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Organocatalytic aqueous formulations: green organocatalytic hydrophobization of heterogeneous polysaccharide-based materials in water through "on-water" mechanisms

A concept for creating stable, water-based colloids enabling simple, eco-friendly, organocatalytic hydrophobization of polysaccharide-based materials is disclosed. Mixing a surfactant, organocatalyst, and alkyl trialkoxysilane in water initiates polymerization in surfactant micelles *via* an "on-water" mechanism, progressing to aggregation and colloid formation upon homogenization. Next, application of these organocatalytic aqueous formulations (OAFs) on diverse cellulose substrates yields hydrophobic or superhydrophobic surfaces via a novel "on-water" mechanism. The dual function of the organocatalyst showcases a sustainable strategy for catalytic transformations in water using small organic molecules.

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Organocatalytic aqueous formulations: green organocatalytic hydrophobization of heterogeneous polysaccharide-based materials in water through "on-water" mechanisms†

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A concept for developing stable, water-based colloids for simple, effective, green, and organocatalytic hydrophobization of heterogeneous polysaccharide-based materials (*e.g.*, cellulose, wood, and paper) in water is disclosed. The addition of a surfactant, an organocatalyst, and a hydrophobic agent (*e.g.*, alkyl trialkoxysilane) to water results in organocatalytic polymerization and the formation of a water-based suspension, which, upon homogenization, forms a stable colloid. The mechanism for the generation of this organocatalytic aqueous formulation (OAF) is elucidated by microscopy and spectroscopy. It is initiated by organocatalytic alkyl alkoxysilane polymerization within the nanomicelles formed by the surfactant in water through an "on-water" Type IIa mechanism. Next, these micelles expand to a microsize upon further polymerization, eventually leading to aggregation and the formation of a suspension through an "on-water" Type III mechanism. Homogenizing this suspension yields a stable colloid with water as the medium. The OAFs were then applied to various cellulosic substrates (*e.g.*, cellulose paper, paper sheets, cotton, and wood) by spraying, roll-coating, or dipping. Organocatalytic colloidal particle modification of a wide range of cellulosic substrates (*e.g.* paper, cotton, and wood) in water through an "on-water" mechanism, which we here classify as Type IV, results in hydrophobic (contact angles of >145°) or superhydrophobic (contact angles of >150°) cellulosic surfaces. Thus, the OAFs can be utilized for modifying a wide range of industrially relevant cellulose-based materials under eco-friendly conditions. The dual role of the organocatalyst in mediating colloidal particle formation and green hydrophobic modification of heterogeneous polysaccharides exemplifies a novel approach for harnessing the catalytic potential of small molecules for organic reactions in water.

> ### Green foundation
>
> 1. The development of stable and water-based formulations for simple, effective, and environmentally friendly hydrophobization of heterogeneous polysaccharide-based materials (*e.g.*, cellulose, wood, and paper) in water offers a sustainable alternative for industrial applications.
> 2. No toxic chemicals: replacing forever chemicals such as fluorocarbons and plastics with sustainable alternatives that are easy to transport and utilize on a large scale, with a concept and theory for catalytic reactions on heterogeneous surfaces in water.
> 3. Expanding the water-based formulations to naturally occurring hydrophobizing agents such as fatty acids.

Introduction

Cellulose is the world's most abundant biopolymer and a perfect starting material for the development of sustainable

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materials.[1–5] However, sensitivity to water and moisture limits its use for several applications (*e.g.* packaging, construction materials, wood protection, and recyclable straws) if the cellulose is not hydrophobized. As a consequence, fossil-based plastics (*e.g.* poly(ethylene), expanded polystyrene, and poly(vinylalcohols)) are used instead or together with cellulose. Thus, the fabrication of water-resistant cellulose-based materials plays a crucial role in addressing these challenges. Applications such as printing,[6] packaging,[7–9] coating,[10,11] water purification,[12–15] and others that require water barrier

