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Durable Superamphiphobic Wood Surfaces from Cu₂O Film Modified with Fluorinated Alkyl Silane

Likun Gao¹, Shaoliang Xiao¹, Wentao Gan¹, Xianxu Zhan^{2*}, Jian Li^{1*}

A simple hydrothermal process with further hydrophobization was developed for fabricating durable superamphiphobic film of cuprous oxide (Cu₂O) microspheres on wood substrate. With the advantages of simple operation, low cost, short reaction time, and environmental friendliness, the present method can be well adopted to fabricate Cu₂O microstructures on the wood surfaces. Meanwhile, the wood coated with a hydrolysis product from long chain fluoroalkyl silane of (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane has a durable superhydrophobic and superoleophobic surface and the coating shows excellent durability to acid, high temperature and humidity, and abrasion. The coatings effectively protect the substrate from damages, expanding the wood application fields. The functional coating may have a broad prospect of applications from the bridges and buildings to automobiles and other possible aspects.

Keywords: durable, superamphiphobic, wood, cuprous oxide (Cu₂O), fluoroalkyl silane

Introduction

Recently bioinspired materials with extraordinary properties and functions provide a wide range of applications from photocatalytic clothing to corrosion-resistant, pollutant-degrading surfaces.¹ The studies of lotus and other living things with unusual wetting characteristic of super-liquid-repellent surfaces have attracted much attention in both scientific and industrial areas.² Super-liquid-repellent surfaces by combining micro- and nanoscaled structures with low-surface-energy materials are often deemed superhydrophobic and superoleophobic up to the repelled liquid. Superhydrophobic surfaces with the water contact angle larger than 150° offer emerging applications including separation of oil from water, nonsticking, self-cleaning, anti-contamination, protection of devices, etc. Moreover, superoleophobic surfaces are defined as the structured surfaces that resist wetting of liquids with the surface tension below 35 mN/m, such as hexadecane ($\gamma_{lv} = 27.5$ mN/m).³⁻⁵ In addition, superoleophobic surfaces have great potential applications in preventing the substrates from fouling of hazard chemicals and biological contaminants. Being called as superamphiphobic surfaces, the combination of the

^aMaterial Science and Engineering College, Northeast Forestry University, Harbin 150040, P.R. China

^bDehua TB New Decoration Material Co., Ltd, Huzhou, 313200, P.R. China

*Corresponding author. Tel: +86-451-82192399; fax: +86-451-82192399

E-mail addresses: gaolknefu@163.com (Likun Gao), and nefulijian@163.com (Jian Li).

superhydrophobicity and superoleophobicity on the same substrate, have an impact on a wide range of phenomena, including biofouling by marine organisms, anti-icing, anti-corrosion, self-cleaning and biomedical applications.⁶

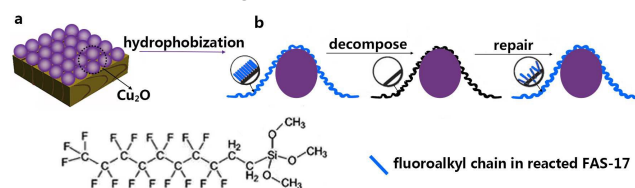
However, no material would remain its properties for long time. The daily used materials will lose their efficacy in three ways: aging, abrasion and rupture. Moreover, the durability of artificial super-liquid-repellent coatings faced enormous threatens and challenges when exposed to acid rain, high-temperature-humidity conditions, or scratched away by sand in the wind or by animals. Redepositing the low-surface-energy materials is a common method for recovering the super-liquid-repellent properties of artificial coatings⁷, which is not convenient. Durable function is defined as that plants maintain their super-liquid-repellent properties by regenerating the epicuticular wax layer after they are damaged. Recently, it is believed that the endowing artificial coatings with durable ability provide an efficient way to solve the problem of the poor durability. Inspired by the durable super-liquid-repellent properties of living plants, the study presents an artificial way through the two key surface parameters, roughness and surface energy, to fabricate durable superamphiphobic coatings. Wang et al. recently reported a durable superamphiphobic surface on anodized alumina that was prepared by filling the intrinsic pores with a low-surface energy liquid⁸. Wang et al. also reported that the durable superhydrophobic and superoleophobic surfaces could be obtained from the fluorinated-decyl polyhedral oligomeric silsesquioxane and hydrolyzed fluorinated alkyl silane⁹.

