cytotoxicity of the hemp-based sustainable slippery titania surfaces was determined using a lactate dehydrogenase (LDH) cytotoxicity assay kit (Cayman Chemical). The as-received titanium, titania nanotube (without hemp oil), and hemp-based sustainable slippery titania surfaces were incubated in blood plasma for 2 h under a 5% CO_2 humidified atmosphere. The samples, as well as the positive control (blood plasma without contact with any sample) and negative control (blood plasma with 10% triton-X100 to ensure the maximum release of LDH), were then transferred to a 96-well plate. A reaction solution consisting of 96% v/v assay buffer, 1% v/v NAD+, 1% v/v lactic acid, 1% v/v tetrazolium salt (INT), and 1% v/v diaphorase was added in equivalent amounts (1:1) to all surfaces. This solution was incubated with gentle shaking on a horizontal shaker plate at 100 rpm for 30 min at room temperature. After incubation, the absorbance of 100 μL of the solution from each surface was immediately measured at 490 nm to evaluate the cytotoxic effect.

RESULTS AND DISCUSSION

Design of Robust Slippery Surfaces. One way of making slippery surfaces is by employing lubricant-infused porous surfaces, which use porosity (or texture/roughness) within the solid to trap pockets of a liquid, which is immiscible with the contacting liquids.[22,23] The trapped immiscible liquid acts as a liquid lubricant, reducing the solid−liquid interfacial area and inducing slip at the liquid−liquid interface.[24] In order to design a lubricant-infused porous surface with robust slipperiness to contacting liquids, three important criteria must be satisfied: (1) the lubricant must completely wet the porous solid surface, (2) the contacting liquid must not displace the lubricant from the porous solid surface, and (3) the lubricant must not "cloak" (or wrap or encapsulate) the contacting liquid droplet. To identify the necessary conditions for fabricating hemp-based sustainable surfaces with robust slipperiness, we examined the interfacial energy of the possible wetting states for each criterion (see Figure 1).

Criterion 1: The lubricant must completely wet the porous solid surface. Consider a dry porous solid surface (Figure 1a) and a lubricant-infused porous solid surface (Figure 1b). The interfacial energy of the dry porous solid is $E_1 = r\,\gamma_{sa}$, where r is the roughness factor of the porous solid surface (i.e., the ratio of the actual surface area to the projected area; $r > 1$ for porous solid surfaces) and γ_{sa} is the solid surface energy. The interfacial energy of the lubricant-infused porous solid surface is $E_2 = r\,\gamma_{sa} + \gamma_{oa}$, where γ_{so} is the solid−lubricant interfacial energy and γ_{oa} is the lubricant surface tension. For the lubricant to completely wet the porous solid surface, E_2 must be a lower energy state compared to E_1, i.e., $E_2 < E_1$.

Criterion 2: The contacting liquid must not displace the lubricant from the porous solid surface. Consider a lubricant-infused porous solid surface with the contacting liquid displacing the lubricant (Figure 1c) and unable to displace the lubricant (Figure 1d). The interfacial energy when the

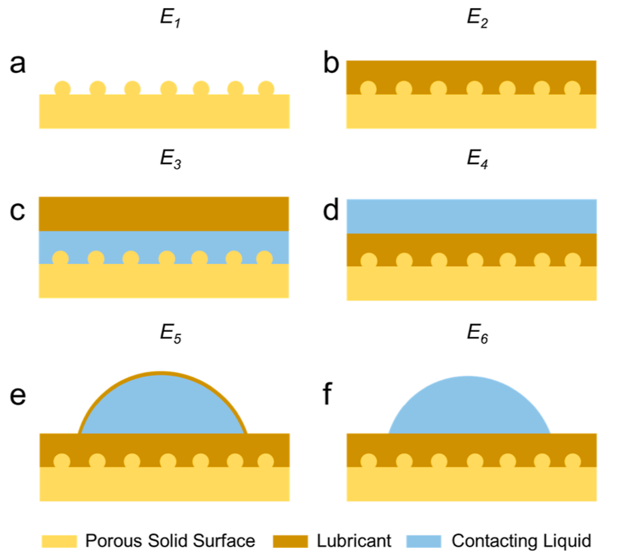

Figure 1. Possible wetting states on a porous solid surface. (a) Dry porous solid surface in contact with air. (b) Porous solid surface infused with a lubricant. (c) Porous solid surface on which the lubricant is displaced by the contacting liquid. (d) Porous solid surface on which the lubricant is not displaced by the contacting liquid. (e) Contacting liquid droplet cloaked by the lubricant. (f) Contacting liquid droplet not cloaked by the lubricant.