properties[16–18] are a central focus of research both in academia and industry. Wettability, the study of how surfaces interact with water, has been studied for over 200 years to design durable materials that resist humidity. By studying the interaction between a droplet and a surface, valuable information about the surface's wettability can be obtained when the solid and liquid phases are in contact.[19] Young first described the force acting on a liquid droplet spreading on a surface, a concept now known as the contact angle.[20] According to the definition, a surface with a contact angle less than 90° is considered hydrophilic, while one with a contact angle greater than 90° is considered hydrophobic. According to Young's equation, the highest contact angle is achieved when the surface energy is at its lowest. Acylation of cellulose with anhydrides and acyl chlorides is used to produce hydrophobic products from cellulose.[21–25] Although partial water resistance has been achieved in the pulp and paper industry using internal sizing agents such as alkenyl succinic anhydrides (ASAs) and alkyl ketene dimers (AKDs),[26] the development of hydrophobic materials based on cellulose fibers remains underdeveloped. In this century, there is a need to shift from the 20th century's conventional methods, such as the use of AKDs and anhydrides, which are prepared from toxic acyl chlorides, or hydrophobization methods relying on the direct use of acyl chlorides and/or organic solvents towards eco-friendly alternatives. In 2005, Hafren and Córdova introduced organocatalysis as a tool for direct acylation of cellulose and heterogeneous polysaccharides using various organic acids and lactones as substrates.[27] Since then, the application of organocatalysis for hydrophobization and functionalization of polysaccharides by acylation has gained increased attention.[28] Forever chemicals (e.g. fluorocarbons) have been widely used to lower the surface energy of cellulose-based materials.[29] However, they are now being banned due to their toxicity and carcinogenicity.[30] Another approach for lowering the surface energy of cellulose is the use of silicones and silicon-containing polymers.[31] Various techniques, such as grafting, physical adsorption, and chemical vapor deposition, have been employed to modify their surface properties. Silanes, in particular, exhibit a strong affinity for hydroxy groups and have been successfully used for hydrophobization and installation of functional groups for click chemistry on biopolymers such as cellulose, nanocellulose, and starch.[32] However, most of these methods involve the use of organic solvents as the reaction media, and this is also the case for organocatalytic methods.[32d–f] The use of natural substrates like betulin and lignin has also been explored for developing hydrophobic cellulosic materials including textiles, paper, and wood.[33] However, organic solvents were used to solubilize these hydrophobic natural products. Minimizing the environmental risks and enhancing process sustainability are major concerns of scientists today. Replacing organic solvents with water is one of the significant achievements in advancing green chemistry.[34] Water can enhance reaction rates and selectivity of chemical reactions.[35] In the context of catalytic reactions, Kobayashi has elegantly referred to them as "in water" and classified them into seven types. When accelerated

in water as heterogeneous mixtures, the reactions can be regarded as following an "on-water"[35b] mechanism. Inspired by the lectures and research of Breslow, Sharpless, Kobayashi, Lipshutz, Marcus, Karplus, and others on organic reactions using water as the reaction medium,[35] we embarked on the concept of developing water-based formulations for organocatalytic modification of cellulosic materials. Herein, we introduce eco-friendly, scalable, and versatile OAFs for catalytic hydrophobization of heterogeneous polysaccharide-based materials in water (Fig. 1).

The mechanism for the catalytic syntheses of OAFs in water was determined. The water-based synthesis starts with the hydrolysis of the alkoxy silane and is followed by organocatalytic polymerization within nanomicelles via a Type IIa[35d] mechanism. Further catalytic polymerization leads to the expansion of the micelle into a microsize, which is followed by continuous polymerization and collapse of the micelle, aggregation, and the formation of a suspension via a Type III[35d] mechanism. Subsequent homogenization gives the resulting water-based colloid OAF, which is applied to heterogeneous polysaccharide substrates. Next, organocatalytic colloidal particle modification of the cellulose substrates in water through an "on-water" Type IV mechanism results in the corresponding hydrophobic polysaccharide surfaces (water contact angles (WCAs) > 145°). The implementation of the overall process is green, facile, scalable, and can be used for the fabrication of hydrophobic cellulosic products such as paper, wood, and textiles.

