

# Biomimetic Surface Modification of (Nano)cellulose<sup>1</sup>

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**Abstract.** The remarkable efficiency of biochemical reactions is the result of biological evolution, often involving confined water. We elaborate on the role of confined water in cellulose chemistry and demonstrate that such water promotes chemical surface reactions and can be used to control their regioselectivity, i.e., it enables the preparation of spatially selectively modified cellulose. Based on this concept, we propose new straightforward avenues to functional cellulose (nano)fibers, which allow precise tuning of their surface chemistry, under mild, sustainable, and aqueous conditions. We expect that these new methods will support in advancing currently used (nano)cellulose modification protocols, and the development of future high-performance materials.

**Keywords:** surface acetylation, biopolymers, nanomaterials, confined reaction

## 1 INTRODUCTION

Water as the solvent of life is ubiquitous in the chemical processes of living organisms[1] and all known living systems only thrive in aqueous systems. Water controls the activity of enzymes, acts as a nucleophile and mediates charge and proton transfers in biological reactions. In the presence of water, nature enables the miraculous array of complex biochemical reactions - at high efficiency and under mild conditions. These also include processes which are unfavoured under aqueous conditions[2], such as dehydrations and esterifications. They do nevertheless occur due to presence of optimized enzymes[3]; and the fact that water is spatially confined in cells and organelles[1], [4]. Water in confinement is restricted in mobility and features anomalous behaviour, if compared to the fluid in bulk, this directly affects its chemical and physical properties[5], [6]. Exploiting the potential of this anomalous water state for chemical reactions, has led to very important scientific contributions, which take advantage of the confined water in artificial porous solids[7]–[11] or biphasic fluid systems[12]–[14]. Current limitations are the restrictions to small molecules

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as reactants, the use of organic solvents and the rather complex design of these reaction systems. Expanding this concept to naturally occurring and sustainable materials, which confine water due to their intrinsic native structure, would be a major contribution to the field. This is especially true in times of climate[15] and plastic crisis[16]. This renders the development of green and resource-efficient reactions, and materials, most timely and necessary. Native cellulosic materials[17] are based on nano-scaled assemblies, covered by surface-confined water under ambient conditions. Cellulose is used herein as representative example for this class of hierarchically structured biopolymers. Cellulose[18], from the molecular viewpoint, has the rather simple chemical structure of  $\beta$ -D-1,4-linked glucopyranose repeating units that give strictly regular and rigid “one-dimensional” fibrils, as its smallest subunit. These fibrils are composed of axially twisted crystallites[19] with a chemically accessible and hydrophilic surface, which under ambient conditions is covered with a hydration layer[20], [21]. The presence of water would make either reactions unfavourable or water would act as a competitor to cellulosic hydroxyl groups; and thus, be feared as the major cause of low yield, side reactions and unwanted reagent consumption. As a consequence, such reactions have been mainly performed under anhydrous or anhydrous homogeneous conditions[22]–[24]. This stays in stark contrast to recent efforts to use water as reaction promoter[25], [26].

