# SYNERGISTIC REINFORCEMENT: HARNESSING NANOCELLULOSE FOR ROBUST DOUBLE NETWORK HYDROGELS

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*In memoriam Acad. Bogdan C. Simionescu*
*(1948-2024)*

Double-network (DN) hydrogels combine two interpenetrating polymer networks with contrasting roles: a brittle, rigid primary network that dissipates energy through sacrificial bond breakage, and a flexible secondary network that maintains integrity. This architecture imparts exceptional toughness, stretchability, and crack resistance, making DN hydrogels valuable for biomedical, soft robotics, and energy-storage applications. Incorporating natural polymers, particularly nanostructured biopolymers like nanocellulose, enhances biocompatibility, sustainability, and tunability. This review outlines DN hydrogel design principles and nanocellulose structures, focusing on their role in polyacrylamide (PAM) and polyvinyl alcohol (PVA) matrices. Emphasis is placed on how cellulose nanofibers (CNF) improve mechanical strength, stability, and dynamic response through entanglement, hydrogen bonding, and nanoconfinement. The review concludes with challenges and future opportunities for nanocellulose-based DN hydrogels in multifunctional and sustainable material design.

***Keywords***: cellulose, nanocellulose, double network, hydrogel, nanofibers, flexible electronics

## INTRODUCTION

The significant amount of water of hydrogels, which are networks of water-swollen polymers, grants them special qualities including biocompatibility, sensitivity to different stimuli, extremely low surface friction, and environmental friendliness.[1–7] Hydrogels are regarded as cutting-edge pharmaceutical, industrial, and medicinal materials, due to their intrinsic characteristics. Hydrogels have revolutionized a number of technical fields during the last few decades. They are used in biomedicine as matrices for regulated drug delivery, scaffolds for tissue engineering, and elements in regenerative treatments and wound healing. Superabsorbent hydrogels are essential for wastewater treatment, agriculture, and personal hygiene goods in industrial settings. Furthermore, the development of stimulus-responsive (or "smart") hydrogels has led to new developments in flexible electronics, biosensing, and soft robotics, where adaptive and programmable functions are made possible by the hydrogels' dynamic reaction to external stimuli.

When combined with developments in polymer design and crosslinking techniques, hydrogels' capacity to replicate biological settings propels innovation and broadens their use as enabling materials in cutting-edge biomedical and technology applications. However, a significant advantage might occasionally become a disadvantage, as is frequently the case. Specifically, the main drawback of hydrogels is their high water content, which weakens them and restricts their use. The creation of double-network (DN) gels, the toughest and strongest hydrogels with resilience comparable to industrial rubber and a high water content (about 90% by weight), is the most noteworthy of the several methods used to reinforce hydrogels. Improved DN gels have outstanding toughness (tearing energy: 100–4500 J/m$^2$), strength (tensile fracture stress: 1–10 MPa, strain 100–3000%), and hardness (elastic modulus:

0.1–1.0 MPa).[8,9] Because of these exceptional qualities, researchers have focused a lot of effort on DN hydrogels, both to optimize and improve their structure and to apply them in other fields.[10–13]

For large-scale applications, various types of resistant DN gels must be synthesized from different chemical species. However, the materials that can be used to create the rigid network 1 of these "resistant" DN gels are limited to polyelectrolyte gels. Conventional DN gels are synthesized through a two-step network formation process. First, a gel is synthesized and immersed in a solution of the second monomer. Then, the second gel polymerizes within the first gel. When a polyelectrolyte is used for the first gel, it swells considerably in the monomer solution due to high osmotic pressure. This results in a highly expanded, rigid network 1 in the final product. The network 2 content of the final DN gel is much higher than that of network 1. In contrast, when neutral gels with a weaker swelling capacity in the second monomer solution are used to create network 1, neither the rigidity of network 1 nor the high network 2 content is obtained, resulting in a DN gel with very low strength. Synthetic polymers were the first to dominate double cross-linked networks because of their perfect control over network topology, chemical stability, and tunable mechanics. However, growing environmental concerns and the push for biocompatibility have prompted a shift toward natural polymers, such as polysaccharides, in the design of double cross-linked networks.

