Mild and Versatile Functionalization of Nacre-Mimetic Cellulose Nanofibrils/Clay Nanocomposites by Organocatalytic Surface Engineering

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ABSTRACT: Development of surface-engineering strategies, which are facile, versatile, and mild, are highly desirable in tailor-made functionalization of high-performance bioinspired nanocomposites. We herein disclose for the first time a general organocatalytic strategy for the functionalization and hydrophobization of nacre-mimetic nanocomposites, which includes vide supra key aspects of surface engineering. The merging of metal-free catalysis and the design of nacre-mimetic nanocomposite materials were demonstrated by the organocatalytic surface engineering of cellulose nanofibrils/clay nanocomposites providing the corresponding bioinspired nanocomposites with good mechanical properties, hydrophobicity, and useful thia-, amino, and olefinic functionalities.

INTRODUCTION

Nature has the ability of producing lightweight materials with robust stability and excellent properties from simple building blocks. Thus, material scientists and engineers have garnered important lessons from nature on fabrication of lightweight materials with exceptional properties.1,2,3 In this context, nacre has gained significant research interest because it has exceptional stability and excellent properties derived from its unique brick-and-mortar structure, which comprises well-aligned inorganic platelets “glued” together by an organic matrix (chitin and proteins).3-6 Despite the many types of inorganic “bricks”, which have been investigated when mimicking the nacre’s brick-and-mortar structure, the present research is on clay platelets of nanometer thickness.7-11 Clay is also useful in reinforcing other types of composites.12,13 In seminal work, Kotov and co-workers introduced a general concept of nacre-mimetic materials for clay nanoplatelet-neat polymer systems.7 It is based on forming micron-thick films by sequential deposition of clay and polyelectrolytes. Another ground-breaking work is the introduction of cross-linking to reach excellent material properties with unprecedented levels of Young’s modulus (>100 GPa).3,5 A novel core-shell approach was introduced by Walther and co-workers.13,14 Here, a polymer is absorbed on the clay nanoplatelets and subsequently the nonsorbing polymer is removed by centrifugation. This allows for the formation of core-shell particles with a minimum amount of polymer (ideally a monolayer) and the possibility of scalability. Most of the vide-supra nacre-mimetic systems are built up of montmorillonite (MTM) as the bricks and a fossil-based polymer (e.g., poly(vinyl alcohol) (PVA) and poly-diallyldimethylammonium chloride (PDDA)) as the mortar. An elegant and sustainable approach for constructing nacre-mimetic nanocomposite systems using cellulose nanofibrils (CNFs) as the renewable mortar instead of fossil-based polymers such as PVA and PDDA was introduced.15-22 The CNFs, which are the primary reinforcement component in the wood cell wall, have been derived from delignified wood pulp fibers and provide good mechanical properties to lightweight...
Composite materials,\textsuperscript{23–25} CNFs also provide unique characteristics in the shape of the nanoscale geometry (diameter $3–15$ nm, length $0.7–2$ $\mu$m) and beneficial mechanical properties of the individual fibrils (crystal modulus $\approx 137$ GPa, tensile strength $\approx 2–6$ GPa, low density $\approx 1.6$ g cm$^{-3}$).\textsuperscript{26,27} Moreover, modifications of the renewable CNFs can allow for surface functionalization of the nanofibril, providing CNFs with tailored characteristics (e.g., charge, size, and surface chemistry).\textsuperscript{28,29} However, the CNF surface is highly moisture-sensitive as it is a natural polysaccharide with a multitude of hydroxyl groups. Moisture and water-sensitivity is also an issue for nacre-inspired clay-polymer nanocomposites in general, since they are mostly based on water soluble polymers such as PVA with an intrinsic hydropphilicity and high moisture sorption. Nacre-mimetics can also be made using graphene and ceramic particles as reinforcing agents, also exhibiting intrinsic water sensitivity.\textsuperscript{30,31} This is also the case when constructing nacre-like materials by, for example, 3D-printing.\textsuperscript{32} In addition, the possibility for tailor-made surface properties is also highly desirable when looking for industrial and biomedical applications of clay nacre-mimetic composites. Today there are methods for making nacre-mimetic materials hydrophobic relying on, for example, covalent cross-linking or ionic supramolecular bonds.\textsuperscript{20,53–55} However, there is a lack of a general technology that in addition to hydrophobicity can install a large variety of functional groups. In addition, many disclosed methods are not practical and rather difficult to scale up for industrial applications. To address these challenges, we have developed an eco-friendly and general method for direct modification of nacre-mimetic nanocomposites. The MTM/CNF system was chosen since it is sustainable and can serve as a general model for both renewable (e.g., MTM/polysaccharide) and fossil-based nacre-mimetic systems (e.g., MTM/PVA).