Results and discussion

Preparation of organocatalytic aqueous colloids

We began preparing various suspensions by adding a surfactant, an organocatalyst and an alkoxysilane into water (Scheme 1A). The components of the resulting OAFs are shown in Table 1. Hexadecyltrimethoxysilane (HDTMS) and octadecyltrimethoxysilane (OTMS) were selected as the organoalkoxysilanes. Naturally occurring organic acids (citric acid, fumaric acid, lactic acid, and maleic acid) were investigated as the organocatalysts (Table 1).
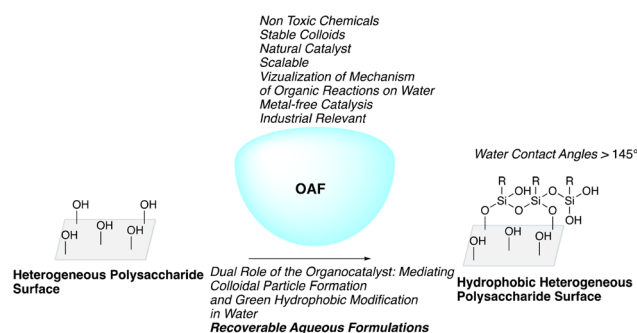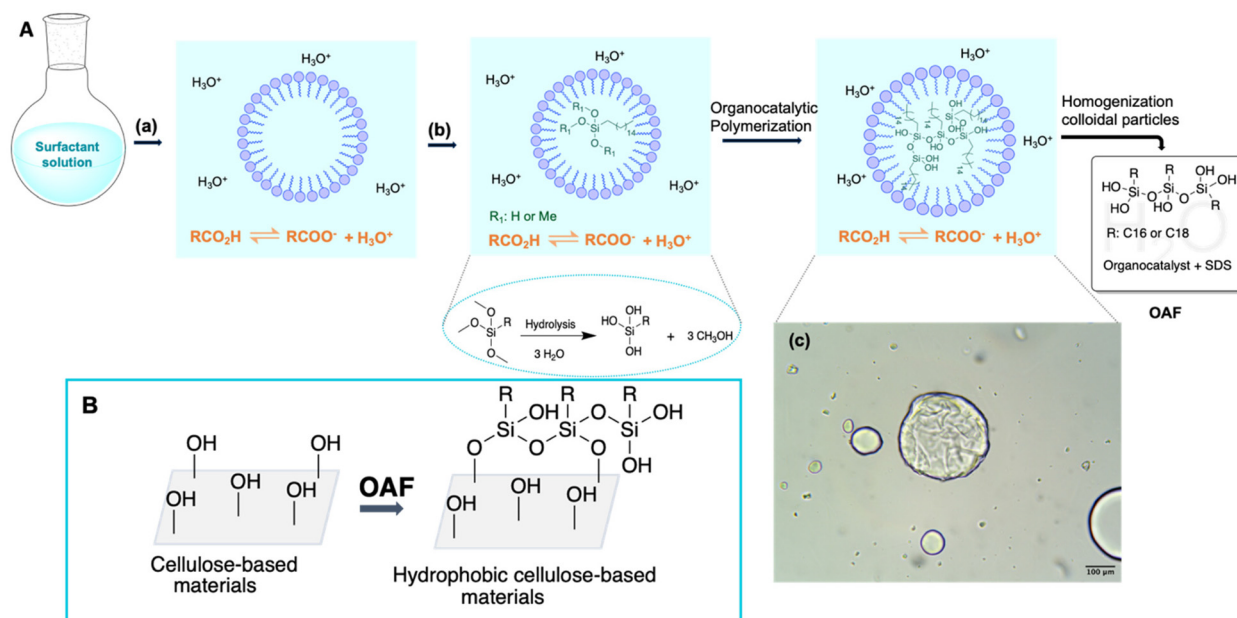

Non Toxic Chemicals
Stable Colloids
Natural Catalyst
Scalable
Vizualization of Mechanism of Organic Reactions on Water
Metal-free Catalysis
Industrial Relevant

Water Contact Angles > 145°

OAF

Heterogeneous Polysaccharide Surface

Dual Role of the Organocatalyst: Mediating Colloidal Particle Formation and Green Hydrophobic Modification in Water
Recoverable Aqueous Formulations

Hydrophobic Heterogeneous Polysaccharide Surface

Fig. 1 Features of this work.