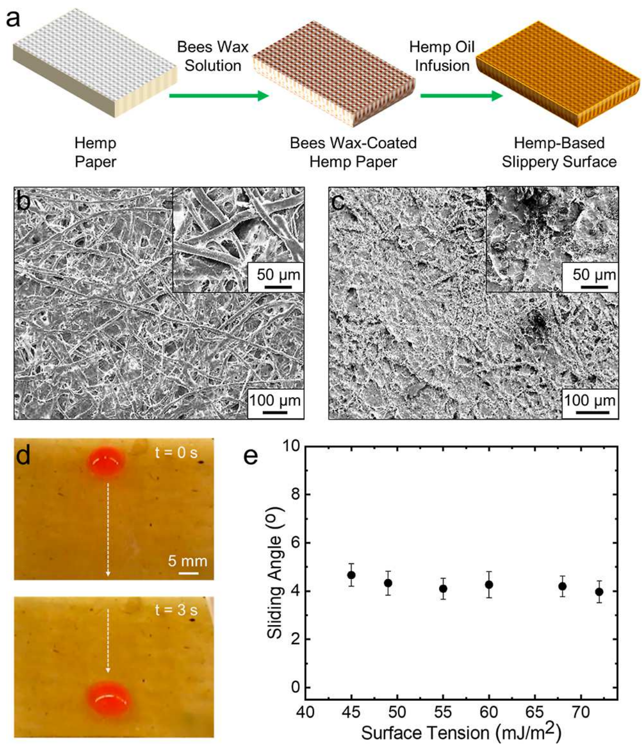

Figure 2. Hemp-based sustainable slippery surfaces. (a) Schematic depicting the fabrication of hemp-based sustainable slippery surfaces. (b,c) SEM images showing the morphology of the hemp paper and the hemp paper coated with beeswax, respectively. Insets show SEM images at a higher magnification. (d) A 20 μL water droplet (colored red) sliding on a hemp-based sustainable slippery surface tilted by 4° relative to the horizontal. (e) Sliding angles of 20 μL droplets of water and aqueous beverages including Gatorade (~68 mJ/m^2), honey (~60 mJ/m^2), milk (~55 mJ/m^2), Coca-Cola (~49 mJ/m^2), and agave syrup (~45 mJ/m^2).

contacting liquid displaces the lubricant is $E_3 = r\,\gamma_{sw} + \gamma_{ow} + \gamma_{oa}$, where γ_{sw} is the solid-contacting liquid interfacial energy and γ_{ow} is the lubricant-contacting liquid interfacial energy. The interfacial energy when the contacting liquid is unable to displace the lubricant is $E_4 = r\,\gamma_{so} + \gamma_{ow} + \gamma_{wa}$, where γ_{wa} is the contacting liquid surface tension. For the contacting liquid to not displace the lubricant (i.e., wash away the lubricant) from the porous solid surface, E_4 must be a lower energy state compared to E_3, i.e., $E_4 < E_3$.

Criterion 3: The lubricant must not cloak the contacting liquid droplet. Consider a lubricant-infused porous solid surface with cloaked (Figure 1e) and uncloaked (Figure 1f) contacting liquid droplets. The interfacial energy of the cloaked contacting liquid droplet is $E_5 = \gamma_{ow} + \gamma_{oa}$. The interfacial energy of the uncloaked contacting liquid droplet is $E_6 = \gamma_{wa}$. For the lubricant to not cloak (and wash away with) the contacting liquid droplet, E_6 must be a lower energy state compared to E_5, i.e., $E_6 < E_5$.

Fabrication of Hemp-Based Sustainable Slippery Surfaces. To ensure robust slipperiness, we evaluated these criteria for hemp oil-infused hemp paper. We chose hemp paper ($\gamma_{sa} \approx 68$ mJ/m^2, assuming that it is predominantly composed of cellulose fibers)[25] and hemp oil ($\gamma_{oa} = 32$ mJ/m^2) because they are sustainable materials. Our analysis indicated that $E_2 < E_1$ (see Supporting Information Section S1), implying that hemp oil completely wets the hemp paper, which was also confirmed by experiments. Assuming that the contacting liquid is water ($\gamma_{wa} = 72$ mJ/m^2), our analysis also indicated that $E_3 < E_4$ (see Supporting Information Section S1), implying that water displaces and washes away the hemp oil from hemp paper, which is undesirable.

