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Organic Synthesis on A Green Scaffold: The Role of Modified and Native Nanocellulose

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ABSTRACT

Nanocellulose (NC), a renewable, bio-derived nanomaterial obtained from cellulose, has gained significant attention as a green scaffold in the advancement of sustainable materials and catalytic systems. Due to its high surface area, inherent biodegradability, mechanical strength, and modifiable surface functionalities, nanocellulose serves as an effective platform across diverse applications such as packaging, biomedicine, filtration, and notably, organic synthesis. In the context of green chemistry, nanocellulose supports the development of eco-friendly, heterogeneous catalytic systems by enabling surface functionalization for targeted chemical transformations. Classified into bacterial nanocellulose (BNC), cellulose nanocrystals (CNCs), and cellulose nanofibers (CNFs), each form offers unique structural features that contribute to their reactivity and versatility in synthetic applications. This review highlights recent advancements in the use of both native and chemically modified nanocellulose in organic synthesis, emphasizing its role as a sustainable, recyclable, and efficient support for catalytic processes aimed at greener synthetic methodologies.

Keywords: Nanocellulose, Green scaffold, Supported nanocatalyst, Bacterial nanocellulose (BNC), Cellulose nanocrystals (CNC), Cellulose nanofibers (CNF), Sustainable synthesis, Organic transformations.

INTRODUCTION

Cellulose, the most abundant biopolymer on Earth, consists of repeating D-anhydroglucopyranose monomers linked via β-(1$\rightarrow$4) glycosidic bonds[1]. Upon acid hydrolysis, these glycosidic bonds are selectively cleaved, yielding nanoscale crystalline domains collectively referred to as nanocellulose (NC)[2]. Nanocellulose is frequently utilized in aqueous-phase reactions and is typically stabilized as colloidal dispersions or hydrogels in water at concentrations below 5%[3]. Its surface is rich in hydroxyl groups, which serve as reactive sites for the formation of nanocomposites and hybrid materials, including conjugates with metal nanoparticles (NPs), metal oxide nanowires, and metal–organic frameworks (MOFs), all of which have demonstrated significant potential in organic synthesis as catalysts, catalyst supports, or reaction media.

Nanocelluloses (NCs) have rapidly gained attention worldwide due to their vast

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potential in sustainable technologies and green chemistry[4]. Their surface chemistry can be tuned through various chemical modifications such as acetylation, benzoylation, or alkylation to enhance hydrophobicity, or sulfonation and oxidation to increase hydrophilicity[5]. These modifications aim to improve nanocellulose's stability and performance in catalytic applications, especially when used as a heterogeneous support in organic transformations.

Nanocellulose is primarily classified into three nanoforms based on their morphology, crystallinity, and synthesis methods: bacterial nanocellulose (BNC)[6], cellulose nanocrystals (CNCs)[7], and cellulose nanofibers (CNFs)[8]. These materials can be synthesized using a variety of mechanical, chemical, and biological methods[9]. Common features of these nanoforms include a high surface area, excellent mechanical strength, tunable porosity, and superior sustainability due to biodegradability and broad availability.

CNCs are typically produced via acid hydrolysis, a top-down method that removes the amorphous regions of cellulose to yield highly crystalline rod-like particles. Alternatively, enzymatic hydrolysis offers a milder approach to generate nanoscale cellulose with less structural degradation. In contrast, BNC is synthesized via a bottom-up biosynthetic pathway, often using strains of Gluconacetobacter, resulting in a highly pure and crystalline material. The surface of nanocellulose contains functional groups such as $–OSO_3^-$, $–PO_4^{3-}$, $–COO^-$, and hydroxyls, which facilitate electrostatic interaction with metal cations. This allows the *in situ* generation of hybrid catalytic systems such as cell–metal NPs, cell–MOFs, and cell–TiO_2 nanowires[10].