“Organocatalysis” portrays the acceleration of chemical reactions through the addition of a substoichiometric quantity of an organic compound. The interest in this field has increased spectacularly during this century as a result of both the novelty of the concept and, more importantly, the fact that the efficiency and selectivity of many organocatalytic reactions can improve established organic reactions. In this context, we have developed scalable organocatalytic methods for direct esterification and silylation of polysaccharides.\textsuperscript{38–43} In fact, these metal-free transformations have been performed on a multi-ton scale by industry, which includes preparing water-repellent textiles by organocatalytic silylations (e.g., Organo-Tex).\textsuperscript{41} Here, the use of a metal-free catalyst significantly accelerates the rate of reaction.\textsuperscript{42,43} In addition, silanes are highly useful reagents in surface engineering of different inorganic materials (e.g., modification of metal surfaces for adhesives, silica nanoparticles, and glass fibers). The merging of organocatalysis with the design of nacre-mimetic materials should allow for a synergistic expansion of the design and application of this type of bioinspired future materials in a variety of industrial applications (e.g., coatings for buildings, spaceships, and biomedical implants). Herein, we disclose a highly versatile strategy for functionalization and hydrophobization of nacre-mimetic nanocomposites derived from simple building blocks using naturally occurring catalysts.

\section*{RESULTS AND DISCUSSION}

\subsection*{Processing and Catalytic Modification.} The fabricated MTM/CNF clay nanocomposite papers are prepared by scalable vacuum-filtration and drying procedures similar to paper-making (Figure 1a). The enzymatically derived CNFs are on average $6.6$ nm in diameter with a length of about $1$ $\mu$m. The processing starts with the preparation of separate suspensions of CNF and MTM. In the latter case, only the highly stable exfoliated MTM supernatant fraction obtained after centrifugation is used. The mixed MTM and CNF suspension shows optical transparency; the filtration is relatively fast in the beginning but slows down as the MTM/CNF nanocomposite film starts to form on top of the filtration membrane. Next, the resulting wet nanocomposite is dried to form a strong, transparent, and flexible film of MTM “bricks” dispersed in a CNF “mortar” inspired by nacre.\textsuperscript{44} With these results in hand, we explore the merging of nacre-mimetic nanocomposite fabrication with organocatalytic surface modification (Figure 1).

We began an initial catalyst screen for the hexadecyltrimethoxysilane (C16Si) and (3-thiopropl)trimethoxysilane (TPSi) modification of MTM/CNF nanocomposite films. Natural organic acids were investigated as catalysts, since we have previously used them as Brønsted acid catalysts for direct surface modification of cellulose with various fatty acids, epoxides, polyesters, and silanes (Scheme 1).\textsuperscript{38–43}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Scheme 1. Brønsted Acid-Catalyzed Silylation}
\end{scheme}

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The organocatalytic reactions proceeded smoothly and the highest contact angles of the corresponding modified MTM/CNF nanocomposites were obtained when using citric acid or L-tartaric acid as the catalysts (Table 1).

| Entry | Catalyst | Silane | Time | Contact angle (°) |
|-------|----------|--------|------|------------------|
| 1     | -        | -      | 48   | 38               |
| 2     | -        | -      | 48   | 93               |
| 3     | L-tartaric acid | MeO | 24 | 105 |
| 4     | L-tartaric acid | MeO | 48 | 120 |
| 5     | acetic acid | MeO | 48 | 111 |
| 6     | citric acid | MeO | 48 | 134 |
| 7     | -        | -      | 48   | 90               |
| 8     | L-tartaric acid | MeO | 24 | 114 |
| 9     | L-tartaric acid | MeO | 48 | 146 |
| 10    | citric acid | MeO | 24 | 106 |