Scheme 1 (A) Organocatalytic preparation of the OAF. (a) An organocatalyst is added. (b) Silane is added. (c) Light microscopy image of micrometer-sized SDS micelles with ongoing organocatalytic silane polymerization, scale: 100 μm. (B) Example of organocatalytic hydrophobization of a heterogeneous polysaccharide material using the OAF.

Table 1 Organocatalytic aqueous formulation (OAF) preparation[a]

Entry	Formula name	Catalyst[b]	Catalyst (mol%)	Silane (mmol)	pH
1	OAF0	—	—	HDTMS:35	7
2	OAF1	CA	2.8	HDTMS:35	3
3	OAF2	CA	4.0	HDTMS:35	2.9
4	OAF3	CA	5.4	HDTMS:35	2.8
5	OAF4	CA	8	HDTMS:35	2.7
6	OAF5	CA	5.4	OTMS:35	2.8
7	OAF6	CA	2.7	HDTMS:70	2.8
8	OAF7	CA	2.7	OTMS:70	2.8
9	OAF8	FA	2.7	HDTMS:70	2.8
10	OAF9	LA	2.7	HDTMS:70	3
11	OAF10	MA	2.7	HDTMS:70	2.4
12[c]	OAF11	CA	2.7	OTMS:70	2.8
13[c]	OAF12	CA	2.7	HDTMS:70	2.8

[a] Sodium dodecyl sulphate (SDS) (8 mmol) was dissolved in 200 mL water, the catalyst was added to the solution, and then either hexadecyltrimethoxysilane (HDTMS) or octadecyltrimethoxysilane (OTMS) was added to the mixture. [b] CA: citric acid, FA: fumaric acid, LA: lactic acid, and MA: maleic acid. [c] SDS is 4 mmol.
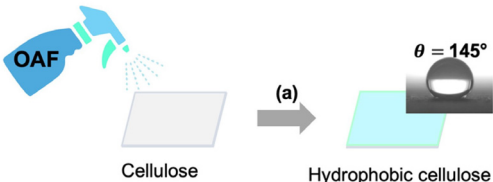
The OAF synthesis begins with organocatalyzed hydrolysis of the methoxy groups of alkoxysilanes within the micelle in water (Scheme 1Ab), which was confirmed by ^{1}H NMR (Fig. S1†).[36] Next, organocatalytic polymerization occurs within the surfactant-generated nanomicelles, followed by their expansion to a micromillimeter size, as determined by light microscopy analysis (Scheme 1Ac). The subsequent organocatalytic polymerization leads to further micelle expansion, aggregation, and the formation of a suspension (Scheme S7†). Finally, homogenization yields stable water-based colloids with

micrometer particle size and pH ranging from 2.4 to 3 (Scheme 1A). Kobayashi and co-workers have classified reactions in water *via* the "on-water" mechanism into different types.[35d] Based on this classification, the initial hydrolysis and subsequent organocatalytic alkyl alkoxysilane polymerization proceed *via* the "on-water" Type IIa mechanism. The further micelle expansion, aggregation, and the formation of a suspension occur through the "on-water" Type IIIa mechanism. All of these are visualized by us (see Scheme 1Ac and S7†). With the OAF colloids in hand, we are ready for investigating the modification of cellulose substrates (Scheme 1B).

Eco-friendly catalytic surface modification and characterization

With the above freshly prepared OAFs in hand (Table 1), we began modifying cellulose paper substrates by spray coating (Table 2). In addition to SDS as the surfactant, we also prepared OAFs with non-ionic surfactants such as polyethylene glycol hexadecyl ether (Brij C10) and nonylphenol ethoxylate product type (Berol 02) as the surfactants (Table S1†). Next, the water contact angles (WCAs) of the resulting OAF-modified cellulose papers were measured. We found that OAFs containing SDS and the organocatalyst were the water-based colloids of choice and gave the corresponding hydrophobic cellulose products with WCAs ranging from 120° to 142° (Table 2). The hydrophobic properties of the modified cellulose paper significantly depended on the amount of the catalyst and silane in the OAF. Increasing the amount of HDTMS in the OAF raised the WCA from 133° to 145° (Table 2, entries 4 and 7). The highest contact angles were obtained when OAF6 and OAF7 were used as modifying agents, resulting in the corresponding