As a natural organic material, wood is one of the widely used structural materials for various applications due to its satisfactory performance, such as low density, thermal expansion, renewability and aesthetically pleasing appearance.¹⁰⁻¹² Wood products with durable superamphiphobic properties would be greatly appreciated by a more discerning and demanding consumer market as high-value-added products.

Hence, our strategy is to design durable superamphiphobic coatings on wood surfaces as shown in Scheme 1. The first step (Scheme 1a) is to build microscaled cuprous oxide (Cu_2O) hierarchical structures on the wood substrate through a simple hydrothermal synthesis for only two hours. To date, most researchers have reported the superhydrophobic surfaces were successfully fabricated based on TiO_2 - or ZnO -treated substrates. However, as a reddish p-type semiconductor, Cu_2O has attracted more and more attention by researchers due to its direct band gap of 2~2.2 eV as a result of the presence of Cu vacancies, which formed an acceptor level 0.4 eV above the valence band.¹³ Cu_2O with unique chemical and physical properties has been widely used in electronics, catalysis, optical devices, biosensing, gas sensors, and antifouling. With its numerous attractive advantages, such as, low toxicity, good environmental acceptability, inexpensive, plentiful and readily available, Cu_2O may become a substitution for TiO_2 and ZnO .^{14, 15} Therefore, we selected Cu_2O film as a rough coating on the wood surfaces.

The second step (Scheme 1b) is the fabrication of long-chain polymer coatings ((heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane, hereafter abbreviated as FAS-17) with

low surface energy. After the deposition of a FAS-17 coating, the wood surface become superamphiphobic because of the formation of a covalently attached fluoroalkyl silane layer. As a most important property, the superamphiphobic coatings can preserve a large number of reacted fluoroalkyl silane moieties as healing agents. When the top fluoroalkyl silane layer of the superamphiphobic coating is decomposed or scratched, the preserved healing agents can migrate to the coating surface to heal the superamphiphobicity like a living plant. Moreover, due to the toxicity of fluoroalkyl silane, the study still needs deep investigation to develop an environmental-friendly and multifunctional material in the future. In the study, we designed harsh conditions, such as acid, high temperature and humidity, and abrasion, to explore the durable properties of the products. The results indicated that the coatings showed excellent durability to acid, high temperature and humidity, and abrasion, and the coatings could effectively protect the substrate from damages.



Scheme 1. Perform mechanism of the durable superamphiphobic wood surfaces: (a) the pristine wood coating with Cu_2O particles provided a rough microstructure; (b) the wood surfaces became superamphiphobic after hydrophobization with FAS-17, and the working principle of the durable process after decomposition.

Methods

Materials

All chemicals supplied by Shanghai Boyle Chemical Company, Limited were of analytical reagent-grade quality and used without further purification. Deionized water was used throughout the experiments. Wood blocks were obtained from the sapwood sections of poplar (*Populus ussuriensis* Kom), which is one of the most common tree species in the northeast of China. The wood specimens were oven-dried (24 h, 103 ± 2 °C) to a constant weight after ultrasonically rinsing in deionized water for 30 min, and oven-dried weight were determined.

Preparation of Cu_2O film on the wood surface

A typical synthesis of the Cu_2O film on wood substrate was performed as follows. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.5989 g) was dissolved in 30 mL deionized water, then D-glucose (0.5 g) and PVP (K-30, 0.3 g) were added under continuous stirring. After 1 h, the resulted solution was transferred into a 50 mL Teflon-lined autoclave and the cleaned wood blocks were immersed in the solution. The autoclave was kept in a vacuum oven at 180 °C for 2 h. After cooling to room temperature in air, the wood loaded with Cu_2O was removed, washed several times with deionized water and ethanol, and dried at 45 °C for more than 24 h in vacuum.