The inherent biodegradability, biocompatibility, renewable source, and varied chemical functionalities, such as hydroxyl, carboxyl, and amino groups, make polysaccharides very appealing for hydrogel design. A key component for the creation of DN hydrogels is cellulose (Fig. 1), which comes in a variety of forms, such as bulk cellulose, chemical derivatives (such as carboxymethyl cellulose and hydroxyethyl cellulose), nanofibrils, nanocrystals, and bacterial cellulose. Figure 1 illustrates the hierarchical structure of lignocellulosic biomass, from plant stems to the molecular level. Figure 1 (a) shows the main components of the plant cell wall: cellulose, hemicelluloses, and lignin, organized into a complex three-dimensional network; while (b) highlights the structural arrangement from fiber bundles to elementary fibrils, emphasizing the crystalline and amorphous regions of cellulose and its association with hemicelluloses and lignin.

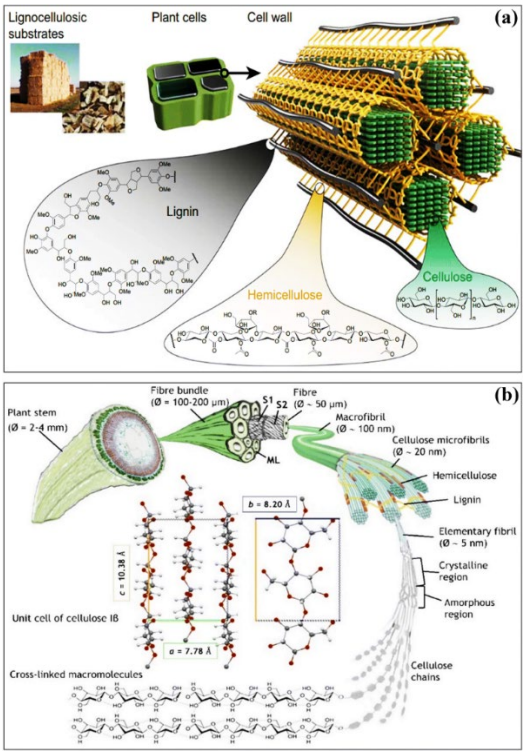


Figure 1: Hierarchical organization of lignocellulosic biomass, showing cellulose microfibrils embedded in a hemicellulose–lignin matrix, forming a multiscale network from fibers to nanoscale fibrils[14]

To attain remarkable mechanical performance, these hydrogels can be made wholly of cellulose or in combination with synthetic polymers, utilizing the complementing capabilities of each network. The many hydroxyl groups that cellulose has along its backbone give it versatility by enabling a variety of crosslinking techniques. Permanent three-dimensional networks can be created via covalent chemical crosslinking, while dynamic or reversible networks that can release energy under stress are made possible by physical entanglement, hydrogen bonds, and ionic interactions. The mechanical strength, toughness, elasticity, and fatigue resistance of the hydrogel are greatly increased by the addition of cellulose nanostructures, such as cellulose nanocrystals (CNCs) or nanofibrils (CNFs), which add high surface area, strong hydrogen-bonding potential, and nanoscale reinforcement. Beyond mechanical resilience, cellulose-based DN hydrogels have customizable physicochemical features, including swelling behavior, porosity, and reactivity to pH, temperature, or ionic strength, making them appropriate for specific applications. For tissue engineering and regenerative medicine, their structural resemblance to extracellular matrices and biocompatibility promote cell adhesion, proliferation, and differentiation. Additionally, cellulose nanostructures' hydroxyl-rich surfaces enable functionalization with medicines, bioactive compounds, or nanoparticles, increasing their potential for flexible electronics, biosensing, and controlled drug administration. Cellulose-based DN hydrogels enable the development of soft sensors, actuators, and bioelectronics by combining mechanical resilience with stimuli-responsive conductivity or optical characteristics in flexible and wearable devices.

Overall, cellulose-based DN hydrogels are a very promising platform for advanced biomaterials and soft functional materials, bridging the gap between mechanical performance and multifunctional design, thanks to their renewable origin, chemical versatility, nanoscale reinforcement, and tunable functionality. Therefore, this review aims to summarize the fundamentals of preparing DN hydrogels and highlight the functional and morphological versatility of cellulose at the nanoscale. Then, it will bring these two scientific fields together by demonstrating how the morphological and functional diversity of nanocellulose contributes to preparing new, advanced, and specialized types of DN hydrogels. Next, the applications of these DN nanocellulose-based hydrogels in flexible hydrogels for current technical fields are presented. Finally, the review concludes with a series of conclusions and future research directions that should be explored to further advance the field.