Organic Synthesis Mediated by Nanocellulose-Based Materials

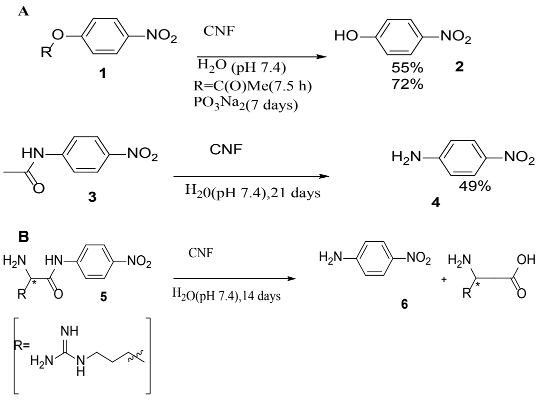
Nanocellulose has been explored in various roles in organic synthesis-including as a solid catalyst, catalyst support, or reaction medium-due to its surface functionalization capabilities, stability, and environmental benignity. While earlier studies often focused on material development and characterization, recent investigations have emphasized its applications in facilitating organic reactions.

This section explores the catalytic behavior of nanocellulose-based materials in organic synthesis. For clarity, the discussion is divided into three parts:

1. Reactions catalyzed by non-functionalized (native) nanocellulose
2. Transformations using metal-modified nanocellulose
3. Reactions involving chemically modified nanocellulose derivatives[11,12].

Chemical Behavior of Non-Functionalized Nanocellulose

In many preparation protocols, the final step in nanocellulose isolation includes an acidic wash, which imparts surface-bound acidic sites. These sites enable native nanocellulose to function as a mild acid catalyst, particularly in hydrolysis reactions. Serizawa and colleagues demonstrated the utility of unmodified cellulose nanofibers (CNFs) as a catalyst for the hydrolysis of esters, monophosphonates, and amides under neutral aqueous conditions (Scheme 1(A))[13]. Remarkably, ester hydrolysis proceeded 8.5 times faster in the presence of CNF compared to control reactions, despite long reaction times. The same group further extended this concept by using a synthetic nanocellulose, not derived from natural sources, to catalyze ester hydrolysis, highlighting the catalytic potential of engineered nanocellulose surfaces. Moreover, the intrinsic chiral environment of CNF was harnessed in aqueous media to selectively hydrolyze protected amino acid derivatives (Scheme 1(B))[14]. This underscores the ability of unmodified nanocellulose to act not only as a catalyst but also as a chiral scaffold in stereoselective transformations.

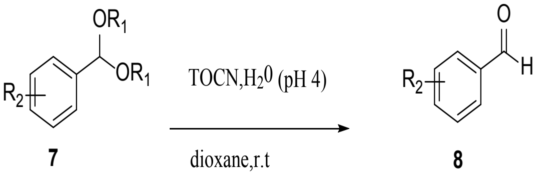


Scheme 1. Neutral Hydrolysis Facilitated by CNF
(A) CNF-Supported Hydrolysis Pathways for Esters, Monophosphates, and Amides.[13]
(B) Hydrolysis of Protected Amino Acids Under Mild Conditions[14]

Catalytic Roles of Organically Functionalized Cellulose Nanofibers

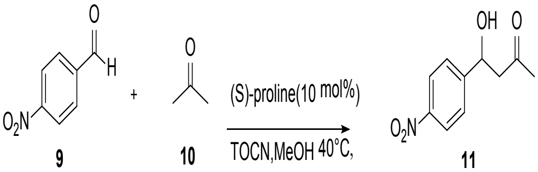
Chemically functionalized cellulose nanofibers (CNFs) have garnered significant attention for their ability to serve as efficient heterogeneous organocatalysts in diverse organic transformations. The incorporation of organic moieties onto the CNF backbone not only enhances catalytic performance but also improves recyclability and environmental compatibility. Several notable advancements in this field have been reported in recent years.

In 2018, two key applications exemplified the catalytic potential of TEMPO-oxidized cellulose nanofibers (TOCNs). In the first example, TOCNs acted as effective organocatalysts in the hydrolysis of acetals (Compound 7) to the corresponding aldehydes (Compound 8), achieving high quantum yields under mild aqueous conditions (Scheme 2)[15].