“The silane derivative (3 equiv, based on CNFs) and nanocomposites, which contains CNFs (1 equiv), were placed in an oven-dried reaction vessel containing the catalyst (5 mol %) and dry toluene (50 mL). After heating the reaction mixture for the time shown, the temperature was decreased to room temperature and toluene was decanted. Next, the modified nanocomposite was washed with acetone (4 × 50 mL) and put in a desiccator and dried under reduced pressure. Contact angle error less than 0.5°.”

Thus, significantly increasing the contact angle from the unmodified MTM/CNF film (entry 1, Figure 2a). For example, the contact angle is 134° for the C16Si-MTM/CNF using citric acid as the catalyst (entry 6, Figure 2b) and the contact angle is 146° for the TPSi-MTM/CNF using L-tartaric acid as the catalyst (entry 9, Figure 2d). In comparison, the reaction without catalyst is much slower and gave a contact angle of 90° (entry 7, Figure 2f).

In Table 2, the results from the simple and mild organocatalytic modification of MTM/CNF films with a variety of functional silanes using manly L-tartaric acid as the catalyst are shown. For example, when using organosilanes with Ph, alkyl, allyl, and thiapropyl functionalities, the corresponding MTM/CNF-films became hydrophobic. The synthesized AllylSi MTM/CNF film had a contact angle of 125° (entry 5, Figure 2c). The catalytic reaction with (1H,1H,2H,2H-heptadecafluorodecyl)Si was much faster than the other silanes in reaching a high contact angle (entry 8). However, it is noteworthy that the TPSi-MTM/CNF (entry 7) had the same contact angle as a (1H,1H,2H,2H-heptadecafluorodecyl)Si-modified MTM/CNF film (entry 8, Figure 2e). Thus, there is a chance of reaching similar levels of hydrophobicity without the use of an environmentally harmful

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c00978)
perfluorocarbon functional group. It should be noted that the thia- and allyl-functional groups are very useful in “click chemistry” transformations and should allow for further degree of diversification, as well as selective attachment of polymers and UV-active groups to the nacre-mimetic nanocomposite films. The silane-modified MTM/CNF films exhibited the same type of flexibility and transparency after the catalytic surface modifications (Figure 3).

**Structure and Characterization of the MTM/CNF Nanocomposites.** The successful modification was confirmed by contact angle measurements, IR analysis, and elemental analysis. In addition, elemental mapping of the MTM/CNF nanocomposites reveals a homogeneous distribution of carbon (CNF) and silicon (MTM) (Figure 4a,b) used as references. It also shows the fluorine (Figure 4c) and sulfur (Figure 4d) distribution with the highest concentration being on the surface of the corresponding (1H,1H,2H,2H-heptadecafluorodecyl)Si-MTM/CNF and TPSi-MTM/CNF films, respectively. This also supported by elemental analysis where the sulfur content of the TPSi-modified film is 0.61 wt % (0.019 mmol S), which is a ratio of 0.042 to the amount of glucose units (0.45 mmol) present in the sample. Thus, only the outer surface is modified by the organosiloxane agent. The cross-sections of the fractured surfaces of modified MTM/CNF and unmodified MTM/CNF nanocomposite films obtained by uniaxial tension at 50% RH were observed by field-emission scanning electron microscopy (FESEM) and micrographs are shown in Figure 4e. Both modified C16Si-MTM/CNF and unmodified MTM/CNF nanocomposites show a lamellar microstructure. Previous XRD measurements of the MTM/CNF has shown that it resembles the brick-and-mortar structure of nacre. The mechanical performance of the nanocomposites was investigated at RH 50% (Table 3). The tensile strength of the C16Si-MTM/CNF is 247 ± 13 MPa (E-modulus = 25.2 ± 1.2 GPa, strain at break = 2.1 ± 0.3%, entry 4) and the strength of the MTM/CNF is 267 ± 18 MPa (E-modulus = 24.8 ± 2.5 GPa, strain at break = 2.7 ± 0.7%, entry 3). Thus, the high strength of MTM/CNF films is maintained after the catalytic surface modifications. In comparison, the tensile strength of the pure CNF film is 277 ± 15 MPa (E-modulus = 17.2 ± 0.9 GPa, strain at break = 5.9 ± 0.6%, entry 1) and for pure MTM is too brittle to measure (entry 2). This result is important and justifies the strategy to modify after the formation of the MTM/CNF nanocomposite since the approach of using hydrophobic CNF-nanoparticles to create films in water failed due to dispersion difficulties. It is the MTM/CNF core that contributes to the mechanical properties of the films and the surface modification is only a small percentage of the functional groups on the film surface. Moreover, at higher humidity (e.g., 90% RH) the mechanical properties are significantly worse at the MTM/CNF core.