Table 2 Water contact angle of OAF-treated cellulose paper

Entry	Formula	WCA[b] (°)
1	OAF0	0
2	OAF1	120
3	OAF2	120
4	OAF3	133
5	OAF4	133
6	OAF5	142
7	OAF6	145
8	OAF7	147
9	OAF8	133
10	OAF9	140
11	OAF10	132
12	OAF11	142
13	OAF12	134
14	Organotex	122

[a] OAF was applied on the cellulose surface by spraying. [b] The contact angle value is the mean value of three spots, measured after 300 s of dispensing the water droplet on the treated cellulose paper, error. WCA = water contact angle.

hydrophobic cellulose paper with WCAs of 145° and 147°, respectively (Table 2, entries 7 and 8). Since HDTMS is cheaper than OTMS and approved for use in food applications at an industrial scale, we decided to use HDTMS for our further studies. All of the organocatalysts (fumaric acid, maleic acid, lactic acid, and citric acid) we investigated produced a hydrophobic product, as illustrated by the selected examples in Table 2 (OAF6–AF10). We found that the presence of a catalyst is crucial since omitting it results in no hydrophobicity (WCA = 0°, Table 2, entry 1). Thus, the organocatalysts promote the organocatalytic colloid particle formation and hydrophobization reaction in the water with great success. We also investigated the commercially available hydrophobizing agent Organotex;[37] however, it produced a lower contact angle compared to the disclosed OAFs (Table 2, entry 14). As mentioned, *vide supra*, Kobayashi has classified organic reactions, which proceed through the Sharpless "on-water"[35b] mechanism, into different types.[35d] However, these classifications were made for small molecule substrates that are insoluble liquids/oils in water. In our case, we have colloidal particles reacting at the solid-water interface of polysaccharide substrates. Thus, organic reactions on solid surfaces, which proceed *via* the "on-water" mechanism, are different from Type IIIa and need to be classified. For that reason, we would like to classify it as a Type IVa case where the cellulose is a solid surface reacting "on water" with the colloidal polysilane particles in the presence of a soluble catalyst (Scheme 1B).

The size and shape of the particles in the OAF colloidal suspension were determined by a SYNC particle analyzer. Particle characterization was conducted through laser diffraction and live dynamic imaging. The image analysis provided the shape and distribution of the colloidal particles. A comparison between OAF3 and OAF6 showed that the OAF3 suspension had a narrower particle size distribution (Fig. 2a). Specifically, 65% of particles in OAF3 were less than 80 microns, whereas in OAF6, only 49% of particles were under 80 microns (Fig. 2b). We also examined the particle size of OAF7, which uses OTMS as the silane source, and OAF9, which uses lactic acid as the catalyst. Their particle sizes were approximately 80 microns as well (see ESI†). These results indicate that the higher WCAs of the OAF6-, OAF7-, and OAF9-treated cellulose paper, compared to OAF3, are likely due to the higher organosilane content in these OAF suspensions rather than particle size. When categorizing particles based on sphericity, both OAF6 and OAF3 displayed a mixture of highly spherical particles and agglomerates. Images of particle shapes, categorized by low and high sphericity, are shown in Fig. 2c. In addition, a scanning electron microscopy (SEM) analysis was performed on the freeze-dried OAF sample, with the morphology displayed in Fig. 2g and h. The rheological analysis of OAF6 and OAF3, shown in Fig. 2e and f, reveals a non-Newtonian relationship between the shear rate and shear stress for OAF6 (pseudoplastic) and a linear relationship for OAF3 (Newtonian), respectively. Thus, the viscosity remains constant across shear rates for OAF3, while shear thinning is observed
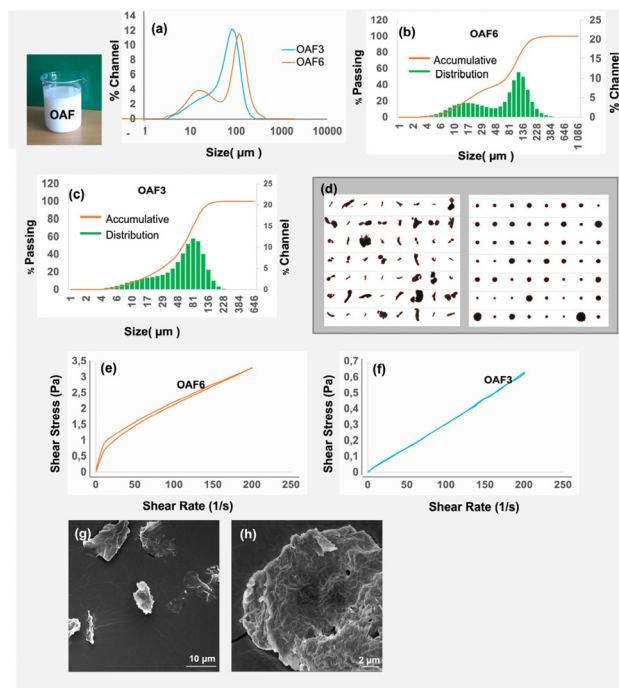