Scheme 2. TOCN-mediated hydrolysis of acetal functional group

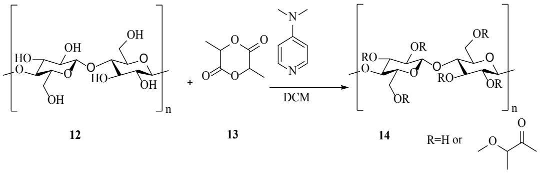
Further developments in 2020 expanded the application spectrum of organically functionalized CNFs. One such example involved surface-initiated ring-opening polymerization (SI-ROP) of rac-lactide, catalyzed by CNFs functionalized with N,N-dimethylaminopyridine (DMAP) in dichloromethane. The approach enabled effective control over polymer growth, demonstrating the utility of CNFs as polymerization initiators (Scheme 4)[17].



Scheme 3. Aldol coupling catalyzed by TOCN-(S)-proline between acetone and 4-Nitrobenzaldehyde

In a parallel study, CNFs were modified with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to catalyze the aqueous-phase synthesis of tetraketones via the coupling of diketones with aldehydes at room temperature. This metal-free, water-compatible catalytic system afforded yields up to 96% and displayed impressive reusability without significant loss of activity[18].

These examples collectively underscore the versatility of organically decorated CNFs in mediating key carbon–carbon bond-forming reactions, nucleophilic additions, and polymerizations. Their biocompatibility, ease of modification, and capacity for catalyst recovery present compelling advantages in the context of green and sustainable organic synthesis.



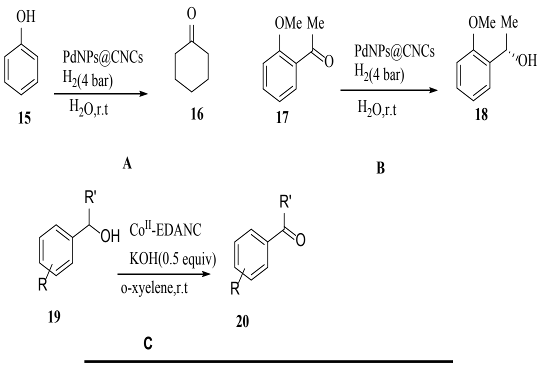
Scheme 4. DMAP-Promoted Surface-Initiated ROP of rac-Lactide

Chemical Reactions Involving Metal-Modified Nanocellulose

The incorporation of metal nanoparticles (MNPs) onto nanocellulose frameworks significantly expands their catalytic utility in organic synthesis. Among the nanocellulose types, cellulose nanocrystals (CNCs) are particularly well-suited for metal modification due to their high crystallinity, abundant surface hydroxyl groups, and defined nanoscale morphology.

A notable example includes the immobilization of palladium nanoparticles on CNCs to form PdNPs@CNCs, which demonstrated efficient catalytic performance in the hydrogenation of phenol to cyclohexanone under mild conditions (Scheme 5(a))[19]. The system showed remarkable activity and reusability, whereas unmodified CNCs and unsupported palladium failed to yield any product. Furthermore, the same PdNPs@CNCs catalyst facilitated enantioselective hydrogenation of benzophenone derivatives, delivering moderate yields and enantiomeric excesses (Scheme 5(b))[20].

Another noteworthy advancement involves the covalent attachment of a Co(II)-ethylenediamine complex to the CNC surface, producing Co(II)-EDANC. This functionalized catalyst exhibited excellent performance in the aerobic oxidation of alcohols to aldehydes and ketones at room temperature, offering yields up to 92% (Scheme 5(c))[21].