The interaction between MTM and CNFs was further investigated by FTIR spectroscopy (Figure 5, see also the Supporting Information). We observed a similar frequency of vibrational bands for MTM/CNF (Figure 5a) and TPSi-MTM/CNF (Figure 5b), dominated by strong hydrogen bonding only in cellulose at 3326 cm⁻¹, whereas the MTM/CNF interface is not expected to be identifiable in the spectrum. Under dry or even 50% RH conditions, we still expect favorable MTM/CNF interface bonding from previous studies. The use of hydrophobic, surface-modified nanoparticles during processing and solidification would penalize the interface interactions between CNF and MTM. The IR also confirmed that (3-thiapropyl)trimethoxysilane had been attached to the nanocomposite film at 2564 cm⁻¹ (Figure 5b).

In order to investigate the surface, we performed atomic force microscopy (AFM) of the MTM/CNF and TPSi-MTM/CNF nanocomposites, respectively (Figure 6). The AFM revealed that the roughness of the nanocomposite film increased from the nm scale to the μm scale after l-tartaric acid-catalyzed thiapropylsilane modification, which is proposed to be due to the catalytic silylation. However, when modifying a MTM/CNF nanocomposite film with a 2.2 times smoother

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**Table 3. Mechanical Data of Various Films at 50% RH**

| entry | sample               | E-modulus (GPa) | tensile strength (MPa) | strain at break (%) |
|-------|----------------------|-----------------|------------------------|---------------------|
| 1     | CNF film             | 17.2 ± 0.9      | 277 ± 15               | 5.9 ± 0.6           |
| 2     | clay-film            | --              | --                     | --                  |
| 3     | MTM/CNF film         | 24.8 ± 2.5      | 267 ± 18               | 2.7 ± 0.7           |
| 4     | C16Si-MTM/CNF film   | 25.2 ± 1.2      | 247 ± 13               | 2.1 ± 0.3           |

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**Figure 4.** Elemental mapping (a–d), (a) homogeneous distribution of carbon (CNF), (b) silicon (MTM), and (c) fluorine at the surface of (1H,1H,2H,2H-heptadecafluorodecyl)Si-MTM/CNF. (d) Sulfur at the surface of TPSi-MTM/CNF. (e) Resulting cross-section of the MTM/CNF nanocomposite before and after modification with C16Si.
surface as compared to the one depicted in Figure 6a, a less rough TPSi-MTM/CNF surface was obtained as compared to the one shown in Figure 6b and a lower contact angle was hence observed (see Figure S8). This is in accordance with the theory of the importance of surface roughness for the design of hydrophobic surfaces with a high contact angle.