To overcome this problem, we coated hemp paper with beeswax and then infused it with hemp oil (Figure 2a). We chose beeswax ($\gamma_{sa} = 28$ mJ/m^2) because it is a sustainable material. Our analysis indicated that $E_2 < E_1$ (see Supporting Information Section S2), implying that hemp oil completely wets the beeswax-coated hemp paper, which was also confirmed by experiments. Our analysis also indicated that $E_4 < E_3$ (see Supporting Information Section S2), implying that water does not displace hemp oil from hemp paper coated with beeswax. Finally, our analysis also indicated that $E_6 < E_5$ (see Supporting Information Section S2), implying that hemp oil does not cloak a water droplet on the surface. These analyses indicate that beeswax-coated hemp paper infused with hemp oil can result in robust slipperiness.

Morphology and Slipperiness of Hemp-Based Sustainable Slippery Surfaces. Based on the above understanding, we fabricated sustainable slippery surfaces using beeswax-coated hemp paper infused with hemp oil (Figure 2a; see the Materials and Methods section). A comparison of the SEM images of the uncoated hemp paper (Figure 2b) and beeswax-coated hemp paper (Figure 2c) shows a uniform coating of beeswax. While an uncoated hemp paper is oleophilic and hydrophilic, the beeswax-coated hemp paper is oleophilic and hydrophobic. The oleophilic nature of beeswax retains the hemp oil trapped in the porous hemp paper, and the hydrophobic nature of beeswax repels water and prevents water from displacing hemp oil from the hemp paper.

We characterized the slipperiness of our hemp-based sustainable slippery surfaces with aqueous liquids. Water droplets (20 μL, colored red) slide easily at tilt angles of ~4° on our hemp-based sustainable slippery surfaces, reaching a sliding velocity of 10 mm/s within ~3 cm (Figure 2d and

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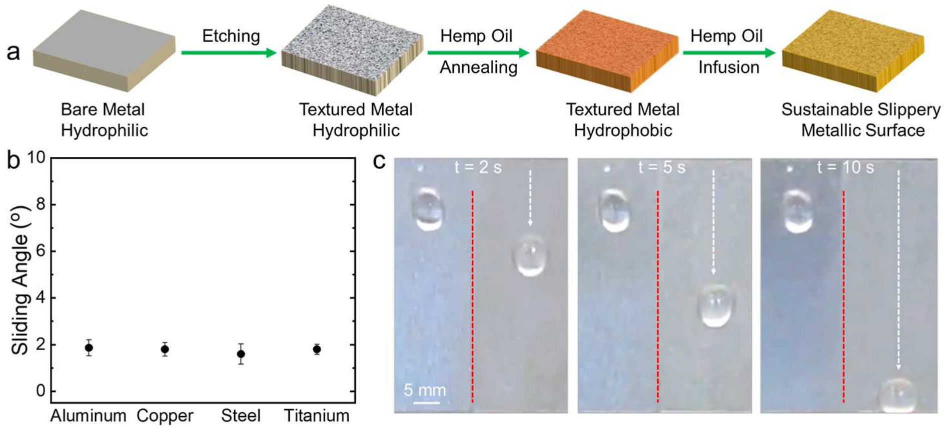

Figure 3. Anti-icing nature of hemp-based sustainable slippery metal surfaces. (a) Schematic depicting the fabrication of hemp-based sustainable slippery metal surfaces. (b) Sliding angles of 20 μL water droplets on hemp-based sustainable slippery metal surfaces. (c) Water droplet adhering and freezing on as-received aluminum (left of the red dashed line) and sliding without freezing on a hemp-based sustainable slippery aluminum surface (right of the red dashed line). Surface temperature was −20 °C.

