Facile Preparation of Stable Superhydrophobic Coatings on Wood Surfaces using Silica-Polymer Nanocomposites

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Superhydrophobic organic-inorganic composite nanocoatings were fabricated on the intrinsically heterogeneous surfaces of wood using silica-polymer hybrid materials, which were prepared through sol-gel chemistry using tetraethoxysilane (TEOS) as an inorganic precursor and hexadecyltrimethoxysilane (HDTMS) as an organic modifier. The long-chain HDTMS acts not only as a hydrophobic agent to lower the surface free energy of the silica particles but also as a bonding agent to aggregate the nanoparticles by polymerization. The degree of aggregation of the silica particles in the coating can be controlled by adjusting the initial concentration of HDTMS, and hence the surface morphology and roughness of the coated wood are tuned. When the concentration of HDTMS reaches a critical level, the formed aggregates of silica particles in combination with the inherent microscale roughness of wood appear to create hierarchical micro/nanostructures on the wood substrate, allowing for the generation of superhydrophobicity. The silica-polymer hybrid coatings on the wood surface are robust enough to withstand high humidity as well as strong acid and alkali whilst retaining its superhydrophobicity. The coatings also exhibit satisfactory durability against water leaching without significantly changing its hydrophobicity, highlighting their potential for outdoor applications.

Keywords: Coatings; Silica-polymer nanocomposites; Sol-gel; Superhydrophobicity; Wood

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INTRODUCTION

Wood is susceptible to water or moisture invasion due to its capillary-porous structure as well as the hydrophilic nature of the cell wall constituent polymers. Wood-water interactions can lead to dimensional instability, accelerated weathering, and biodegradation of wood (Mahltig *et al.* 2008). Conventionally, chemical modifications such as acetylation (Hill and Jones 1999; Chang and Chang 2002), silanization (Donath *et al.* 2004, 2006), *in-situ* polymerization (Trey *et al.* 2010; Li *et al.* 2012), and flavonoid insertion into cell walls (Ermeydan *et al.* 2012) have been attempted to improve the hydrophobicity of wood. Although these methods can be applied to reduce or retard water absorption into wood, they fail to prevent wood-water interaction completely, since most cavities and micropores in wood are still accessible to water following the chemical treatments. The undesired performance of these treatments along with the hazardous chemicals possibly used in these processes highlights the need of developing alternative approaches for wood modification and functionalization.

Superhydrophobic surfaces with a water contact angle (CA) higher than 150° have recently attracted increasing attention due to their potential applications in many areas. Water droplets on a superhydrophobic surface cannot adhere to such a surface but easily roll off the surface, taking away the pollutants and thus exhibiting self-cleaning effects. A superhydrophobic surface tends to minimize the interaction between water and the substrate, keeping the substrate dry even when exposed to water and thereby avoiding problems related to water absorption. Such systems may offer a desirable solution for wood protection against water.

It has been well established that the superhydrophobicity results from the combination of suitable surface roughness owing to the hierarchical micro- and nano-structures and low surface energy materials on top of the rough structures (Neinhuis and Barthlott 1997; Feng *et al.* 2002). Recently, based on this principle, highly hydrophobic or superhydrophobic surfaces have been successfully fabricated on cellulose-based materials and solid wood substrates by roughening the surface with inorganic nanoparticles in combination with low-surface energy treatments (Li *et al.* 2010; Hsieh *et al.* 2011; Jin *et al.* 2011; Sun *et al.* 2011; Wang *et al.* 2011; Fu *et al.* 2012; Jin *et al.* 2012; Wang *et al.* 2012; Wang *et al.* 2014). However, many of these processes involve multistep procedures or expensive reagents, special equipment, and harsh experimental conditions. More importantly, the assessment of the stability and durability of the superhydrophobic coatings on wood surfaces is lacking. The practical application of superhydrophobic surfaces relies on simple and inexpensive fabrication processes as well as the stability of the coatings under operating conditions.

In a previous study the authors fabricated highly hydrophobic wood surfaces based on a two-step process consisting of growing silica nanofilms on wood surfaces followed by low surface energy treatment with hexadecyltrimethoxysilane (HDTMS) (Wang *et al.* 2013). High hydrophobicity with a water contact angle of ~140^{o} but not superhydrophobicity was achieved on the longitudinal surfaces of wood. This was because the formed silica nanoparticles were rather uniformly distributed on the wood surface without aggregation into large clusters, and thus the surface roughness is not high enough to generate superhydrophobicity.

