

Perspective on the Biomimetic Approaches for the Design of Hydrophobic and Antimicrobial Paper Coatings with Hierarchical Surface Structures [†]

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Abstract: The design of functional paper coatings with excellent barrier properties, including water repellence, anti-microbial properties, and recyclability, is highly demanded in view of the sustainable use of paper as flexible substrates for various industrial applications such as packaging. The enhanced coating functionalities should be incorporated through a combination of selected bio-based materials and the creation of appropriate surface textures enhancing coating performance. The bio-inspired approaches through the replication of hierarchical surface structures with multi-scale dimensional features in combination with selection of appropriate bio-based functional groups offer new concepts for coating design. In this short perspective paper, concepts in the field are illustrated with a focus on the combination of hydrophobic and anti-microbial properties. Based on long-term work with the available toolbox of bio-based building blocks and nanoscale architectures, they can be processed into applicable aqueous suspensions for sprayable paper coatings. The macroscopic roughness profile of paper substrates can be complemented through the decoration of nanoscale bio-based polymer particles of polyhydroxybutyrate or vegetable oil capsules with dimensions in the range of 20–50 nm or 100–500 nm depending on the synthesis conditions. The anti-microbial properties can be provided by the surface modification of nanocellulose with biologically active molecules sourced from nature. Besides the more fundamental issues in design and synthesis, the industrial application of the bio-inspired coatings through spray-coating becomes relevant.



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1. Introduction

Paper substrates are preferred carriers generated from renewable fiber sources and present good properties such as high flexibility, specific strength, and stiffness to be used in several application domains, including packaging, batteries, transistors, sensors, or microfluidics. Owing to the organization of cellulosic fibers into a macroscopic web-like structure, the bulk structure of the paper possesses high porosity and permeability, which must be controlled by the application of a barrier layer or coating on the surface. The surface modification of the paper with a thick coating layer is traditionally performed through extrusion or dispersion coatings, but results in the formation of a very dense and closed layer that fully covers the surface pores and protects fibers from being exposed at the surface. The latter rather reflects the formation of a full polymer layer on top of the paper substrate and converts the surface towards a comparable plastic material. The latter

way obviously restricts responsible handling of paper as a natural resource and conflicts with the sustainability issues. As such, the circularity of paper processing is not guaranteed because of the lack of recycling possibilities for a coated paper. Better recovery of paper fibers may be guaranteed by the deposition of a thin coating from aqueous suspension.

Novel coatings with superior performance through a combination of different functionalities should be designed by the exploitation of synergistic effects based on the intrinsic micron-scale roughness of the paper substrate in combination with a micro- to nanoscale coating morphology. The hierarchical structural organizations and presentation of active compounds, as found in nature, should be mimicked at artificial level through the engineering of surface textures and chemistries. The natural surfaces with multi-scale morphological features serve different goals, such as water-repellence/anti-stick, observed in plant leaves and animal toe pads [1], or anti-fouling/anti-adhesion, observed on shark skin or mussel shells [2]. Alternatively, natural products with intrinsic hydrophobicity include plant wax [3], and/or the natural compounds with anti-microbial properties include chitin/chitosan [4] or peptides [5]. The latter products are urgently needed for the replacement of toxic or traditional chemicals such as fluorinated compounds, metallic nanoparticles, or biocides. In a biomimetic approach, the translation of natural systems into a controlled organization of selected species occurs through the chemical self-assembly that is directed through bottom-up or top-down directional forces. The self-assembly of polymer molecules can be controlled using intermolecular interactions [6], either in the presence of mechanical load (e.g., shear) [7], magnetic fields [8], or electrostatic fields [9], which often require special technologies or up-scaling limitation.

In this perspective paper, some concepts are illustrated for the design of paper coatings with improved functionalities using bio-based ingredients and bio-mimetic structures that primarily focus on hydrophobic and anti-microbial properties. Both properties are selected in relation to the practical applications of papers in the packaging industry, while both are simultaneously interconnected to give better protective properties. The novelty in the approach is that the presented methods are not based on lab-scale application procedures, but they are applicable for upscaling towards industrial processes by spray coating.