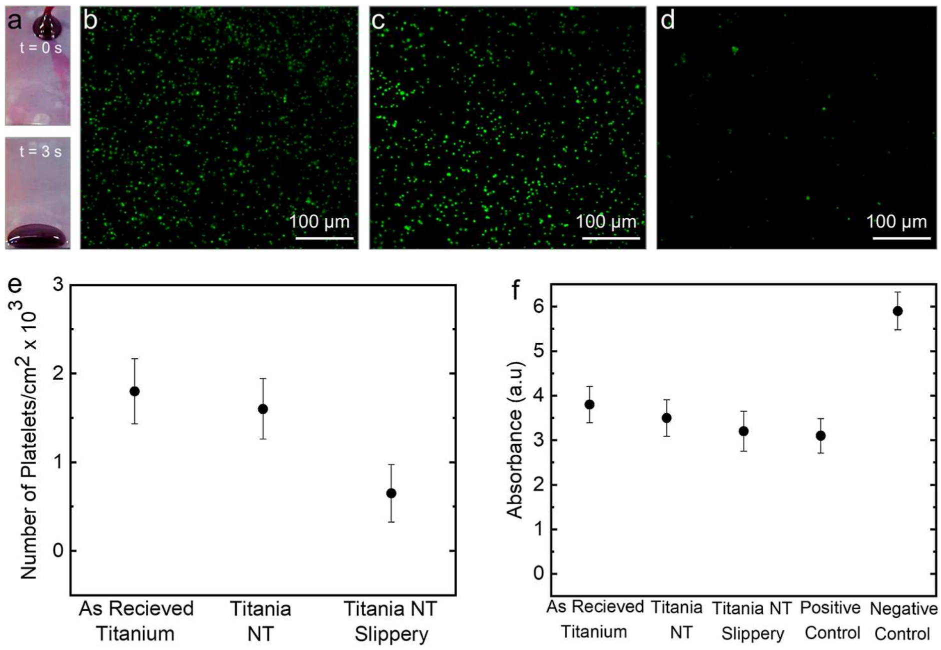

Figure 4. Antithrombotic nature of hemp-based sustainable slippery titania surface. (a) A 20 μL whole blood droplet sliding on a hemp-based sustainable slippery titania surface. (b−d) Fluorescence microscopy images depicting adhesion of platelets (green) on the as-received titanium surface, titania nanotube surface (without hemp oil), and hemp-based sustainable slippery titania surface, respectively. (e,f) Number of platelets per unit area and LDH cytotoxicity, respectively, on the as-received titanium surface, titania nanotube surface (without hemp oil), hemp-based sustainable slippery titania surface, positive control (blood plasma without contact with any sample), and negative control (blood plasma with 10% triton-X100 to ensure maximum release of LDH).

Movie S1). In addition, our hemp-based slippery surfaces display slipperiness to various aqueous beverages (Figure 2e), which have lower surface tension than that of water, including Gatorade (∼68 mJ/m^2), honey (∼60 mJ/m^2), milk (∼55 mJ/m^2), Coca-Cola (∼49 mJ/m^2), and agave syrup (∼45 mJ/m^2). The sliding angles of these beverages are very similar to those of water. Such slipperiness with beverages indicates that our hemp-based sustainable slippery surfaces can be used to effectively reduce losses in industrial processing of beverages and liquid waste in food containers.

Icephobicity of Hemp-Based Sustainable Slippery Surfaces. The accumulation of ice on aircrafts, ships, power lines, oil rigs, and automotives is a severe hazard, which not only endangers human life but also causes enormous financial losses.[26−29] For example, ice accretion on aircraft wings can cause accidents and significant delays.[30,31] Active methods (e.g., heating) for anti-icing (i.e., preventing or delaying the formation of ice) or de-icing (i.e., removal of ice after it has formed) are expensive and energy-intensive.[32−34] Hence, passive methods like coatings and surface modifications are more attractive for anti-icing and/or de-icing.[35−37] Prior work has indicated that lubricant-infused surfaces are icephobic (i.e., both anti-icing and de-icing).[38−40] Building on prior work, we fabricated hemp-based sustainable slippery surfaces on different textured metal substrates (e.g., aluminum, copper, steel, and titanium) to investigate their icephobicity. To accomplish this, we first fabricated textured metal substrates (see the Materials and Methods section; Figure 3a and Supporting

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Information Figure S1). Then, we modified the textured metal substrates by annealing in hemp oil and curing, which allows the long chain fatty acids in hemp oil to adsorb on the textured metal substrates, rendering them hydrophobic and oleophilic. Subsequently, we infused the hydrophobic and oleophilic textured metal substrates with hemp oil, rendering them slippery. Water droplets (20 μL) could easily slide past all the hemp-based sustainable slippery metallic surfaces at a tilt angle of <2° (Figure 3b).