The present study reports a simple one-step dip-coating method for fabrication of stable superhydrophobic coatings on wood surfaces based on silica-polymer nanocomposites. The silica-polymer hybrid coating materials are derived from the inorganic precursor TEOS and the organic modifier HDTMS through sol-gel chemistry. In this process, HDTMS acts not only as a hydrophobic agent to lower the surface free energy but also as a bonding agent to aggregate the silica particles by polymerization. This coating solution is then applied onto wood surfaces by dip-coating, but other techniques such as spin- and spray-coating can be used for large-area fabrication. The subsequent heat treatment transformed the applied solution into an organic-inorganic hybrid nanocoating. The as-prepared superhydrophobic coatings on wood surfaces exhibit good stability and durability against strong acid and alkali, high humidity, as well as water leaching.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH, 25%), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hexadecyltrimethoxysilane (HDTMS) was obtained from Sigma-Aldrich (St. Louis, Minnesota, USA). All chemicals were used as received without further purification. Wood samples of Chinese fir (*Cunninghamia lanceolata*) were cut parallel to grain direction from the sapwood portion of the stem and sawn into cubic blocks of 20 mm × 20 mm × 20 mm (tangential× radial × longitudinal).

Preparation of Hydrophobic Silica Sols

Firstly, monodisperse silica sols were prepared based on a typical Stöber method using ammonia as catalyst. A typical sol preparation procedure was as follows: 3 mL of NH_4OH was mixed with 50 mL of ethanol to form a homogeneous solution with magnetic stirring for 30 min at 50 °C, and 3 mL of TEOS was then added dropwise into the above solution while stirring. The stirring was continued for 2 h to form a transparent silica sol exhibiting a characteristic light blue color. After this, HDTMS was further applied to modify the hydrophilic silica colloid particles and enable aggregation of the particles in the prepared sols. Different amounts of HDTMS with concentrations ranging from 0.1% to 5% of the sol were added into the sol system. All the concentrations used here are based on weight (w/w). The mixed sols were further stirred at 50 °C for 2 h to form a hydrophobic coating solution.

Wood Surface Coating

Prior to coating treatment, the wood samples were ultrasonically washed with ethanol and distilled water for 10 min, respectively and dried at 103 °C for 5 h. The cleaned samples were then dipped into the as-prepared coating solution for ~30 min to allow full deposition of silica particles on wood surfaces. The coated wood samples were then washed with ethanol to remove the residual unreacted monomers and dried at room temperature for 1 h, and finally cured at 103 °C for 6 h to solidify the coatings.

Microstructure and Morphology of the Nanocoatings

The microstructure and aggregation of silica colloid particles of the prepared sols were examined by transmission electron microscopy (TEM, Tecnai G2 F30, FEI, USA). The silica sols were diluted by ethanol with mild stirring to prepare TEM samples. The diluted solution was dropped onto a standard carbon-coated formvar film on a copper grid followed by drying under vacuum. The morphology and elemental composition of the hybrid nanocoatings on wood surfaces were examined by a field-emission scanning electron microscope (FE-SEM, Zeiss SUPRA 55, Germany) combined with energy dispersive X-ray analysis (EDX). A thin platinum (Pt) layer was sputtered onto the sample surfaces to improve conductivity prior to observation. Changes in surface chemistry of the coated samples were analyzed using a Fourier transform infrared spectrometer (FTIR, Nicolet Magna-IR 750, USA) equipped with an attenuated total reflection (ATR) accessory.

Water Contact Angle (CA) Measurement

The hydrophobicity of the coated samples was evaluated by water CA measurements. The static CA was measured by a contact angle meter (Shanghai Zhongchen JC2000D, China) at ambient temperature. The static CA was recorded 60 s after a water droplet of 5 μL was placed on the sample surface, and the average CA value was obtained by measuring more than five positions for each sample.