Hydrophobization of wood surfaces with FAS-17

A 20 mL methyl alcohol solution of 0.2 mL (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane ($\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, hereafter denoted as FAS-17) was hydrolyzed by the addition of 60 mL water at room temperature. Then, 75 mL of the adjusted solution was

transferred into a 100 mL Teflon container. The Cu_2O -treated wood samples were subsequently placed into the above reaction solution. The autoclave was sealed and maintained at 75 °C for 5 h, then allowed to naturally cool to room temperature. Subsequently, the samples were washed with ethyl alcohol to remove any residual chemicals and allowed to dry in air at room temperature. They were then dried at 45 °C for more than 24 h in vacuum. Thus, a superhydrophobic wood surface was obtained.

Characterization

The morphology of the wood surfaces was observed using the field emission scanning electron microscopy (SEM, Quanta 200, FEI, Holland) operating at 12.5 kV in combination with EDS (Genesis, EDAX, Holland). The X-ray diffraction (XRD, Bruker D8 Advance, Germany) was employed to analyze the crystal structures of all samples applying graphite monochromatic with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range from 5° to 80° and a position-sensitive detector using a step size of 0.02° and a scan rate of 4° min^{-1} . The transmission electron microscopy (TEM) experiment was performed on a Tecnai G20 electron microscope (FEI, USA) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. FTIR spectra were obtained on KBr tablets and recorded using a Magna-IR 560 spectrometer (Nicolet) with a resolution of 4 cm^{-1} by scanning the region between 4000 and 400 cm^{-1} . Thermogravimetric and Differential Thermal Analysis (TG-DTA): SDT Q600 thermogravimetric analyzer (TA Instruments, USA), 10 mg sample size, N_2 as carrier gas (150 ml min^{-1}), 10 °C min^{-1} , 25 °C–800 °C. Water contact angles (WCAs) and oil (hexadecane) contact angles (hereafter defined as OCAs) were measured on an OCA40 contact angle system (Dataphysics, Germany) at room temperature. In each measurement, a 5 μL drop of deionized water was injected onto the surfaces of the wood samples and the contact angles were measured at five different points of each sample. The final values of the contact angles were obtained by averaging the five measurement values. Furthermore, the roll-off angle (α) could be expressed as the difference between advancing and receding contact angle. The roll-off angle (α) is minimized on the surface expected to induce the drop roll off. The roll-off angle measurements were made at room temperature following tilted plate methodology.^{16, 17} In this method, a water or hexadecane drop of volume $\sim 10 \mu\text{L}$ was suspended with the needle and brought in contact with the superamphiphobic surfaces using a computer controlled device. The roll-off angle (α) was measured by inclining objective table when drops land on the sample surface. And roll-off angle (α) was calculated as the angle between the horizontal plane and the inclined plane when the drop started to sliding.

Results and discussion

The SEM images of the pristine wood and the Cu_2O -treated wood are presented in Fig. 1. The pristine poplar wood has a quite smooth surface and it is observed that the polar wood is a type of heterogeneous and porous material (Fig. 1a).

After the wood is immersed in the hydrothermal system for 2 h, high density particles on the surface is formed (Fig. 1b). The corresponding high magnification SEM image reveals that the wood cell walls and the pits of the wood surface are coated with irregular particles with the size ranging from 3.9 μm to 2.7 μm (Fig. 1c). In the system, the microscaled particles and the heterogeneous wood substrate form a rough hierarchical morphology, which helps to endow the wood with improved wettability. The surface chemical elemental compositions of the Cu_2O -treated wood are determined using the energy-dispersive X-ray spectroscopy (EDS), and the results are presented in Fig. 1d. The evidence of only carbon, oxygen, copper, and gold elements could be detected. The gold element is originated from the coating layer used for SEM observation, and carbon element is from the wood substrate. Since no other elements were detected, the Cu_2O -treated wood is composed of Cu and O elements.