## NETWORK STRUCTURE OF DN HYDROGELS

Hydrogels are networks of crosslinked polymers that are three-dimensional and have the ability to hold a lot of water while yet being structurally sound. They are appealing materials in a variety of industries, from soft robotics and flexible electronics to tissue engineering and delivery of drugs, thanks to their high water content, biocompatibility, and adjustable physicochemical characteristics. However, typical hydrogels generally suffer from innate tensile weakness, notably low toughness and poor resistance to deformation, which restricts their practical usage in demanding applications. The idea of DN hydrogels has surfaced as a potent way to overcome these constraints and balance a high-water content with remarkable mechanical strength. Two interpenetrating polymer networks with different structures and functions: a brittle, tightly crosslinked first network and a ductile, loosely crosslinked second network, are commonly used to create DN hydrogels (Fig. 2). The two of these components work together to provide distinctive mechanical behavior. While the second network retains its flexibility and avoids a complete breakdown, the first network splits sacrificially under stress, releasing energy. DN hydrogels may attain toughness levels that are many orders of magnitude greater than those of traditional single-network (SN) hydrogels, thanks to their architectural design.

The first DN hydrogel was developed by Gong and co-workers in 2003.[15] This DN was created by using PAMPS/PAM, where poly(2-acrylamido-2-methylpropanesulfonic) acid (PAMPS) was the first layer and polyacrylamide (PAM) the second layer. Since then, researchers around the world have been trying to find new recipes for manufacturing DN hydrogels, which are perhaps the toughest soft-wet materials.

Since their introduction, DN hydrogels have generated a lot of interest due to their performance and versatility, beginning with this intriguing finding. To customize the ratio of stiffness, toughness, and functionality, researchers have

investigated a wide range of polymer combinations, crosslinking techniques, and preparation approaches. DN hydrogels are promising candidates for load-bearing biomedical applications like cartilage replacement, as well as in cutting-edge fields like soft actuators, sensors, and energy storage devices, as they can demonstrate enhanced resilience, fatigue resistance, and self-recovery, in addition to mechanical reinforcement. Since their introduction, DN hydrogels have generated a lot of interest due to their performance and versatility, beginning with this intriguing finding. To customize the ratio of stiffness, toughness, and functionality, researchers have investigated a wide range of polymer combinations, crosslinking techniques, and preparation approaches.

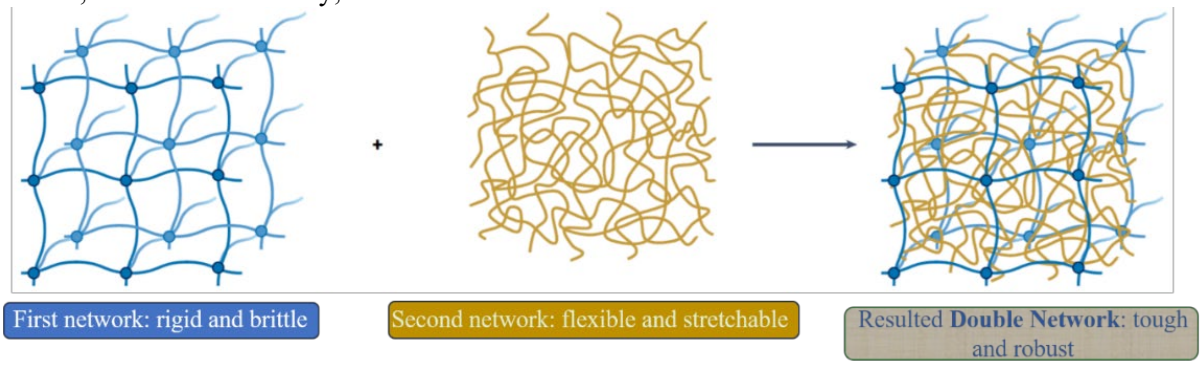


Figure 2: Schematic illustration of the formation of a double network hydrogel from two component networks[16]