2. Biomimetic Approaches for Water-Repellent Paper Coatings

As inspired by the Lotus leaf, the superhydrophobic properties are evoked by a combination of macro- and nanoscale surface roughness together with coverage of a hydrophobic wax layer. For paper substrates, the microscale surface roughness is given by the organization of the cellulose fibers in the paper web structure, while the surface decoration in the nanoscale range can be obtained by the precipitation of nanoparticles [10] and/or the organization of natural polysaccharide materials in nanoscale crystalline forms [11]. A number of examples are known from the literature, where bio-inspired crystallization of CaCO_3 results in the precipitation of calcite microtubes or nanoscale needles onto cellulose fibers [12]; here, *in situ* templated synthesis is directed by the presence of cellulose fibers and suitable concentrations of the poly(acrylic acid) as a crystal growth modifier. Also, the combination of SiO_2 nanoparticles and multi-wall carbon nanotubes dispersed into a PDMS matrix with butyl acetate dispersing agent formed a flexible superhydrophobic coating onto paper substrates for electronic applications [13]. The combination of biowax with mineral hybrids and proteins has created the structural reinforcement and waterproofing of paper wasps, where biowax–silica hybrids were mineralized and gelatin acts as a functional additive to facilitate the anchorage of hybrids to paper [14].

In our own work, we explored the role of bio-based ingredients in hydrophobic paper coatings, including vegetable oils, biopolymers, or biowax [15]. The hydrophobic papers were created by deposition of nanoparticles with encapsulated vegetable oils, including

up to 70% content of palm oil, rapeseed oil, castor oil, and corn oil [16]. The surface structure of coated paper resembles Lotus leaf petals, where the organic nanoparticle shell acts as a binder with the cellulose fibers and anchorage for the fatty acid molecules of the oil (Figure 1a); the deposition from aqueous dispersion with high solid content forms a continuous coating with the oil as a binder. Alternatively, the specific structuring of rose petals was mimicked through the synthesis of poly(hydroxybutyrate) or PHB micro- and nanoparticles with open-structured surfaces (Figure 1b); depending on the precipitation conditions of the PHB during solvent exchange at various concentration ratio, the particle morphology could be altered [17]. In another example, the layered brick-and-mortar structure of nacre, equally occurring in natural clay minerals, could be mimicked by a modified kaolinite with intercalated nanoparticles of styrene-co-maleimide nanoparticles (Figure 1c); as the interlayer spacing of mineral platelets can be enhanced through intercalation of polymer species, an open layered structure and hydrophobic protection is provided [18]. As such, efficient paper barrier coatings against water vapor transmission consist of parallel ordered additives providing a tortuous path for gas diffusion. The spiky surface of insects enables to control adhesion and repellent properties (Figure 1d), which other authors duplicated through the controlled crystallization of a biowax (e.g., soybean wax) onto a superhydrophobic paper coating for liquid food [19].

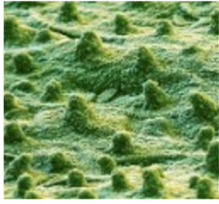
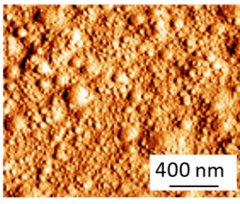
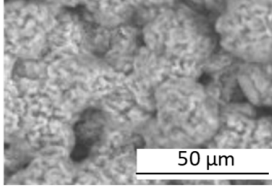
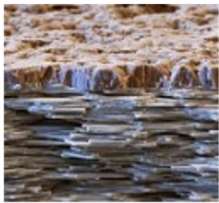
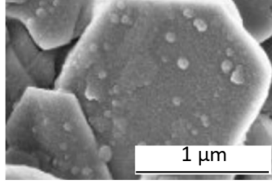
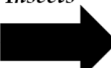
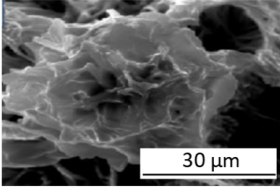
Representative bio-surface		Detail of synthetic coating on paper	Water contact angle range
(a)	  <i>Lotus Leaf</i>		$140 \pm 5^\circ$
(b)	  <i>Rose Petal</i>		$151 \pm 5^\circ$
(c)	  <i>Nacre</i>		$130 \pm 5^\circ$
(d)	  <i>Insects</i>		$159 \pm 2^\circ$