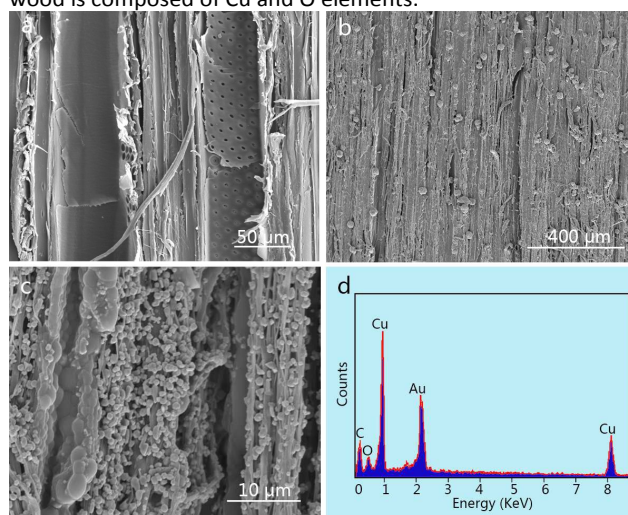
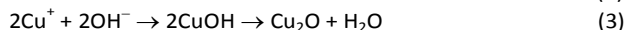
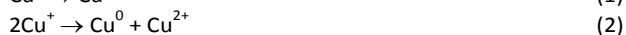


Fig. 1. SEM images of the surfaces of (a) the pristine wood, (b, c) the Cu_2O -treated wood at different magnifications, and (d) EDS spectrums of the Cu_2O -treated wood.

Fig. 2 shows the XRD patterns of the pristine wood and the Cu_2O -treated wood, and the selected electron diffraction (SAED) pattern, the representative TEM image and high-resolution transmission electron microscopy (HRTEM) image of the Cu_2O -treated wood. In Fig. 2a, the diffraction peaks at 14.8° and 22.5° belonging to the (101) and (002) crystal planes of cellulose in the wood are observed in both the spectrum of the pristine wood and the Cu_2O -treated wood.^{18, 19} For the Cu_2O -treated wood, all reflectance peaks are indexed to cuprite Cu_2O (JCPDS card no. 05-0667) and Cu species (JCPDS card no. 65-9026).^{20, 21} The peaks at 2θ values of 29.5°, 36.4°, 42.3°, 61.6°, 73.8° and 77.6° correspond to (110), (111), (200), (220), (311) and (222) planes of pure cuprite Cu_2O crystal, respectively. In addition, the diffraction peaks located at 43.4° and 50.5° can be indexed to (111) and (200) planes of Cu, which may be from the intermediate material in the process of preparing the Cu_2O film. In view of the observation and analysis mentioned above, the Cu^{2+} ions are reduced first to Cu^+ by D-glucose. The possible chemical reaction for the

formation of Cu_2O film is described with the following equations²²:



When the D-glucose powders are added into the Cu^{2+} salt system, the D-glucose powder are firstly touched with organic additives (PVP) and reaches the reaction zone, then the Cu^{2+} ions are reduced to Cu^+ by D-glucose. Meanwhile, due to the existence of enough OH^- ions on the wood surfaces and in the aqueous solution, the main reaction tendency of Eq. (3) becomes dominant.

Moreover, the corresponding selected area electron diffraction (SAED) pattern of the Cu_2O -treated wood is shown in Fig. 2b. The different crystal planes are identified as (111), (200), (220), (311) and (222) diffraction planes of cuprite Cu_2O , which is in agreement with XRD pattern results in Fig. 2a. As shown in Fig. 2c, the TEM image shows that a large quantity of cuprite Cu_2O particles are attached onto the surface of the wood substrate. To further investigate the distribution of Cu_2O particles, the HRTEM image is displayed in Fig. 2d. The clear lattice fringe of $d=0.25$ nm matches that of the (110) plane of Cu_2O .²³ No other impurities such as CuO are detected.