DN hydrogels are promising candidates for load-bearing biomedical applications like cartilage replacement, as well as in cutting-edge fields like soft actuators, sensors, and energy storage devices, as they can demonstrate enhanced resilience, fatigue resistance, and self-recovery, in addition to mechanical reinforcement. Following their studies, the authors of the first DN hydrogel developed a set of necessary conditions for successfully obtaining a DN hydrogel. These preliminary conditions include the following:[17] (1) the first polymer network should consist of a rigid polyelectrolyte with an asymmetric, brittle network, and the second network should consist of a soft, tough neutral polymer; (2) the molar concentration of the neutral monomer forming the second network must be in large excess (about 20–30 times higher) than the concentration of the first polyelectrolyte monomer forming the first network; (3) the first network should be highly cross-linked at a low concentration, and the second network should be weakly cross-linked (possibly uncross-linked) at a relatively high concentration. Applying these conditions has led to considerable improvements in the methods and properties of DN hydrogels. Depending on the method by which the crosslinking of the two networks is ensured, DN hydrogels include fully chemically crosslinked DN hydrogels, hybrid, in which crosslinking occurs both physically and chemically, and fully physically crosslinked DN hydrogels.

**Fully chemically crosslinked DN hydrogels**

Fully chemically crosslinked DN hydrogels were initially synthesized mainly by two-step polymerization and molecular stent methods.[18] In this approach, the first network made of a robust polyelectrolyte permanently broke into pieces to release the energy when the DN hydrogel was stretched. These pieces improved the second network's resistance to crack propagation by acting as sacrificial bonds.[17] In an attempt to develop a material that closely mimics native cartilage and that can act as a synthetic replacement strategy and avoid the disadvantages of current autograft treatments, the authors designed a fully chemically cross-linked DN hydrogel, composed of asymmetrically cross-linked networks of PAMPS and N-isopropylacrylamide (NIPAAm) copolymerized with acrylamide (AAm) [P-(NIPAAm-co-AAm)].[19] Notably, DN hydrogel's cartilage-like elastic modulus increased by around 1 MPa when compared to SN hydrogel, and its compressive strength increased by about 50 times to reach about 25 MPa. With all these special remarks, we must point out that the high cross-link density results in irreversible network damage and a significant drop in mechanical strength during stretching, even though fully chemically cross-

linked DN hydrogels sacrifice covalent bonds of the initial rigid polymer network to preserve good mechanical strength under deformation.[20] Furthermore, the hydrogels have virtually no self-healing ability due to their frequent lack of fatigue resistance and extreme softening,[21] which severely limits their applicability, particularly in biological tissue engineering.

**Hybrid physically/chemically crosslinked DN hydrogels**

The high bonding strength of chemical bonds creates chemical DN hydrogels with high structural strength. However, the breakage of these bonds is irreversible and adversely affects the hydrogel's mechanical properties. Therefore, the mechanical properties of chemically crosslinked DN hydrogels decrease significantly after tensile testing. Conversely, damage to noncovalent interactions (*e.g.*, hydrogen bonds, ion-ligand interactions, hydrophobic interactions, and electrostatic interactions) is reversible under external forces. Thus, introducing noncovalent interactions into DN hydrogels can improve their fatigue resistance. Additionally, noncovalent units can be responsive to stimuli, enabling the creation of multifunctional hydrogels (including self-healing and shape-memory hydrogels), which greatly expands their range of applications. Ionic and coordination interactions, as well as van der Waals forces, are examples of dynamic and reversible bonds that are required to address the deficiencies noted in the case of chemically crosslinked hydrogels. Physical cross-linking points within the network can be established by crystallization, hydrogen bonding, hydrophobic interactions and many other interactions. DN gels are classified as hybrid physically/chemically cross-linked DN hydrogels when one network is physical and the other is a chemical network. In recent years, numerous hybrid DN hydrogels have been reported.[22–26] Using the physical cross-linking method, they can be broadly classified into three groups: ionic networks, hydrogen bonding networks, and hydrophobic association networks. Physical cross-linking enhances the DN hydrogels' toughness, ductility, and self-healing properties by acting on reversible sacrificial bonds. Examples of such networks include acidic polysaccharides, such as sodium alginate, carrageenan, and carboxymethyl cellulose, which coordinate with metal ions. When a Ca-Alg/PAAm DN hydrogel is created, the ionic bonds unzip and dissipate significant quantities of energy during the stretching process. In this process, the ionic bonds act as “sacrificial bonds”. Unlike fully chemically cross-linked DN hydrogels, which break “sacrificial bonds”, hybrid DN hydrogels exhibit a continual energy dissipation process.