To test the anti-icing performance of the hemp-based sustainable slippery metallic surfaces, we used aluminum substrates as an example. We placed the as-received aluminum surface and a hemp-based sustainable slippery aluminum surface in a −20 °C freezer. Our results indicate that frost starts forming on the as-received aluminum surface within 20 s, while it takes ∼15 min for frost formation on the hemp-based sustainable slippery aluminum surface, confirming the anti-icing nature. Furthermore, when water droplets (20 μL) were placed on surfaces tilted at 45° relative to the horizontal, the water droplet on the as-received aluminum surface remained adhered and froze to form ice, while the water droplet on the hemp-based sustainable slippery aluminum surface slid past the surface without forming ice (Figure 3c and Movie S2), reaffirming the anti-icing nature. In addition, to test the de-icing performance of the hemp-based sustainable slippery aluminum surface, we measured the ice adhesion strength (see the Materials and Methods section). The ice adhesion strength of the hemp-based sustainable slippery aluminum surfaces was ∼5 kPa, which is very low, confirming the de-icing nature. If ice contacted the underlying aluminum substrate, the ice adhesion strength would be orders of magnitude higher, similar to the ice adhesion strength of the as-received aluminum surface (∼1000 kPa).[41] These results indicate that hemp-based sustainable slippery surfaces can be used to impart icephobic properties to metallic surfaces.

Antithrombotic Properties of Hemp-Based Sustainable Slippery Surfaces. Thrombosis is one of the most common and persistent challenge in biomedical materials and medical devices.[42] Thrombus formation on the medical devices often requires expensive device replacement or treatment with anticoagulants that increases the risk of severe complications and death.[43] Prior work has indicated that lubricant-infused surfaces display antithrombotic properties due to the presence of a molecularly smooth liquid interface.[44,45] Building on prior work, we investigated the antithrombotic properties of our hemp-based sustainable slippery metallic surfaces, using titanium substrates as an example. To accomplish this, we first fabricated textured titania nanotube surfaces by electrochemical anodization (see the Materials and Methods section). Then, we modified the textured titania nanotube substrates by annealing in hemp oil and curing, rendering them hydrophobic and oleophilic. Subsequently, we infused the hydrophobic and oleophilic textured titania nanotube substrates with hemp oil, rendering them slippery. Whole blood droplets (20 μL) could easily slide past the hemp-based sustainable slippery titania surfaces, without any residue (Figure 4a and Movie S3).

To test the antithrombotic properties, we compared platelet adhesion on the as-received titanium surface, titania nanotube surface (without hemp oil), and hemp-based sustainable slippery titania surface by incubating them in human blood plasma for 2 h and subsequently imaging them using a fluorescence microscope (see the Materials and Methods section). While the fluorescence microscopy images indicated significant platelet adhesion on titanium and titania nanotube surfaces, there was negligible platelet adhesion on the hemp-based sustainable slippery titania surface (Figure 4b−d). The number of platelets per unit area was significantly less on the hemp-based sustainable slippery titania surface compared to that on titanium and titania nanotube surfaces (Figure 4e). This is significant because platelet adhesion plays a key role in the blood coagulation cascade and serves as an early indicator of thrombosis.[46] Furthermore, we compared the cytotoxicity of these surfaces using an LDH cytotoxicity assay kit (see the Materials and Methods section).[47] The cytotoxicity results indicate that hemp-based sustainable slippery titania surfaces are comparable to titanium surfaces, which are currently used in several implants (Figure 4f).[48,49] These results indicate that hemp-based sustainable slippery surfaces have potential for use as antithrombotic coatings on medical devices.[50]

■ CONCLUSIONS

In conclusion, building on the thermodynamics of wetting, we designed and fabricated hemp-based sustainable and robust slippery surfaces by coating hemp paper with beeswax and subsequently infusing it with hemp oil. Droplets of water and many aqueous beverages (Gatorade, honey, milk, Coca-Cola, and agave syrup) slide on our hemp-based sustainable slippery surfaces without leaving a trace, indicating their potential to liquid waste in food containers. Furthermore, we fabricated hemp-based sustainable slippery surfaces using different textured metal substrates. Our hemp-based sustainable slippery metal surfaces display anti-icing and de-icing properties, indicating their potential as icephobic coatings on aircrafts, ships, power lines, oil rigs, or automotives. Our hemp-based sustainable slippery metal surfaces also display antithrombotic properties, indicating their potential for use in medical devices. With these attributes, we envision that our hemp-based slippery surfaces will pave the path to more sustainable slippery surfaces.

Finally, it is important to note that the practical utility of any lubricant-infused slippery surface depends on its durability; and the durability requirements are application-specific. Preliminary investigation of the durability of our hemp-based sustainable slippery surfaces demonstrated retention of slipperiness (i.e., negligible change in sliding angles of water) after exposure to air for 7 days, immersion in water for 7 days, and 20,000 water droplets sliding past the surface (see Supporting Information Figure S2). A more extensive characterization of durability (e.g., mechanical durability, thermal durability, chemical durability, radiation durability, etc.) is required to thoroughly assess the practical utility of hemp-based sustainable slippery surfaces in product development.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06233.