**CONCLUSIONS**

In summary, we disclose a general organocatalytic strategy for the versatile functionalization and hydrophobization of nacre-mimetic nanocomposites. The merging of metal-free catalysis and the design of nacre-mimetic nanocomposite materials allows for facile and mild surface engineering of this important class of nanocomposites. The concept is demonstrated by the sustainable assembly of strong, transparent, hydrophobic, renewable, and flexible MTM/CNF films using several silanes with useful functionalities (e.g., −SH, −NH₂, olefin, and aryl). In order to obtain transparent films, the organocatalytic silylation reactions were made after the assembly of the MTM/CNF nanocomposites. Since there are a large variety of available silanes, it is possible to attach a plethora of molecules to nacre-mimetic nanocomposites using the disclosed strategy. Furthermore, the −SH and olefinic groups are excellent reactive groups for attachment of biopolymers and bioactive molecules. Such multifunctional combinations make these nanomaterials interesting for broader applications, such as drug delivery and tissue engineering, as well as packaging, construction, and advanced functional materials. Thus, further development of multifunctional nanocomposites inspired by the architecture of nacre is envisioned based on the disclosed strategy.

**EXPERIMENTAL SECTION**

**General.** Chemicals (e.g., hexadecyltrimethoxysilane (C16Si) from Sigma-Aldrich, (3-thiapropyl)trimethoxysilane (TPSi) from Sigma-Aldrich, (1H,1H,2H,2H-heptadecafluorodecyl)trimethoxysilane (1H,1H,2H,2H-heptadecafluorodecyl)Si from TCI) and solvents were used as purchased without any further purification. Tartaric acid from Sigma-Aldrich and citric acid from Merck were dried in a desiccator over phosphorus pentoxide. Fourier-transformed infrared spectroscopy was recorded by Thermo Scientific NICOLET 6700 FTIR, Smart orbit, Diamond 30,000−200 cm⁻¹ using transmission mode (160 scans) directly on the films. The AFM experiments were carried out with dimension icon and tapping mode with Bruker TAP525A as a cantilever. Resonance frequency for these experiments was 445 kHz with a 0.32 lines/s scanning rate.

**Materials. CNF.** The CNF suspension (1.5 wt %) in Milli-Q water was prepared by high-pressure homogenization of an enzymatically pretreated sulfite pulp (Nordic AB, Sweden), as reported by Henriksson et al.²³ Thus, pulp fibers were washed and beaten prior to addition of an endoglucanase under slight heating. After enzyme hydrolysis, the CNFs were washed and homogenized resulting in the 1.5 wt % suspension.

**Clay Suspension.** A stable MTM suspension (approx. 0.35 wt %, Na⁺ Cloisite, BYK additives, Germany) was prepared by intense mixing and ultrasonication of MTM powder in Milli-Q water using a probe shear-mixer (Ultra-Turrax) for 30 min. Notably, only the supernatant fraction of the MTM suspension after centrifugation (4500 rpm, 30 min) was used and the aggregates were removed. Sonication/centrifugation cycles were repeated until all aggregates were removed, which is typically 3−4 times. The yield of the processes is 70%.

**Preparation of Nanocomposites.** The MTM/CNF nanocomposites were prepared by filtration and drying, as reported Medina et al.¹⁷ Briefly, CNF water suspension was diluted to 0.15 wt % and sheared with an Ultra-Turrax apparatus. After 10 min, the above MTM suspension was added and the mixture was mixed for 5 more min. The well-dispersed aqueous MTM/CNF suspension was filtered with a microfiltration membrane with a pore size of 0.65 μm for several hours. The resulting wet cake was dried in a hand sheet dryer (Rapid Kothen, Austria) under reduced pressure at 93°C.

![Figure 5](https://pubs.acs.org/doi/10.1021/acsomega.0c00978)

**Figure 5.** FTIR spectrum of the CNF/Clay nanocomposite. (a) MTM/CNF. (b) TPSi-MTM/CNF (c) (3-thiapropyl)trimethoxysilane (TPSi).

![Figure 6](https://pubs.acs.org/doi/10.1021/acsomega.0c00978)

**Figure 6.** AFM images of nanocomposites. (a): MTM/CNF nanocomposite, RMS roughness (sq): 296 nm, surface area: 3187 μm² (b) TPSi-MTM/CNF, RMS roughness (sq): 1.028 μm, surface area: 4039μm².
°C for 15 min. The nanocomposite contained 20 wt % MTM and 80 wt % CNF.