**Fully physically crosslinked DN hydrogels**

Due to irreversible bond breaking in networks and the high likelihood of using hazardous chemical cross-linkers, fully chemically crosslinked DN hydrogels typically have poor self-healing characteristics and low biocompatibility, as we have already mentioned.[27] Although hybrid DN hydrogels are robust and mechanically strong, their sluggish diffusion of polymer chains typically prevents them from self-healing. Furthermore, the design and synthesis of next-generation physical hydrogels were investigated in order to overcome the low fatigue life and poor self-recovery of DN hydrogels. This is because irreversible damage cannot be completely controlled due to the unavoidable covalent bond breakage in the chemically cross-linked network.[28] The network's physical linkages distort under extreme loading when DN hydrogels are stretched, breaking first to release energy. The physical linkages allow the hydrogels to repair and rejoin when they are unloaded. The creation of completely physically cross-linked, non-toxic DN hydrogels is growing in popularity. Although fully physically cross-linked DN hydrogels exhibit good self-healing ability, require no additional chemical cross-linking agents, and have straightforward preparation procedures, their overall mechanical strength is still inferior to that of fully chemically cross-linked DN hydrogels or hybrid DN hydrogels. For this reason, it is now crucial to improve the physical properties of fully physically crosslinked DN hydrogels in order to insure the remarkable self-healing capacity of such hydrogels.

All things considered, DN hydrogels mark a paradigm change in hydrogel design by emphasizing the value of sacrificial connections and hierarchical organization in reaching enhanced material performance. The selection of polymer networks, level of crosslinking, interplay between the two networks, and possible incorporation with functional elements like nanoparticles, conductive additives, or bioactive compounds are general factors for their creation. Together, these elements influence the material’s mechanical strength, as well as its responsiveness, biocompatibility, and appropriateness for particular uses.

## NANOCELLULOSE AS A FUNCTIONAL COMPONENT

Nanocellulose as a functional component is a renewable and biodegradable nanomaterial, being eco-friendly, non-toxic, and biocompatible. Owing to its stable physical and chemical characteristics, extensive specific surface area, and high mechanical strength and crystallinity, nanocellulose has been a hot topic of investigation in nanomaterials.[29] Nanocellulose is defined by its nanoscale size, elevated aspect ratio, and remarkable mechanical strength. It is classified into three primary types: CNCs, CNFs, and bacterial nanocellulose (BNC) – Figure 3. CNCs are inflexible, rod-shaped nanoparticles measuring in the nanometer range. Conversely, CNFs are elongated, pliable fibrils with dimensions ranging from tens to hundreds of nanometers. BNC is synthesized by certain bacteria and constitutes a distinct, very pure variant of nanocellulose. Each category presents unique benefits and uses across multiple applications.[30]

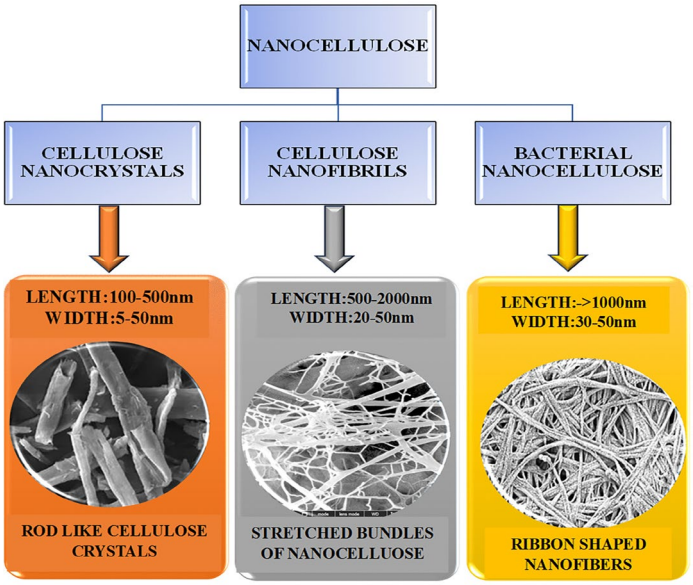


Figure 3: Classification of nanocellulose[29]