Fig. 2 OAF characterization: (a) Comparison of particle size distribution in OAF3 and OAF6. (b) Particle size distribution of OAF3. (c) Particle size distribution of OAF3. (d) Images of particle shapes: (left) Least spherical. (right) Most spherical. (e) Rheology study of OAF6 with shear stress as a function of shear rate with a continuous ramp. (f) Rheology study of OAF3. (g) and (h) SEM images of freeze-dried OAF6.

for OAF6. The identical upward and downward ramps confirm that the sample's behavior remains time-independent during shearing. Notably, the solid content of OAF6 is twice that of OAF3, resulting in a viscosity for OAF6 that is five times higher than that of OAF3. Complete characterization details for OAF3 and OAF6 are provided in Fig. 2, as well as in Fig. S3–S6 in the ESI.†

SEM analyses were conducted to examine the surface of cellulose paper modified with OAF3 and OAF6, respectively (Fig. 3). The SEM images reveal that both OAF3 and OAF6 share similar distribution patterns on the cellulose surface (Fig. 3b and d). However, the water contact angle was higher for the OAF6-modified cellulose surface. The SEM analysis also revealed that the colloidal particles had aggregated at the cellulosic surfaces (Fig. 3). FTIR analyses revealed that all of the substrates had been modified with polysilane particles, with new signals appearing at 2925, 2855, and 1468 cm^{-1}, representing signals for the symmetric and asymmetric stretching of the –CH$_3$ and –CH$_2$ groups and the C–O bond, respectively (see ESI†). We also performed TGA analysis of cellulose paper before and after OAF6 modification (Fig. S9†). The analysis determined that OAF6 modification made the thermal degradation of the material slower. XRD analysis demonstrated that the crystallinity did not significantly change after modification (see Fig. S12†).

Polysaccharide substrate screening

Given the higher water contact angle achieved with OAF6 on cellulose paper, we decided to explore this formulation for its effectiveness on other cellulose-based substrates such as Chemi-ThermoMechanical (CTMP) paper, cotton, and wood (Table 3). A coating of 1 to 2 mg cm^{-2} of the OAF was applied to these surfaces (Fig. 4). As can be seen in Table 3, all of the substrates got hydrophobic. It is noteworthy that in the case of cotton and wood, the OAF-modified products became superhydrophobic (WCA of >150°). The water contact angles of cotton

Fig. 3 The SEM images of cellulose paper. (a) Cellulose paper, (b) modified cellulose paper with OAF3, and (c) colored water droplets on OAF-modified cellulose paper. (d–f) The OAF6-modified cellulose paper at different magnifications.

Table 3 The results of treated cellulose-based substrates with OAF6^a

Entry	Substrate	WCA^b (°)
1	Cellulose paper	145
2	CTMP sheet	145
3	Cotton	151
4^c	Wood	150

^{a} The substrate was treated with OAF6 using spray coating. ^{b} The contact angle value represents the mean of three spots, measured 300 seconds after dispensing the water droplet on the treated substrates (error margin = ±2°). ^{c} Wood (Aspen veneer) was impregnated with OAF6 under reduced pressure.
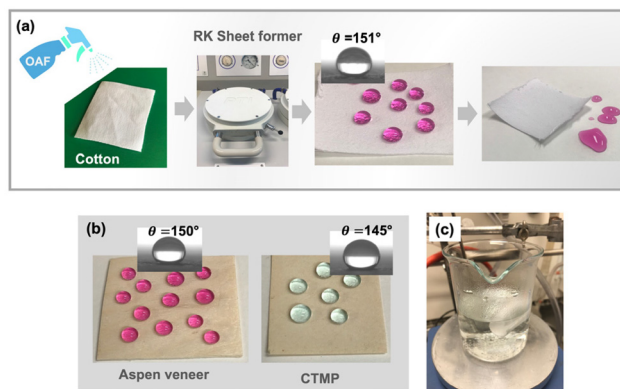