Figure 1. Illustrative examples of biomimicry in creating water-repellent paper coatings with hierarchical surface structures based on (a) vegetable-oil nanocapsules [16], (b) polyhydroxybutyrate particles [17], (c) intercalated kaolinite clay [18], and (d) biowax precipitation [19].

3. Biomimetic Approaches for Anti-Microbial Paper Coatings

Anti-microbial and anti-adhesion surface design is strongly determined by intertwined wettability, roughness, and surface patterning [20]. The increase in hydrophobicity postulated in the previous section is a first step in controlling the affinity for microbial/bacterial attachment, proliferation, and growth, as creation of a water-depleted environment disfavors comfort of adhering organisms. In addition, specific anti-microbial chemical moieties found in nature should be incorporated in the coating composition in combination with the control of the surface topography.

3.1. Bio-Inspired Selection of Anti-Microbial Coating Chemistry

The anti-microbial properties in packaging materials and paper coatings are often introduced through metallic nanoparticles, such as silver (Ag) or zinc oxide (ZnO), which may pose negative environmental concerns, health effects, and toxicity after eventual leaching or contact. They should therefore be preferentially immobilized onto a biobased carrier material such as cellulose nanofibers (CNFs) that form a dense network of fibrillated fibers with film forming properties and good intrinsic barrier properties against oxygen permeation, but have no intrinsic anti-microbial properties. The surface chemistry of nanocellulose plays a pivotal role in coating performance, and tailored surface functionalization can introduce various properties to nanocellulose for paper coatings [21]. Therefore, the chemical functionalization of the CNFs with anti-microbial moieties has been performed. The reactivity of the CNFs with large surface area and hydroxyl groups allows for the chemical grafting and/or physical absorption. In particular, functional groups like aldehyde groups, quaternary ammonium, metal, metal oxide nanoparticles, and chitosan are employed to enhance the anti-microbial efficiency. The deposition of Ag nanoparticles onto CNFs was performed by the in situ reduction from AgNO₃ precursors, where the CNFs act as a catalyst and forms a template structure for the deposition of the anti-microbial compounds (Figure 2a) [22]. Alternatively, a range of anti-microbial peptides (AMPs) with analogs in nature was discovered, and they can be chemically grafted onto the nanocellulose surface. The bio-inspired AMPs are generally short peptides with 12–50 amino acids, specifically containing charged residues (e.g., arginine, lysine, histidine) or a significant portion (over 50%) of hydrophobic moieties providing anti-microbial activity. Researchers synthesized oxidized CNF and grafted it with tryptophan-based peptides using a two-step coupling method [23]: first, CNF was activated using N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide hydrochloride forming a stable active ester; then, the active ester reacted with the amino groups of the peptide, resulting in an amide bond between ester groups and the peptide. Otherwise, the bioactive peptides were also successfully grafted onto nano-CuO impregnated cellulose membranes [24]; the process involved a simple and rapid method, including atmospheric argon plasma treatment, without the need for additional solvents or emulsifiers. Furthermore, peptides were covalently grafted onto microcrystalline cellulose using a benzyl thiosuccinic linker, where the modified peptides exhibited anti-microbial properties [25]. The functional groups modifying the nanocellulose surface make it effective against a wide range of microorganisms, including viruses, bacteria, fungi, algae, and protozoa [26].

The other natural compounds with anti-microbial properties include certain extracts of plant oil, such as eucalyptus oil, neem oil, coconut oil, thyme essential oil, or oregano essential oil, which are known to combat bacteria and preserve food [27]. In our work, the plant oils were used for creating anti-microbial paper coatings after encapsulation of the plant oils in polymer nanocapsules, the precipitation of the nanocapsules onto CNFs through physical interactions, and the controlled release of the plant oils (Figure 2b) [28].