> Energy analysis for possible wetting states on hemp paper, energy analysis for possible wetting states on beeswax-coated hemp paper, SEM images of various textured metal surfaces, and durability of hemp-based sustainable slippery surfaces (PDF)

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Sliding of different droplets including water, milk, and coke on a hemp-based sustainable slippery surface (MP4)

Anti-icing property of the as-received aluminum and hemp-based sustainable slippery aluminum surface (MP4)

Sliding of a whole blood droplet on a hemp-based sustainable slippery titania surface (MP4)

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Author Contributions

D.J.S and A.M.R contributed equally to this work. A.K.K conceived the idea. D.J.S, A.M.R, R.M.S, S.V, and W.W conducted the experiments. D.J.S, R.M.S, A.M.R, S.V, W.W, and A.K.K conducted the analysis. D.J.S, A.M.R, K.C.P, and A.K.K wrote the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information

Hemp-based Sustainable Slippery Surfaces: Icephobic and Antithrombotic Properties

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Section S1. Energy analysis for possible wetting states on hemp paper

Consider the interfacial energies of dry hemp paper (E_1) and hemp oil infused hemp paper (E_2). The interfacial energy $E_1 = r\gamma_{sa}$, where r is the roughness factor of hemp paper (i.e., ratio of the actual surface area to the projected area; note that $r > 1$) and $\gamma_{sa} \approx 68$ mJ/m^2 is the solid surface energy of the hemp paper.[1] So, $E_1 = 68r$ mJ/m^2. The interfacial energy $E_2 = r\gamma_{sa} + \gamma_{oa}$, where γ_{so} is the hemp paper-hemp oil interfacial energy and γ_{oa}= 32 mJ/m^2 is the hemp oil surface tension [2]. Using Fowkes equation,[3] we estimated hemp paper-hemp oil interfacial energy, $\gamma_{so} = \gamma_{sa} + \gamma_{oa} - 2\sqrt{\gamma_{sa}^{d}\gamma_{oa}^{d}} = 41$ mJ/m^2, where $\gamma_{sa}^{d} = 27$ mJ/m^2 and $\gamma_{oa}^{d} = \gamma_{oa} = 32$ mJ/m^2 are the dispersive components of hemp paper solid surface energy and hemp oil surface tension, respectively.[2] So, $E_2 = 41r + 32$ mJ/m^2. Upon comparing E_1 and E_2, it is evident that $E_2 < E_1$ (i.e., hemp oil completely wets the hemp paper) when $r > 1.2$, which is reasonable based on the morphology of the hemp paper (see Figure 2b). Furthermore, our experiments show that hemp oil indeed wets the hemp paper completely, which also confirms that $E_2 < E_1$ (i.e., $r > 1.2$ for the hemp paper).

Now, consider the interfacial energies of hemp paper on which hemp oil is displaced by water (E_3) and hemp paper on which hemp oil is not displaced by water (E_4). The interfacial energy $E_3 = r\gamma_{sw} + \gamma_{ow} + \gamma_{oa}$, where γ_{sw} is the hemp paper-water interfacial energy and γ_{ow} is the hemp oil-water interfacial energy. Using Owens and Wendt equation,[4] we estimated hemp paper-water interfacial energy, $\gamma_{sw} = \gamma_{sa} + \gamma_{wa} - 2\sqrt{\gamma_{sa}^{d}\gamma_{wa}^{d}} - 2\sqrt{\gamma_{sa}^{p}\gamma_{wa}^{p}} = 2$ mJ/m^2, where γ_{wa}= 72 mJ/m^2 is water surface tension, $\gamma_{wa}^{d} = 21$ mJ/m^2 and $\gamma_{wa}^{p} = 51$ mJ/m^2 are the dispersive and polar components, respectively, of water surface tension, and $\gamma_{sa}^{d} = 27$ mJ/m^2 and $\gamma_{sa}^{p} = 41$ mJ/m^2 are the dispersive and polar components, respectively, of hemp paper solid surface energy.[1] So, $E_3 = 2r + \gamma_{ow} + 32$ mJ/m^2. The interfacial energy $E_4 = r\gamma_{so} + \gamma_{ow} + \gamma_{wa} = 41r + \gamma_{ow} + 72$ mJ/m^2. Upon comparing E_3 and E_4, it is evident that $E_3 < E_4$ (i.e., water displaces hemp oil), which is undesirable.