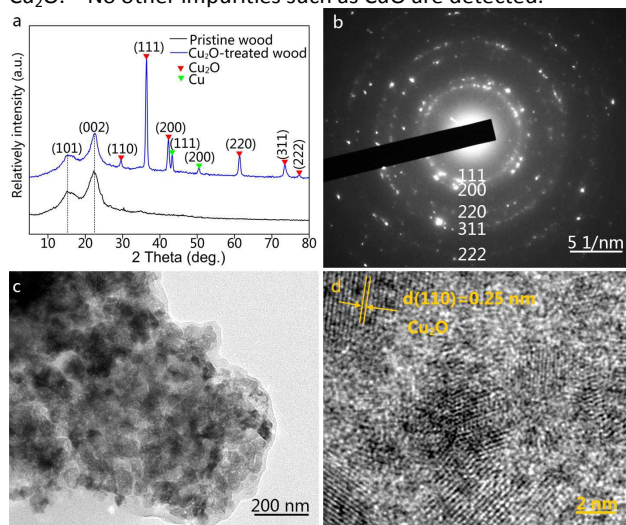


Fig. 2. (a) XRD patterns of the pristine wood and the Cu_2O -treated wood, and (b) the selected electron diffraction (SAED) patterns, (c) TEM image and (d) HRTEM image of the Cu_2O -treated wood, respectively.

The TG profiles and DTG profiles of the pristine wood and the hydrophobized Cu_2O -treated wood are shown in Fig. 3. In Fig. 3b, the DTG curves of both the samples show an initial peak between 50 °C and 160 °C, which correspond to a mass loss of absorbed moisture less than 5%. After this peak, the DTG curve of the pristine wood shows two decomposition steps²⁴: (1) the first decomposition shoulder peak at about 295 °C is attributed to thermal depolymerisation of hemicellulose or pectin (weight loss 15%); (2) the major second decomposition peak at about 375 °C is attributed to cellulose decomposition (weight loss 62%). However, the DTG curve of the hydrophobized Cu_2O -treated wood shows only one major

decomposition peak at about 380 °C, which may be due to the protection effect of modifying agent (FAS-17). In addition, the hydrophobized Cu_2O -treated wood exhibits higher maximum decomposition temperature, because the composition of the sample that has the hydrophobic property may be responsible for the thermal insulation of cellulose degradation. As shown in Fig. 3a, it can be observed from the TG curves that carbon residues with the weight of 16.4% for the pristine wood remains, while the hydrophobized Cu_2O -treated wood is able to keep 22.8% of the weight left. The results indicate that the film combined with Cu_2O and FAS-17 provides wood with the protection.