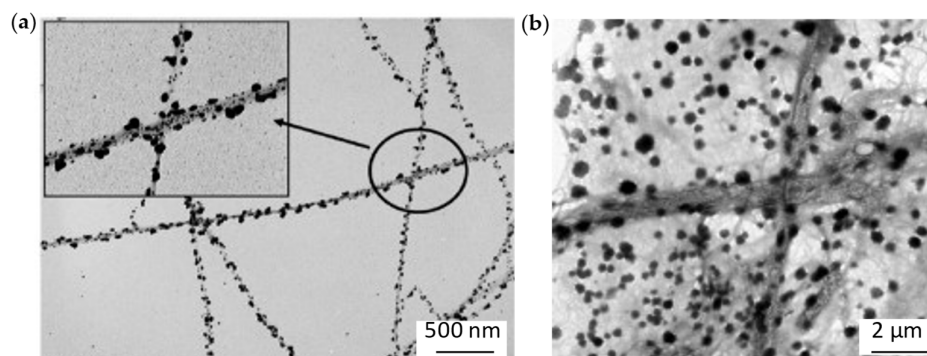


Figure 2. Illustrative examples of biomimicry in creating anti-microbial paper coatings with selection of specific anti-microbial chemical compounds, such as, e.g., (a) functionalized nanocellulose with Ag nanoparticles [22]. Reprinted with permission from © 2010 American Chemical Society. (b) Functionalized nanocellulose with encapsulated plant oil [28].

3.2. Bio-Inspired Selection of Anti-Microbial Coating Topography

Understanding and manipulating surface topography additionally contributes to designing more effective anti-microbial paper coatings. By optimizing roughness and periodic features, the ability to resist microbial colonization on paper coatings can be enhanced. A textured or rough surface could enhance the interaction between the coating and micro-organisms, potentially inhibiting their growth, while rough surfaces also provide a larger area for the release of anti-microbial agents. Consequently, they exhibit higher anti-microbial activity compared to smooth surfaces. The combination of nano- and microscale topographies significantly limits bacterial attachment, and they reduce the chances of bacterial colonization and biofilm formation [29]. When bacteria encounter a surface with controlled features (such as grooves, ridges, or irregularities), their ability to adhere is compromised. This limits their ability to form biofilms, which are often associated with infection and anti-microbial resistance. Therefore, the synergy between different anti-bacterial mechanisms on heterogeneous surfaces are enhanced either by the intrinsic topography of the paper coating and/or the artificial structuring of paper coatings.

4. Industrial Processing of Biomimetic Paper Coatings

The industrial processing of functional paper coatings, including anti-microbial agents, is favored in the presence of functionalized CNFs, owing to their inherent rheological properties and shear thinning effects that allow for continuous application under spray coating. The latter technique provides conformal coatings that preserve the intrinsic roughness of the substrate, in case of the macroscale roughness of the paper, and decorates it with a 1–5 μm thin coating on top with eventual nanoscale roughness.

In addition, we have recently demonstrated that femtosecond laser texturing of spray-coated nanocellulose layers can introduce organized linear patterns in micrometer range (as determined by the laser-spot size) or create anti-microbial patterns that control the hydrophobic and anti-microbial resistance [30]. The latter technology has recently reached industrial maturity and is readily available for upscaling.

5. Conclusions

According to the state of the art, the spray coating with aqueous suspensions provides ample opportunity for mimicking hierarchical surface structures with combined hydrophobic and anti-microbial resistance on paper substrates through the control of surface topography and selection of bio-based compounds (e.g., nanocellulose, plant oil, biowax, peptides) that occur in organized structures or have inherent anti-microbial properties.

Future explorations will rely on the combination of properties that can be obtained through the surface modification of nanocellulose in combination with appropriate patterning technologies for coatings through laser texturing. The latter combination of spray coating and laser patterning is ready for application at the industrial scale.

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