Section S2. Energy analysis for possible wetting states on beeswax coated hemp paper

Consider the interfacial energies of dry beeswax coated hemp paper (E_1) and hemp oil infused beeswax coated hemp paper (E_2). The interfacial energy $E_1 = r\gamma_{sa}$, where r is the roughness factor of beeswax coated hemp paper (i.e., ratio of the actual surface area to the projected area; note that $r > 1$) and $\gamma_{sa} \approx 28$ mJ/m^2 is the solid surface energy of beeswax coated hemp paper.[5] So, $E_1 = 28r$ mJ/m^2. The interfacial energy $E_2 = r\gamma_{sa} + \gamma_{oa}$, where γ_{so} is the beeswax coated hemp paper-hemp oil interfacial energy and $\gamma_{oa} = 32$ mJ/m^2 is the hemp oil surface tension.[2] Using Fowkes equation,[3] we estimated beeswax coated hemp paper-hemp oil interfacial energy, $\gamma_{so} = \gamma_{sa} + \gamma_{oa} - 2\sqrt{\gamma_{sa}^d \gamma_{oa}^d}$ = 1 mJ/m^2, where $\gamma_{sa}^d = \gamma_{sa} = 28$ mJ/m^2 and $\gamma_{oa}^d = \gamma_{oa} = 32$ mJ/m^2 are the dispersive components of the beeswax coated hemp paper solid surface energy[5] and hemp oil surface tension,[2] respectively. So, $E_2 = r + 32$ mJ/m^2. Upon comparing E_1 and E_2, it is evident that $E_2 < E_1$ (i.e., hemp oil completely wets the beeswax coated hemp paper) when $r > 1.2$, which is reasonable based on the morphology of the beeswax coated hemp paper (see Figure 2c). Furthermore, our experiments show that hemp oil indeed wets the beeswax coated hemp paper completely, which also confirms that $E_2 < E_1$ (i.e., $r > 1.2$ for beeswax coated hemp paper).

Now, consider the interfacial energies of beeswax coated hemp paper on which hemp oil is displaced by water (E_3) and beeswax coated hemp paper on which hemp oil is not displaced by water (E_4). The interfacial energy $E_3 = r\gamma_{sw} + \gamma_{ow} + \gamma_{oa}$, where γ_{sw} is the beeswax coated hemp paper-water interfacial energy and γ_{ow} is the hemp oil-water interfacial energy. Using Fowkes equation,[3] we estimated the beeswax coated hemp paper-water interfacial energy, $\gamma_{sw} = \gamma_{sa} + \gamma_{wa} - 2\sqrt{\gamma_{sa}^d \gamma_{wa}^d}$ = 52 mJ/m^2, where $\gamma_{wa} = 72$ mJ/m^2 is water surface tension and $\gamma_{wa}^d = 21$ mJ/m^2 is the dispersive component of water surface tension. So, $E_3 = 52r + \gamma_{ow} + 32$ mJ/m^2. The interfacial energy $E_4 = r\gamma_{so} + \gamma_{ow} + \gamma_{wa} = r + \gamma_{ow} + 72$ mJ/m^2. Upon comparing E_3 and E_4, it is evident that $E_4 < E_3$ (i.e., water is unable to displace hemp oil) for all $r > 1$.

Finally, consider the interfacial energies of water droplet cloaked by hemp oil (E_5) and water droplet not cloaked by hemp oil (E_6). The interfacial energy $E_5 = \gamma_{ow} + \gamma_{oa}$. Using Fowkes equation,[3] we estimated hemp oil-water interfacial energy $\gamma_{ow} = \gamma_{oa} + \gamma_{wa} - 2\sqrt{\gamma_{oa}^d \gamma_{wa}^d} = 51$ mJ/m^2. So, $E_5 = 83$ mJ/m^2. The interfacial energy $E_6 = \gamma_{wa} = 72$ mJ/m^2. Upon comparing E_5 and E_6, it is evident that $E_6 < E_5$ (i.e., water droplet is not cloaked by hemp oil).