Durability of the Nanocoatings

The leaching durability of the superhydrophobic coatings was examined by submerging the coated wood samples in a volume of distilled water 10 times that of the samples for 24 h at room temperature with magnetic stirring, followed by drying in an oven at 103 °C for 5 h. The leaching procedures were conducted for 10 cycles, and the water CA was measured following each leaching cycle. The environmental stability of the coatings was evaluated by exposing the coated samples in a high humidity atmosphere (98% RH) at room temperature up to 60 days. The chemical stability of the coatings was tested by submerging the coated samples in a sodium hydroxide (NaOH) solution of pH 12 and a hydrochloric acid (HCl) solution of pH 2 for 10 h at room temperature, respectively, followed by water rinsing and air drying. The CA of the treated samples was measured at certain intervals.

RESULTS AND DISCUSSION

The hydrophobic modification of silica sols and aggregation of silica colloid particles are schematically illustrated in Fig. 1.

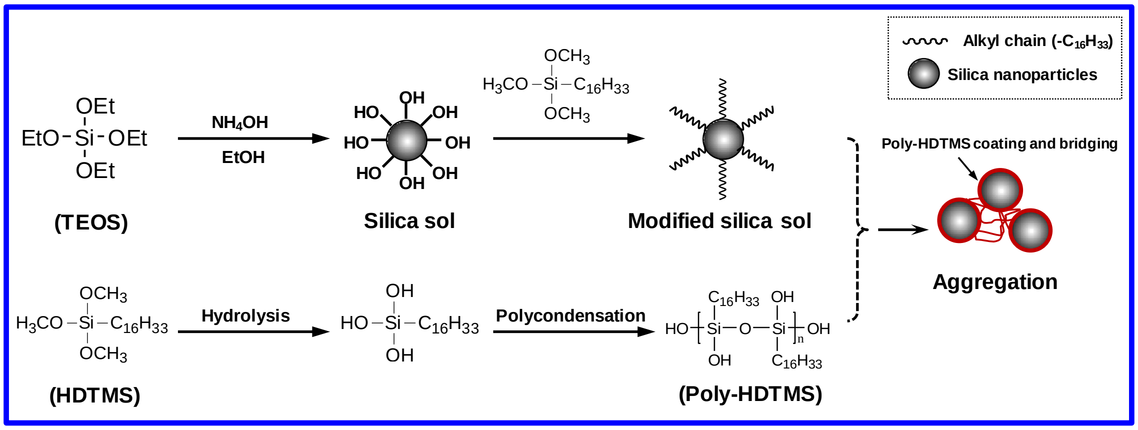

Fig. 1. Schematic illustration of hydrophobic modification of silica sols and aggregation of silica colloid particles

Monodisperse silica colloid particles were firstly prepared by hydrolysis and condensation of TEOS under an alkaline condition based on the typical Stöber method. HDTMS was then applied to hydrophobize the silica particles owing to the long-chain alkyl group ($-C_{16}H_{33}$) in its molecule. Meanwhile, dehydration or dealcohol polycondensation may occur between the remaining HDTMS molecules to form poly-HDTMS with a siloxane structure. As a result, the modified silica particles are covered and bridged by the formed poly-HDTMS. In this process, HDTMS acts not only as a hydrophobic agent to lower the surface free energy but also as a bonding agent to aggregate the silica particles by polymerization.

Figure 2 shows the TEM images of the modified silica colloid particles. When a small amount of HDTMS (0.5%) was added into the sol, the initial smooth surface of the silica particles become fuzzy, and the silica particles were covered by a thin layer of the formed polymer, exhibiting an obvious tendency to aggregate with each other. When the HDTMS concentration was increased up to 1%, more polymer materials were formed in the sol, and the silica particles were densely coated by the polymer, forming a core-shell structure. Obviously, the silica particles were connected tightly by the net of polymer, causing intensified particle aggregation. With a further increase of the HDTMS concentration up to 5%, an extremely dense polymer network was formed at such high concentration level, and all of the silica particles were entirely enclosed in the polymer network.