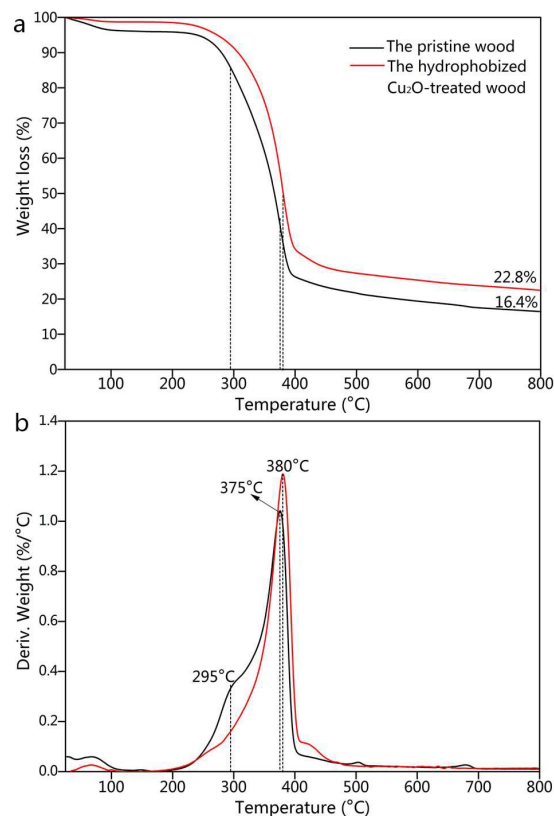


Fig. 3. (a) TG profiles and (b) DTG profiles of the pristine wood and the hydrophobized Cu_2O -treated wood, respectively.

The wetting properties of the Cu_2O -treated wood before and after the hydrophobization are investigated by measuring the drop CAs for both water and hexadecane as shown in Fig. 4. The combined effect of CA and α determines the super-liquid-repellent properties of the surfaces. A surface owning CA more than 150° and α less than 10° shows super-liquid-repellent properties. The Cu_2O -treated wood presents hydrophobicity with the WCA of 130.6° and the α of 13.7° (Fig. 4a), and superoleophilicity with the OCA of 0° (Fig. 4c). After being modified with FAS-17, the hydrophobicity of the Cu_2O -treated wood surface is raised to superhydrophobicity, and the WCA reaches 153.8° and the α is 3.6° (less than 10°). At the same time, the hydrophobized Cu_2O -treated wood possesses a superoleophilicity with OCA of 152.1° and the α of 4.5° (less than 10°). The results indicate that the

superamphiphobic properties of wood surfaces are significantly increased.

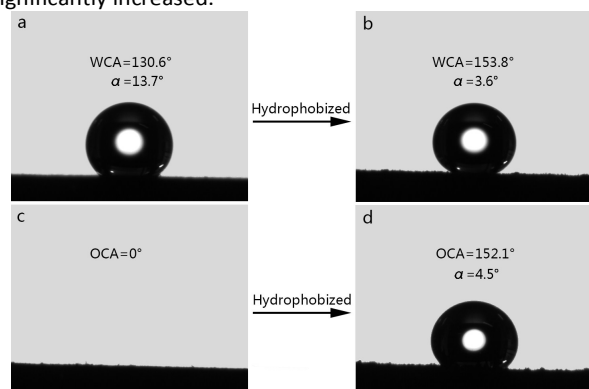


Fig. 4. (a, b) WCAs and roll-off angles (α) of the Cu_2O -treated wood before and after hydrophobization, (c, d) OCAs and roll-off angles (α) of the Cu_2O -treated wood before and after hydrophobization.

In outdoor applications, it needs that superamphiphobic wood surfaces can survive harsh conditions. To investigate the mechanical resistance of the as-prepared coating, sand abrasion test is performed in Fig. 5a. Sand grains 100 μm in diameter are introduced to impact the surfaces from a height of 20 cm. Then, the contact angles (WCA and OCA) of the as-prepared superamphiphobic wood surfaces after sand impact tests are measured to estimate the physical and mechanical stability of the coatings as shown in Figs. 5b and c. It is obvious that the as-prepared superamphiphobic wood surfaces still remain superhydrophobicity with the WCA of 153.2°, and superoleophobicity with OCA of 151.8°.

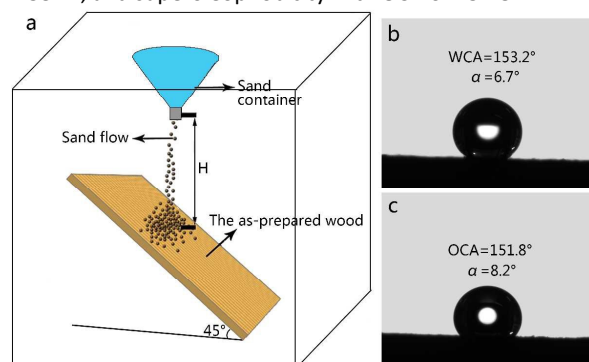


Fig. 5. Mechanical resistance quantified by sand abrasion. (a) Schematic drawing of a sand abrasion experiment. (b) Water drop and (c) hexadecane drop deposited on the as-prepared wood surface after 20 g of sand abrasion from 20 cm height.