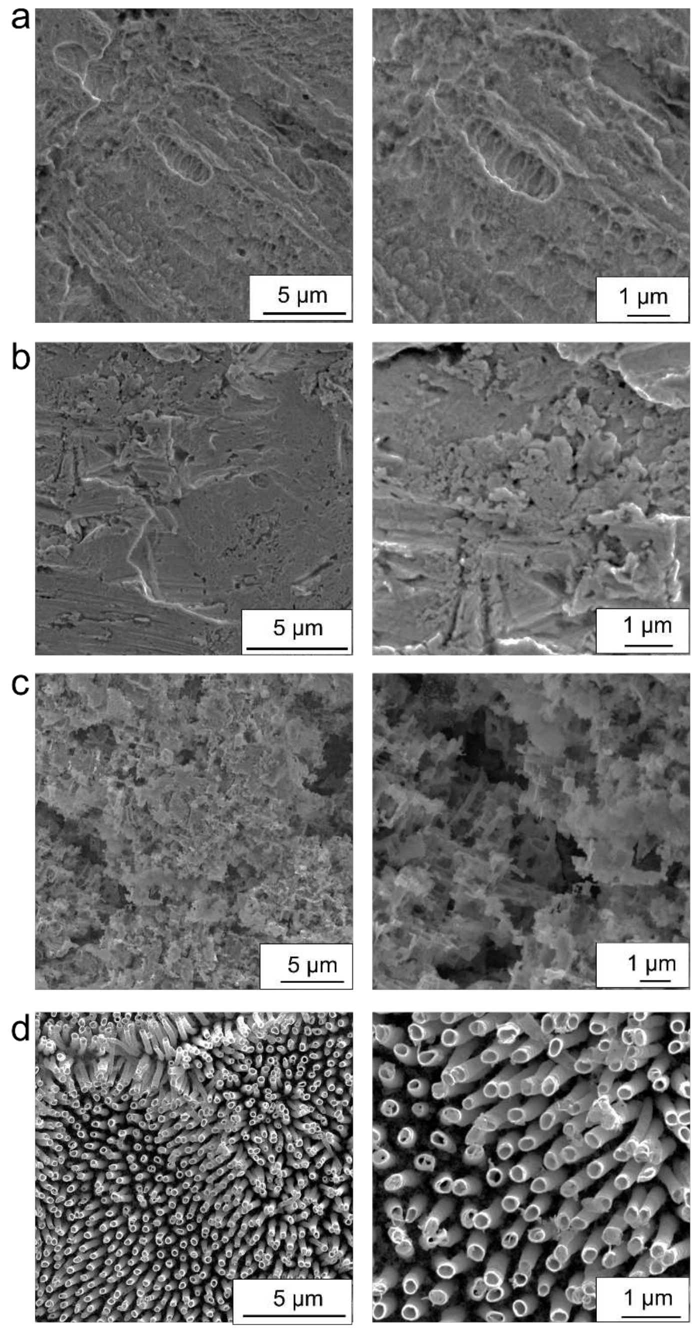

Figure S1: SEM images depicting the morphology of different textured metal surfaces. (a) steel, (b) copper, (c) aluminum, and (d) titanium.

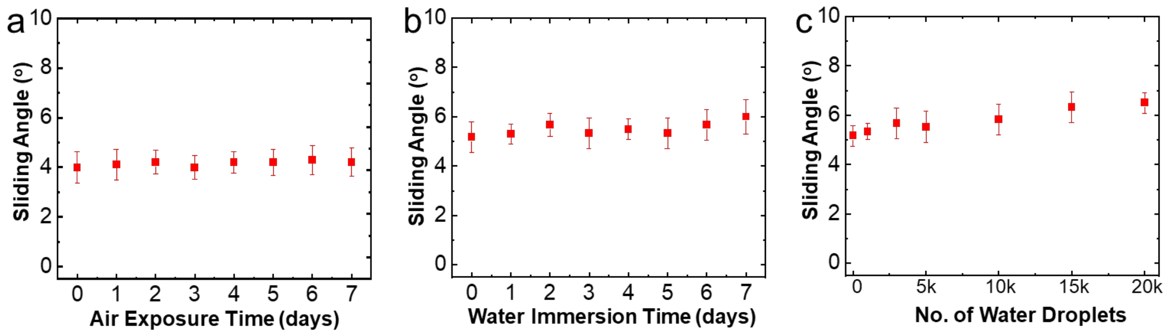

Figure S2: Durability of hemp-based sustainable slippery surfaces. Sliding angles of water on hemp-based sustainable slippery aluminum surfaces as a function of (a) air exposure time, (b) water immersion time, and (c) number of water droplets sliding past the surface. Similar results were observed with all the other hemp-based sustainable slippery surfaces (both paper and metal).

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