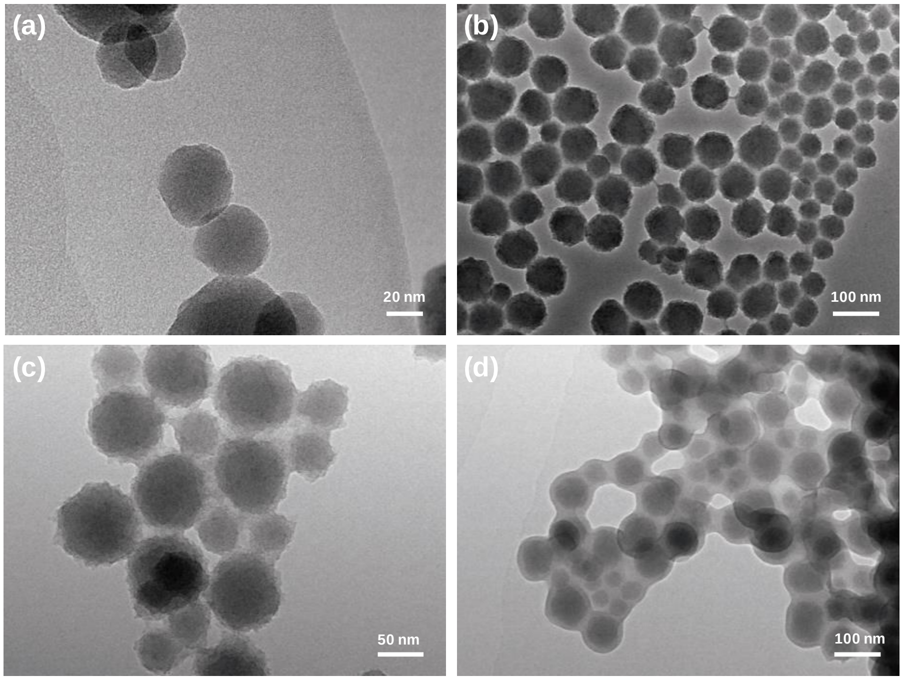

Fig. 2. TEM images of the synthesized silica nanoparticles modified with HDTMS at different concentration levels: (a) 0, (b) 0.5%, (c) 1%, and (d) 5%

The molecular structure of the modified silica particles was characterized by FT-IR. The corresponding spectra of the silica-polymer hybrid coating material applied on wood surfaces are shown in Fig. 3. In the spectra of the coated wood, the increased absorption at 2853 and 2953 cm^{-1}, which can be respectively assigned to the C-H stretching vibrations of $-CH_2$ and $-CH_3$ (Pandey 1999), indicates the grafting of long-chain alkyl groups ($-C_{16}H_{33}$) of HDTMS on the silica particle surface. Moreover, the appearance of new bands at 802 cm^{-1} corresponding to the stretching vibration of the Si-C bond further confirms the grafting of alkyl groups in the hybrid coating system (Li *et al.* 2007). The typical absorption peak of the Si-O-Si bond of the siloxane components at 1130 to 1000 cm^{-1}, which appears to overlap with the C-O stretching of wood cellulose, was remarkably intensified after the coating treatment, suggesting that poly-HDTMS with a siloxane structure was formed in the hybrid coating system. This is in good accordance with the polymeric material covering the silica particles as observed in the TEM images.

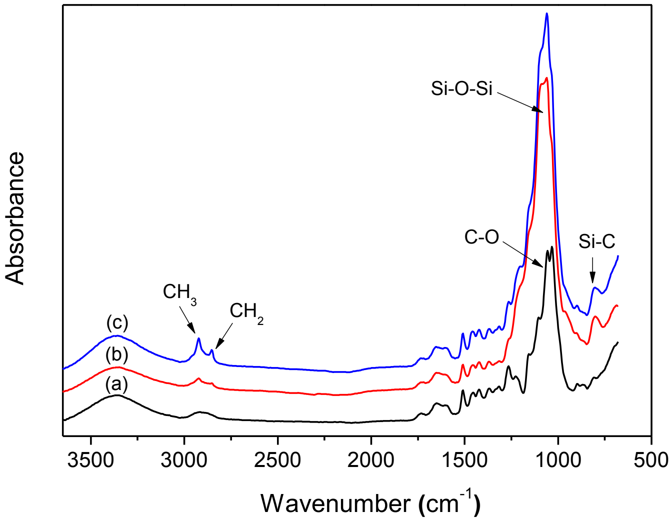

Fig. 3. FTIR spectra of (a) native wood and wood coated with (b) 0.1% and (c) 1% HDTMS modified silica sols