Fig. 4 Description of the process for preparing hydrophobic cellulose-based materials. (a) Preparation of hydrophobic cotton textile. (b) Images of examples of modified samples in Table 3. Water droplets dyed with potassium permanganate and copper sulfate to illustrate hydrophobicity. (c) Photograph of the washing process of hydrophobic cotton at 60–65 °C.

and wood were 55° and 26°, respectively. In order to verify the covalent attachment of the colloidal particles to the cellulose surface, we performed extensive Soxhlet extraction with acetone on the OAF-modified cellulose paper with a WCA of 145°. We found that only 15–20% of the coating material was removed after Soxhlet extraction and the WCA is maintained at 145°. Thus, most of the colloidal silane particles are covalently bound to the cellulose. Scrubbing the OAF-modified paper also did not change the contact angle. It should also be mentioned that the excess OAF from the coating can be reused for hydrophobization of another substrate, demonstrating the green chemistry of surface modification. In another test, the OAF6-modified cotton sample was washed with water at 60–65 °C for 1.5 hours and then dried in an oven overnight at 60 °C for two washing cycles. Measuring the contact angle of the cotton sample after each washing cycle revealed that the WCA was maintained at 150°. Thus, the OAFs can be suitable for the treatment of textiles and as a replacement for toxic fluorocarbons.

The above results demonstrate that organocatalysis of colloidal silane particles at the water–cellulose interface effectively creates a hydrophobic polysaccharide surface across a broad range of substrates. Comparing organocatalytic silanization
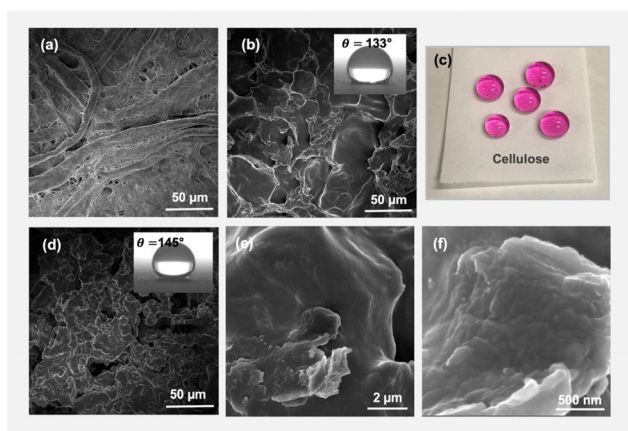
performed in water to that in organic solvents, such as toluene,[32d] shows that the corresponding hydrophobic cellulose products modified in water reach a higher contact angle. This can be explained by the fact that the multilayer of the colloid particle coating forms a rougher surface compared with the more monolayered coating in an organic solvent. The preparation of OAFs can be readily scaled and applied, for example, in the large-scale fabrication of hydrophobic paper by continuous hot-pressing (Fig. S8†).

Experimental

Chemicals and methods

Chemicals were purchased from commercial suppliers and were used without any purification. Hexadecyltrimethoxysilane (HDTMS) was obtained from Sigma Aldrich, octadecyltrimethoxysilane (OTMS) from ACROS ORGANICS, and sodium dodecyl sulphate (SDS) from VWR CHEMICALS. Citric acid and maleic acid were obtained from KEBO Lab. Lactic acid and fumaric acid were purchased from Sigma Aldrich. MUNKTELL 00H laboratory cellulose filter paper was used as the cellulose source. In addition, Aspen veneer, Chemi-ThermoMechanical Pulp (CTMP) and cotton were used as cellulose-based materials in this study.

Water contact angle measurements

The static water contact angles (WCAs) were recorded using a PGX + Pocket Goniometer. The contact angle between a 4 μL drop of water and the modified surface was measured from the captured image after 300 s (5 minutes). The reported contact angles are the mean value of three measurements.