To assess the durable ability, the superamphiphobic wood surfaces is damaged artificially by sand impact tests for 100 times. Fig. 6a demonstrates water drop and hexadecane drop on the superamphiphobic wood surface after 100 cycles sand abrasion tests. It can be seen clearly that the water drop and hexadecane drop appear as spheres. Fig. 6d shows the change of the WCAs and OCAs with the abrasion cycles. The results indicate that the superamphiphobic wood surfaces can withstand at least 100 cycles of abrasion damages without changing its super-repellent feature. As shown in Fig. 6e, after immersed in an aqueous HCl solution (pH 1) for 24 h, the superamphiphobic wood surface results in a slight reduction in

water and hexadecane contact angles, being reduced from 153.8° to 151.6° and 152.1° to 150.1°, respectively. Furthermore, Figs. 6b and c demonstrate snapshots of the captured videos of the superamphiphobic wood surface while being separately exposed to streams of water and hexadecane. It can be noted that the surface is able to effectively shed off the liquids without getting wet, which indicates that the superamphiphobic wood surface has the self-cleaning property that would scour off the dust during raining. In Fig. 6f and g, it could be observed that the global water and hexadecane drops on their surfaces with the WCA of 151.3° and the OCA of 150.5° after boiling at 100 °C for 30 h. The result powerfully proved that the thin film made of Cu_2O and FAS-17, as a barrier, effectively protected the wood substrate from acid and other degradations. Thus, the wood coated with the film shows robust anti-acid, mechanical resistance, and high temperature-humidity-resistant superamphiphobic property. All the above results indicate that the superamphiphobic wood surfaces possess excellent durable superamphiphobicity.

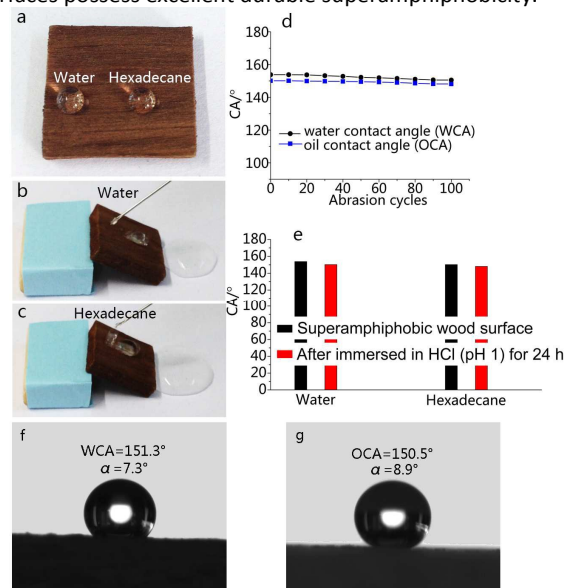


Fig. 6. (a) Digital photographs of water drop and hexadecane drop on the superamphiphobic wood surface after sand abrasion tests. (b, c) the surfaces exposed to the stream of water and hexadecane showing the chemical and physical roughness of surface in shedding the liquids, respectively. (d) CAs changes depending on the abrasion cycles. (e) CAs of the superamphiphobic wood surface before and after immersed in HCl (pH 1) for 24 h. (f) Water drop and (g) hexadecane drop deposited on the as-prepared wood surface after boiling at 100 °C for 30 h.

Conclusions

In summary, this study demonstrates that wood surfaces coated with hydrophobized Cu_2O films have a remarkable superamphiphobic surface with excellent durability against acid exposure, severe abrasion and high-temperature-

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humidity conditions. Such the functional coating may be useful for the development of innovative protective clothing for various applications, such as bridges, buildings, automobile, etc.

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Graphical Abstract