The microstructure and morphology of the nanocoatings on wood surfaces were examined by FE-SEM. Figure 4 shows typical top views of the native and coated wood surfaces as well as the corresponding water droplets on the surfaces. The native wood presents a highly-textured cellular structure with a smooth lumen surface (Fig. 4a). The longitudinally arranged cells constitute the wood surface featured by concave cell lumens and projected cell walls, forming an alternating “valley” and “ridge” structure, which produces the primary roughness of wood surfaces at the microscale level. When water droplets was placed on the surface, they penetrated instantly into the underneath structure due to the hydrophilic nature of wood.

A thin layer of silica particles was observed on the lumen surface when a coating solution with a 0.5% HDTMS concentration was applied on the wood surface (Fig. 4b). The nanoscaled particles appeared to aggregate with each other, resulting in a heterogeneous lumen surface. The coated wood showed notably improved water repellency, with a CA of ~137°. With an increase of the HDTMS concentration to 1%, a more heterogeneous wood surface was created by the large clusters or bumps derived from intensified aggregation of the silica particles (indicated by arrows in Fig. 4c). The incorporation of larger bumps of silica particles enabled the formation of hierarchical micro- and nano-structures and accordingly generated high surface roughness on wood substrates. In consequence, the coated wood displayed superhydrophobic properties with a CA of 152°. However, a further increase of the HDTMS concentration to 5% resulted in relatively smooth lumen surfaces, and the silica particles and their aggregates were deeply embedded in the dense network of polymer (Fig. 4d). In this case, the water repellency of the coated wood was not further improved. The quantitative relationship between the HDTMS concentration levels and the resulting CAs of the coated wood is presented in Fig. 5.