Scanning electron microscopy

SEM images of the samples were recorded using a Tescan Maya-2016. The samples were sputter-coated with a 5 nm layer of iridium using a Quorum Q150T ES. The experiment was conducted at an accelerating voltage of 5 kV. For the SEM analysis of the OAF suspension, the experiment was performed on a freeze-dried sample.

Dynamic image analysis

The particle size and morphology of the OAFs were measured using SYNC from MICROTRAC MRB. The OAF suspension was introduced through FLOWSYNC (a wet application using water as the dispersant) until the optimal concentration was determined by the software. Particle characterization was performed using laser diffraction and live dynamic imaging. The reported particle size, distribution, and particle shape distribution are the results of three measurements.

Rheology study of the OAF

The rheology of the OAF was studied using a Physica Anton Paar MCR 300 and Rheoplus/32 v3.62 software (21001478-33025). CC27 was used as a measuring system, the measurement cell used was TEZ 150P-C, and the shear rate was fixed from 0 to 200 s^{-1} with a continuous ramp.

Optical microscopy

For optical microscopy, a drop of the sample was placed on a glass slide and covered with a coverslip. The sample was then observed using a Leitz Wetzlar microscope equipped with a microscope lens adapter (FMA050, Toupcam™) and a digital camera (U3CMOS, Toupcam™).

Fabrication of hydrophobic cellulose-based materials

Typical procedure for preparing organocatalytic aqueous colloidal formulations (OAFs). Sodium dodecyl sulphate (2.3 g, 8 mmol) was added to a round-bottom flask (500 mL) containing 200 mL of Milli-Q water. After stirring the resulting mixture slowly for 30 minutes at room temperature, citric acid (400 mg, 1.9 mmol) was added, and the temperature increased to 40 °C. After stirring for 5 minutes, hexadecyl trimethoxysilane (24 g, 70 mmol) was added slowly to the flask, and the mixture was stirred for 5 minutes. Next, the stirring was stopped. After letting the mixture stand for 2 hours at 40 °C, the temperature was decreased to room temperature and the mixture was maintained for an additional 46 hours. Next, the prepared suspension was homogenized using an ULTRA TURRAV mixture (IKA 25 digital) at 6000 rpm for 10 minutes.

Coating of cellulosic substrates. The OAF was applied on the surface of the cellulosic substrate by spray coating. The treated surface was left at room temperature until the suspension was fully adsorbed, leaving the surface nearly dry. This drying time varied between 15 and 25 minutes, depending on the substrate. After drying, the treated surface was covered with protective paper (RKP 220 Pappersrondeller) and transferred to a Rapid-Köthen sheet former. The sample was subjected to a temperature of 93 °C under an applied pressure of 96 kPa for 20 minutes.

Conclusions

A concept is presented for developing stable, water-based colloidal OAFs for green, organocatalytic hydrophobization of heterogeneous polysaccharides *via* an "on-water" mechanism. OAFs form through organocatalytic polymerization of alkyl alkoxysilane within surfactant nanomicelles, progressing from "on-water" Type IIa to Type III mechanisms as micelles expand, aggregate, and burst. When applied to cellulosic substrates, these OAFs enable hydrophobic (WCA of >145°) or superhydrophobic (WCA of >150°) surfaces through an "on-water" Type IV mechanism. This eco-friendly approach offers a versatile solution for modifying cellulose-based materials. The dual functionality of the organocatalyst, which facilitates colloidal particle formation and enables green hydrophobic modifications of heterogeneous polysaccharides, exemplifies an innovative strategy for utilizing the catalytic power of small molecules in water-based organic reactions. Inspired by the OAF concept, we also developed water-based betulin colloids

for green modifications and the synergistic fabrication of high-performance materials.[38] Ongoing studies in our laboratories are exploring the extension of the OAF concept to construct superhydrophobic and hydrophobic lightweight materials, with findings to be disclosed in due course.

Author contributions

A. C. and R. A. conceptualized the research project. R. A., D. F., Z. E. H. and T. M. performed the research. R. A. and A. C. prepared the manuscript. All authors reviewed the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

A patent has been filed.

Acknowledgements

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