Typical Procedure for Catalytic Surface Modification of Nanocomposites. The silane derivative (3 equivalents, based on the CNF) and nanocomposite (338 mg), which contains CNF (270 mg, 1.66 mmol (based on glucose anhydrous unit), 1 equiv) were placed in an oven-dried reaction vessel containing L-tartaric acid (36 mg, 0.24 mmol, 5 mol %) and dry toluene (50 mL). After performing the reaction for 48 h at 95 °C, the temperature was decreased to room temperature and the toluene was decanted. Next, the modified nanocomposite was washed with acetone (4 × 50 mL) and dried under reduced pressure.

Typical Procedure for Catalytic Surface Modification of CNF. A 31 g of suspension of CNF (1.6 wt %, 500 mg dry mass, 3 mmol) was homogenized in EtOH (95%, 60 mL) for 1 h at 6000 rpm. The solvent was exchanged with EtOH (95%, 3 × 60 mL) using centrifugation. The CNF was next transferred to the reaction vessel in EtOH (95%, 30 mL). Next, (3-mercaptopropyl)trimethoxysilane (1.4 mL, 7.5 mmol, 2.5 mequiv) and tartaric acid (23 mg, 0.15 mmol, 5 mol %) were sequentially added. After refluxing the resulting reaction mixture for 24 h, it was cooled down to room temperature and the modified CNF was washed with EtOH (95%, 3 × 60 mL) using centrifugation.

Typical Procedure for Catalytic Surface Modification of MTM. Allylttrimethoxysilane (0.34 mL, 2 mmol) and MTM (500 mg) were placed in an oven-dried reaction vessel containing tartaric acid (25 mg, 0.5 wt %) and dry toluene (10 mL). After stirring the reaction mixture at 80 °C for 6 h, the temperature was decreased to room temperature and toluene was decanted. Next, the modified MTM was Soxhlet extracted (acetone, 24 h) and dried under reduced pressure.

Contact Angle Measurements. The contact angle (CA) was recorded on a DAT 1100-FIBRO-system ab-SWEDEN (acetone, 24 h) and dried under reduced pressure.

Field-Emission Scanning Electron Microscopy (FESEM). High-resolution micrographs of the sample surface and cross-sections were recorded using a Hitachi S4800 Field-Emission scanning electron microscope (Japan). The typical accelerating voltage was 1 kV and the working distance was 3−4 mm. Additionally, elemental mapping was carried out using an energy-dispersive X-ray detector (Oxford Instruments, UK) at 15 kV and high probe current.

Tensile Testing. Tensile properties of the modified and unmodified films were determined on a Universal Testing Machine, Instron 5944 (USA). The samples were first conditioned at 50% relative humidity and 22 ± 1 °C for at least 40 h. Rectangular strips of 3−5 mm in width were then cut and tested, using a gauge length of 22 mm and a strain rate of 0.1 mm·min⁻¹. The instrument was equipped with a noncontact video extensometer for strain measurement, and the load was measured with a 500 N load cell. All reported values are averaged data from at least five specimens.

Atomic Force Microscopy. The AFM experiments were carried out with dimension icon and tapping mode with Bruker TAP525A as a cantilever. Resonance frequency for these experiments was 445 kHz with a 0.32 lines/s scanning rate.
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(44) It should be noted that we also separately modified the CNF with thiapropylsilane (TPSi) and MTM with allylsilane (AllylSi), respectively, using l-tartaric acid as the catalyst (see the Supporting Information). The catalytic reaction worked well and gave the corresponding hydrophobic TPSi-CNFi and AllylSi-MTM, respectively. Thus, MTM can also be highly functionalized by organocatalysis, which should find application in a lot of different areas ranging from catalysis to toxic metal purification (For a review see: Varadwaj, G. B. B.; Parida, K.; Nyamori, V. O. *Inorg. Chem. Front.* 2016, 3, 1100.). However, trying to prepare a transparent AllylSi-MTM/TPSi-CNFi nanocomposite in organic solvent (e.g., EtOH) using the above described filtration technique failed. Instead agglomeration occurred and a white film with TPSi and AllylSi groups was formed.

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