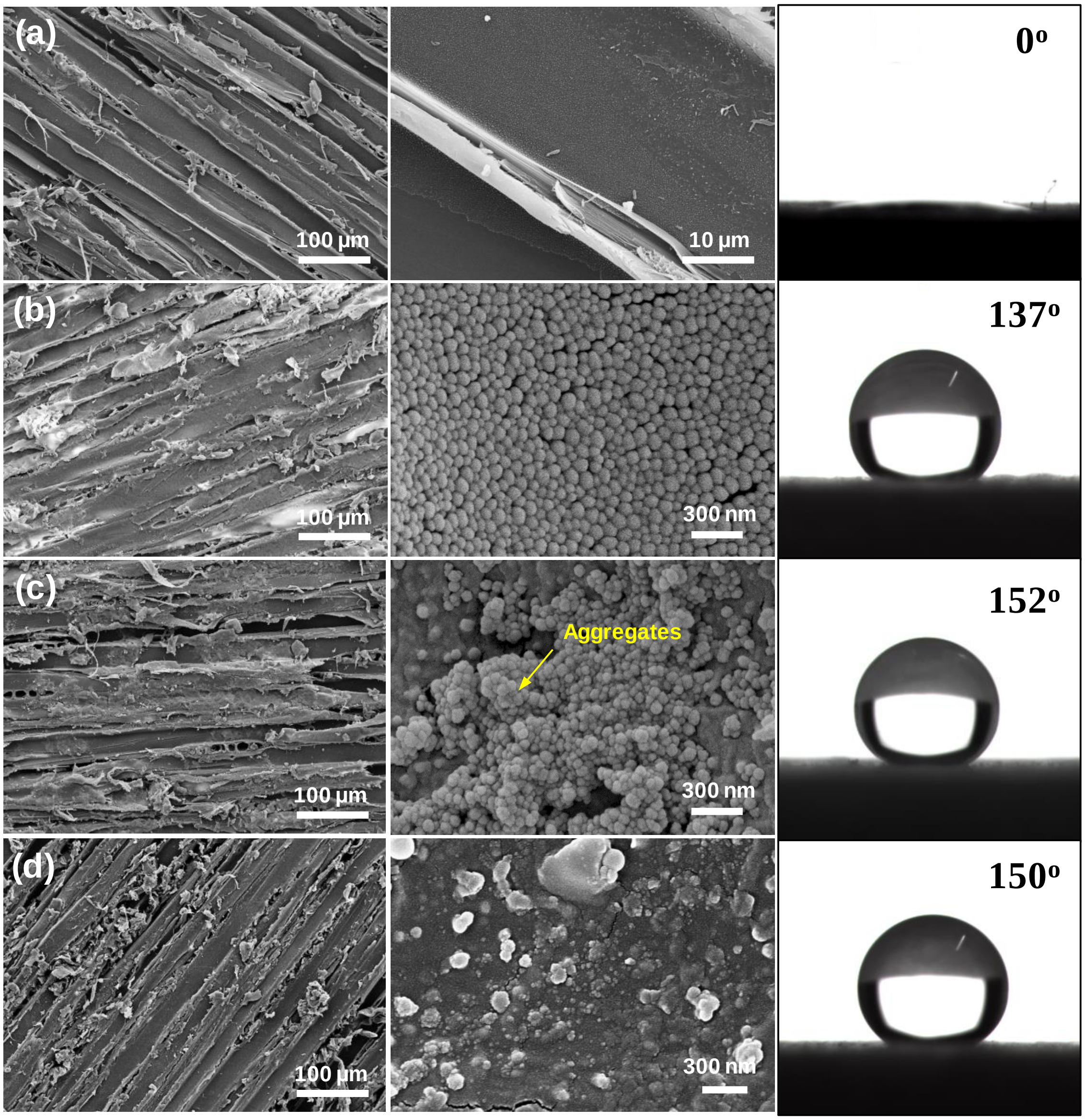

Fig. 4. SEM images of (a) native and wood surfaces coated with HDTMS modified silica sols at different concentration levels: (b) 0.5%, (c) 1%, and (d) 5%. High-magnification images display the microstructure of the coatings on the lumen surface. The corresponding images of water droplets on the wood surfaces are presented on the right panel.

It has been established that the superhydrophobicity of a material is governed not only by its surface chemistry but also by its surface roughness. When the surface chemistry is kept the same, the surface structure is the key factor affecting the CA (Xu *et al.* 2010). In the present study, the HDTMS functions not only as a hydrophobic agent to lower the surface free energy but more importantly as a bonding agent to aggregate the silica particles to form rough structures on wood surfaces. As schematically illustrated in Fig. 6, when the HDTMS concentration was rather low (less than 0.5%), the silica particles were randomly distributed without obvious aggregation, forming a thin layer of coating on the lumen surface. Hence, the incorporation of silica nanoparticles caused no significant changes in the inherent microscale structure of the wood surfaces, and the water droplets could fill the open lumen space of the longitudinally arranged cells, resulting in full contact between the water droplets and the lumen surface without air being trapped inside. This wetting behavior is consistent with the case of Wenzel model (Wenzel 1936). In this case, the achieved CA was not sufficiently high, and the adhesion force between the water droplets and the wood substrate was large.

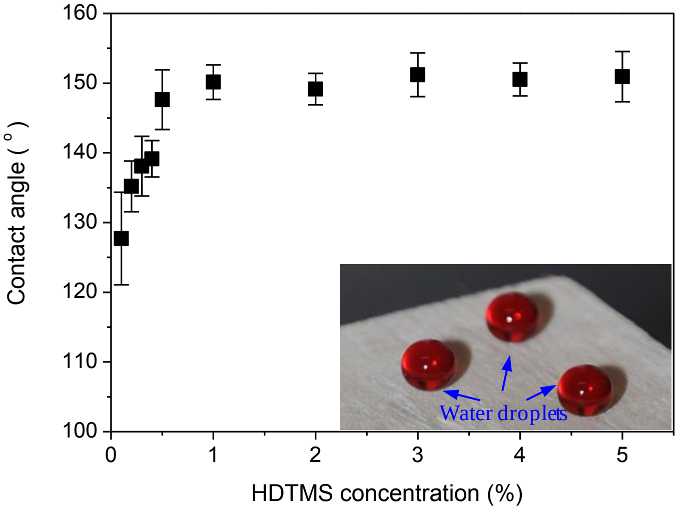

Fig. 5. Water contact angles (CAs) of the coated wood as a function of the HDTMS concentration. The inset shows an optical image of spherical water droplets on the wood surface coated with 1% HDTMS modified silica sol.