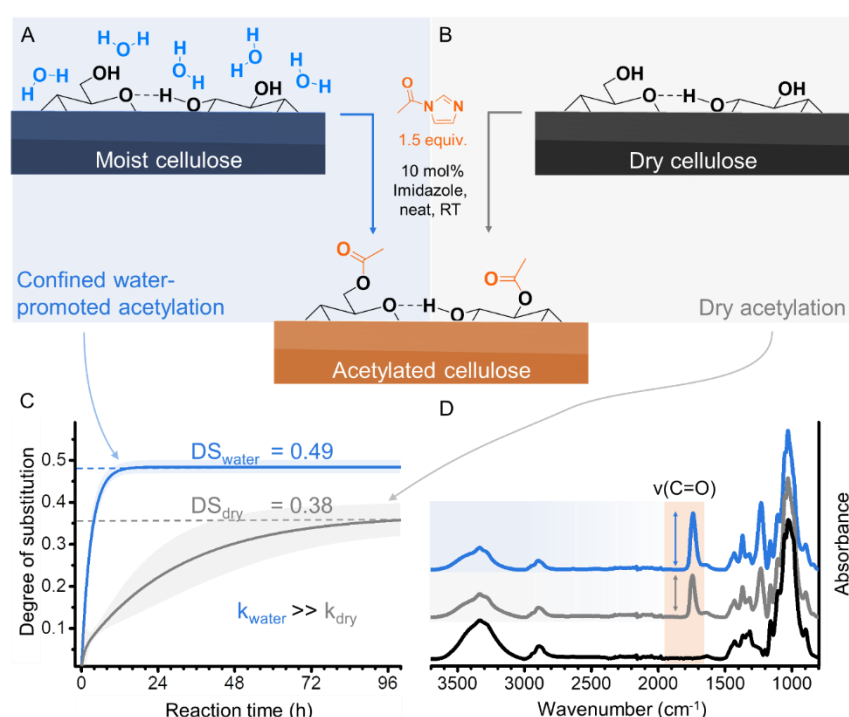
## 2 METHODS

*SOLID-STATE ACETYLATION WITH N-ACETYLMIDAZOLE.* Cellulose fibres at EMC (1.0 g dry mass, 6.2 mmol, 1 Eq) were mixed with the respective amount of *N*-acetylimidazole *i.e.* 0.3 Eq (0.20 g, 1.85 mmol), 1.0 Eq (0.68 g, 6.17 mmol) or 1.5 Eq (1.02 g, 9.25 mmol) in a 0.25 mL grinding jar. 10 mol% imidazole (based on the amount of *N*-acetylimidazole) and stainless-steel grinding balls (17.7 g, 0.5 cm diameter) were added and milled for 0.5 h at 25 Hz in a vibratory ball mill (Retsch CryoMill, Retsch GmbH, Germany). After milling, the samples were equilibrated at room temperature in a closed vessel. The reaction time was defined as the sum of the milling time and equilibration times. The acetylation was quenched by addition of a saturated aqueous solution of NaHCO<sub>3</sub>. The acetylated fibres were finally washed carefully with DI water and dried at 105 °C for further analysis.

## 3 EVALUATION

Wood-based cellulose fibres with a high cellulose content of 92% were used as starting material. Due to their hierarchical and porous architecture, they can structurally confine up to 0.5 mL of water per gram of fibre. In case of the cellulose fibre, only the surface hydroxyl groups of the elementary fibrils are accessible for chemical reactions. In general, experiments were conducted using fibres with equilibrated moisture content (EMC) of 50 % relative humidity, equalling approx. 7 wt% water. The resulting number of water molecules is in the

same stoichiometric range as the cellulose's surface hydroxyl groups and hence strongly bound to the cellulose surface. In this work, we used solely the solid reactants, *N*-acetylimidazole[27]–[29] and the catalyst imidazole to acetylate the cellulose surface. Imidazole was chosen because of its structural analogy to histidine, its associated enzyme-like catalytic behaviour[30] and affinity for cellulose surfaces[31]. The heterogeneous reaction of cellulose and *N*-acetylimidazole was initiated by solid-state mixing using a vibratory ball mill (Fig. 1A) and represents, to the best of our knowledge, the only reported true solid-state polymer acetylation method.



**Fig. 1:** Confined water-promoted acetylation: Cellulose fibres were reacted under solvent-free and heterogeneous (solid-phase) conditions with *N*-acetylimidazole in presence of confined water (A) and dry condition (B). The kinetics (C) and the infrared spectra (D) show that water, seemingly paradoxically, is a key player in the reaction mechanism and increases reaction rate and efficiency (95 % confidence intervals are shown in shaded colour).

Ball milling was chosen as it allows for mild mixing conditions, avoiding depolymerisation and decrystallization of the cellulose. We studied the solid-state acetylation in presence of different water amounts – dry, 7 wt%, 20 wt% and 30 wt% - with respect to kinetics, reaction efficiency and regioselectivity. The calculated reaction efficiency is the ratio of the degree of substitution and the molar amount of used *N*-acetylimidazole. As water is conventionally regarded as a nuisance factor in esterifications, decreasing the efficiency of this type of

reaction, we expected the highest reaction efficiency in case of the dry sample. Paradoxically, we observed the contrary: as shown in **Fig. 1A**, the presence of 7 wt% water in the fibre increased not only the reaction kinetics but also its efficiency. The kinetic scatter plots were exponentially fitted and resemble the shape of typical diffusion-controlled reactions[32]. Considering our results, the solid reactants and the solvent-free reaction conditions; we assume a reaction mechanism based on diffusion through the fibre hydration layers. The reaction is also auto-catalytic as additional formed imidazole (formed after hydrolysis or esterification of *N*-acetylimidazole), can act as a base catalyst[30]. This has the effect of accelerating kinetics inside the fibre as the reaction proceeds.

#### 4 CONCLUSION

Cellulose, as a hierarchically structured biopolymer, is hygroscopic and intrinsically confines water in its fibrillar structure. Our data shows, for the first time, that this structurally confined water can be exploited as special reaction medium. In comparison to a dry acetylation, surface-confined water elevated the reaction efficiency and increased the reaction rate of the cellulose surface acetylation with *N*-acetylimidazole. Considering, that this type of confined water is intrinsically present in a range of biopolymers, our findings have far-reaching impact and can be translated to other hierarchically structured biopolymers.

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