Entry	Catalyst	Yield
A	5%PdNPs@C(4 mg)	38%
	CNCs (40 mg)	0
	0.5% PdNPs@C(40 mg)	90
B	5%PdNPs@C(0.2 mg)	40
	CNCs (40 mg)	0
	0.5% PdNPs@C(40 mg)	68
C	CoII-EDANC	72
	CoII-cellulose	0
	CoII-diamine	92

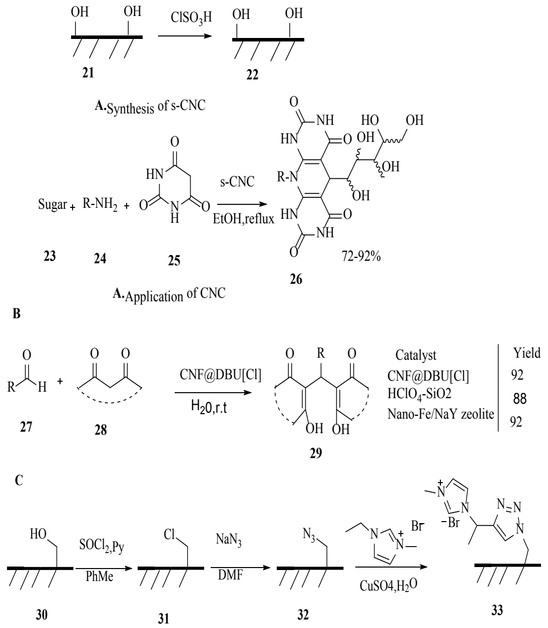
Scheme 5. Metal NP-Catalyzed Reactions on Cellulose-Based Materials
(A). Catalytic Hydrogenation of Phenol[19]
(B). Stereoselective Reduction[20]
(C). Oxidation of alcohols[21]

Nanocellulose Modified Through Alternative Routes

Beyond metal conjugation, nanocellulose can be chemically modified via alternative synthetic routes to introduce novel functionalities that facilitate diverse organic transformations. In one approach, CNCs were functionalized with sulfonic acid groups through reaction with chlorosulfonic acid, yielding sulfated CNC (s-CNC). These materials showed potential as multifunctional catalysts for acid-mediated transformations (Scheme 6(a))[22].

In another example, CNFs were functionalized with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form CNF@DBU[Cl], which catalyzed the condensation of 1,3-dicarbonyl compounds with aldehydes to afford tetraketones (Scheme 6(b))[23]. The catalyst exhibited high activity, delivering up to 92% yields with excellent substrate scope, and reactions were completed in just a few minutes under mild aqueous conditions.

More sophisticated chemical modifications enabled the creation of ion-exchangeable CNCs. For instance, hydroxyl groups on CNCs were first substituted with chlorides, which were then subjected to click reactions to introduce triazole and imidazolium-based ionic functionalities. These ion-exchangeable CNCs open avenues for phase-transfer and ionic liquid-supported catalysis (Scheme 6(c))[24].



Scheme 6. Modified nanocellulose as a functional material in synthetic reactions
(A). Fabrication of s-CNC for multicomponent functional applications[22]
(B). Synthetic Route to Tetraketone Compounds[23]
(C). Development of ion exchange CNC catalyst[24]

CONCLUSION

Nanocellulose has emerged as a powerful and sustainable scaffold in modern organic synthesis, offering a combination of environmental compatibility, chemical tunability, and functional versatility. Various forms of chemically modified and unmodified nanocellulose-including cellulose nanocrystals (CNCs), nanofibers (CNFs), and bacterial nanocellulose (BNC)-have demonstrated remarkable potential as catalysts, catalyst supports, and reaction media in a wide range of transformations. CNCs, in particular, serve as excellent platforms for the growth and stabilization of metal nanoparticles (NPs) and for the integration of organocatalytic moieties, enabling highly selective and efficient transformations. Importantly, the catalytic activity of these systems cannot be solely attributed to the embedded nanoparticles or functional groups; rather, the synergistic interactions between these components and the polysaccharide backbone play a critical role in defining the overall reactivity. These findings highlight that nanocellulose is not merely a passive support but can participate actively in catalytic processes.

The inherent biodegradability, abundance, and low toxicity of nanocellulose, along with its structural modifiability, reusability, and economic feasibility, make it a compelling candidate for the development of next-generation green catalytic systems. Continued exploration of structure–activity relationships and hybrid materials will further expand its applicability in sustainable and scalable chemical processes.

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Conflict of interest

The author declare that we have no conflict of interest.

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