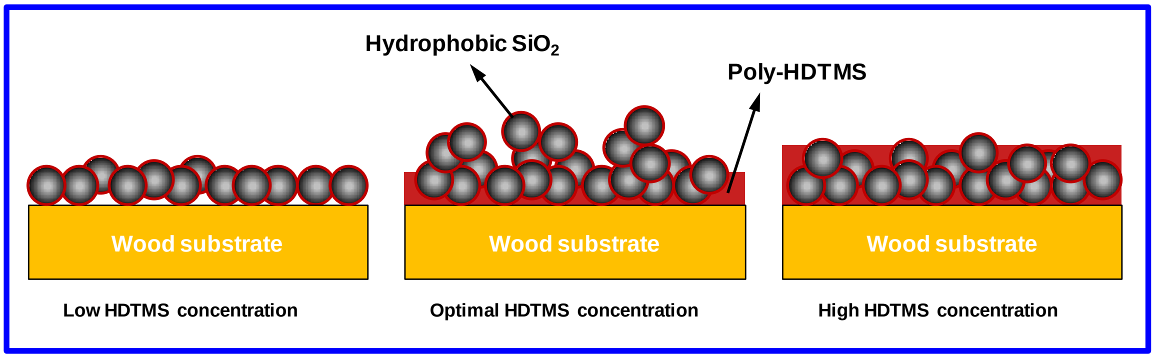

Fig. 6. Schematic illustration of the effect of HDTMS concentrations on the aggregation of silica particles and the resulting microstructures on wood substrates.

By contrast, when the HDTMS concentration was increased up to an optimal level (1%), the silica particles started to aggregate with each other to form large clusters or bumps of various sizes, generating hierarchical micro/nano structures on the wood surface. In this case, the water droplets could not fill the lumen spaces but were suspended beyond the air entrapped in the voids of the substrate, forming a solid/liquid/air interface, which is a typical wetting behavior described by the Cassie model (Cassie and Baxter 1944). Consequently, spherical water droplets were formed on the coated wood surface, displaying a high CA, and the adhesion force between the water droplets and the wood substrate was small. However, when the HDTMS concentration was extremely high (5%), the hierarchical structural features derived from the silica particles became hidden in the formed dense polymer network of the coatings, and the resulting surface roughness of the wood substrate was not further enhanced. As a result, the CA of the coated wood was not further increased.

For practical outdoor application of the superhydrophobic wood, the stability and durability of the coatings against environmental factors such as moisture, rainfall, and temperature during long-term outdoor exposure are crucial. Figure 7a shows the change of water CA of the coated wood with the exposure time in a high humidity environment (98% RH) at room temperature. No obvious change in CA was detected even after exposure for 60 days. In particular, the coatings with 1% and 3% HDTMS maintained superhydrophobicity throughout the humidity test periods. This indicates that the hybrid coatings on the wood surface showed satisfactory stability against high humidity.

Water leaching tests were performed by alternating water immersion and oven-drying of the coated wood samples in order to examine the washing durability of the coatings (Fig. 7b). With increasing leaching cycles, the CA of all the coatings showed a slightly decreasing tendency depending on the concentration levels of HDTMS. The coatings containing 3% HDTMS showed satisfactory durability with CA of greater than 135° after being subjected to water leaching for ten cycles. In general, the coated wood samples were robust enough to withstand water leaching without significantly changing its hydrophobicity.

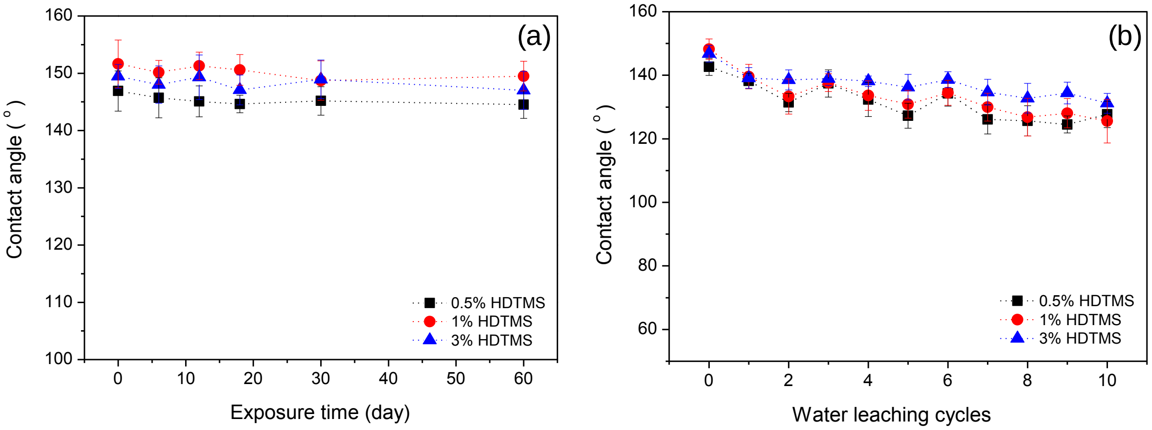

Fig. 7. Changes in water contact angles of the coated wood as a function of (a) exposure time in a high humidity environment (98% RH) at room temperature and (b) water leaching cycles by alternating water immersion (with stirring) and oven-drying

The chemical durability of the silica-polymer coatings on wood surfaces was evaluated by measuring the changes in the CA of the coated wood samples upon treatments with aqueous solutions of a strong acid (pH=2) and a strong base (pH=12), respectively (Fig. 8). The results showed that the CA of all the coatings remained almost constant during the strong acid or strong alkali treatment for a period of 10 h. This indicates that the formed hydrophobic silica particles and the polymer net were very stable in both strong acid and base, and the superhydrophobic coatings were therefore durable enough to resist the attacks by the strong acid and base.

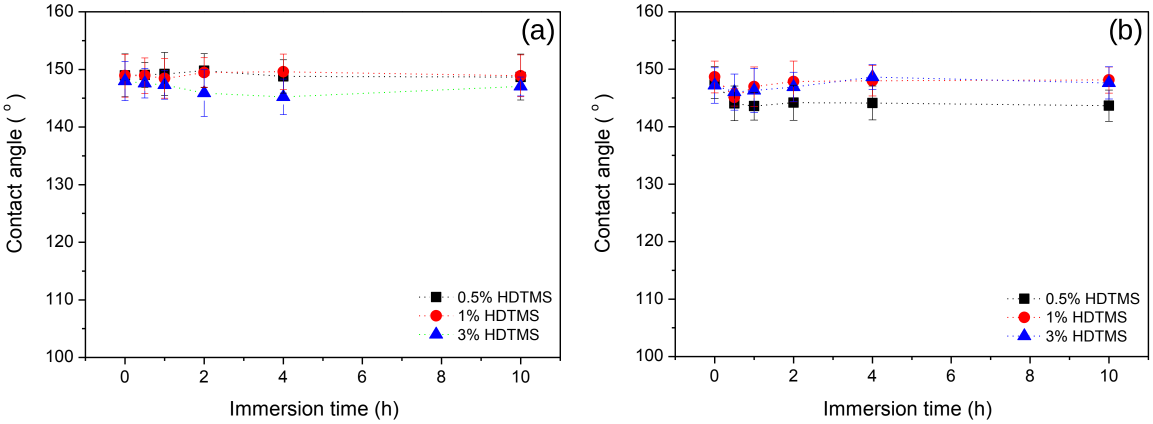

Fig. 8. Changes in water CAs of the coated wood with immersion time in solutions of (a) strong acid (pH=2) and (b) strong base (pH=12) at room temperature

CONCLUSIONS

A facile way to fabricate stable superhydrophobic coatings on the intrinsically heterogeneous wood surfaces has been developed using silica-polymer hybrid materials, which were derived from the inorganic precursor TEOS and the organic modifier HDTMS through sol-gel chemistry. The superhydrophobicity was achieved by the nanoscale roughness imparted by the aggregates of silica particles in combination with the microscale roughness inherent on wood surfaces forming desired hierarchical micro- and nano-structures on the wood substrate. The formed superhydrophobic coatings on wood surfaces exhibited good stability and durability against strong acid and alkali, high humidity as well as water leaching, highlighting their potential in outdoor applications such as garden buildings, flooring and fencing.

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