Due to its distinct mechanical, morphological, and biochemical properties, nanocellulose is a particularly valuable functional component. Mechanical resistance is the main characteristic of nanocellulosic materials. Li *et al.*,[31] in a recent study, reported that by incorporating cellulose nanofibers, especially chemically functionalized (DA-CNF), there is a significant increase in the compressive strength and stability of hydrogels, with both hydrogen and covalent bonds being formed. Similarly, Arsuffi *et al.*[32] demonstrated that by integrating CNC and CNF into a DN, materials with superior mechanical properties are obtained due to the synergy between the interpenetrating polymer networks and nanocellulose. A high aspect ratio and a significant specific surface area provide nanocellulose with an outstanding capability to interact with polymer matrices. Kumar *et al.*[29] highlighted how these characteristics promote effective stress transfer within composites. In addition, other researchers[33] proved that the morphological variations between fibrous and crystalline nanocellulose lead to different interfacial behaviors, which have direct consequences for mechanical performance. Another advantage of nanocellulose is its biocompatibility, being suitable for biomedical applications, including tissue engineering and drug delivery systems.[14,34] To optimize the efficiency of nanocellulose, a key strategy is chemical functionalization.[31] The most efficient method of chemical functionalization is oxidation.[35] Through the oxidation process, carboxyl, aldehyde, or ketone groups can be introduced, facilitating the ability to interact with polymeric substrates, resulting in multi-responsive materials with high mechanical strength.[36,37] Another essential criterion that nanocellulose must meet is to confer dimensional stability to materials against physical factors, such as freezing, temperature variations, *etc.*[14,38]

Nanocellulose has proven to be an effective reinforcing phase in double-network hydrogels, simultaneously improving toughness and enabling additional functionality. Integration of bacterial nanocellulose into three-dimensional DN architectures imparts self-healing behavior, while enhancing mechanical integrity.[39] Dialdehyde-modified cellulose nanofibrils (DA-CNF) serve as rigid, covalently crosslinkable components that, when combined with poly(acrylamide) and AMPS networks, markedly increase compressive strength and chemical resilience.[31] Moreover, the incorporation of CNC and CNF into responsive PNIPAM/PAA–alginate DN systems yields programmable, multi-stimuli responsiveness, in addition to structural reinforcement.[32] Hierarchical designs that combine nanocellulose fibrils with graphene oxide and interpenetrating polyacrylamide–alginate networks further enhance dimensional stability and reliable performance in sensing applications.[38] All these studies position nanocellulose as a multifunctional element in DN hydrogel design, bridging rigid and ductile phases to produce robust, adaptable materials.

**Types and characteristics of nanocellulose**

As mentioned in the previous chapter, nanocellulose is characterized by its high specific surface area, intrinsic biodegradability, and remarkable mechanical performance. Being a renewable material with versatile surface chemistry, it has gained considerable attention in advanced materials science, particularly in the design of hydrogel systems for biomedical and environmental applications.[40–43] Three main classes are generally distinguished: CNCs, CNFs, and BNC, which are schematically represented in Figure 4, where the structural hierarchy and dimensional scale of cellulose and its nanostructured forms are illustrated. Starting from the plant cell wall, cellulose fibrils are organized into microfibrils (MFC), which can be further disintegrated into CNF and CNC, containing both crystalline and amorphous domains. Figure 4 also depicts the biosynthesis of BNC, showing the polymerization of β(1,4)-glucan chains and their assembly into microfibrils, ribbons, and pellicles. This schematic highlights the multiscale nature and structural diversity of nanocellulose originating from both plant and microbial sources. While CNFs are long, entangled fibrils, comprising crystalline and amorphous regions, and BNC is biosynthesized as a highly pure fibrillar network, CNCs are rigid, rod-like nanoparticles obtained through the selective removal of amorphous cellulose domains.[45]

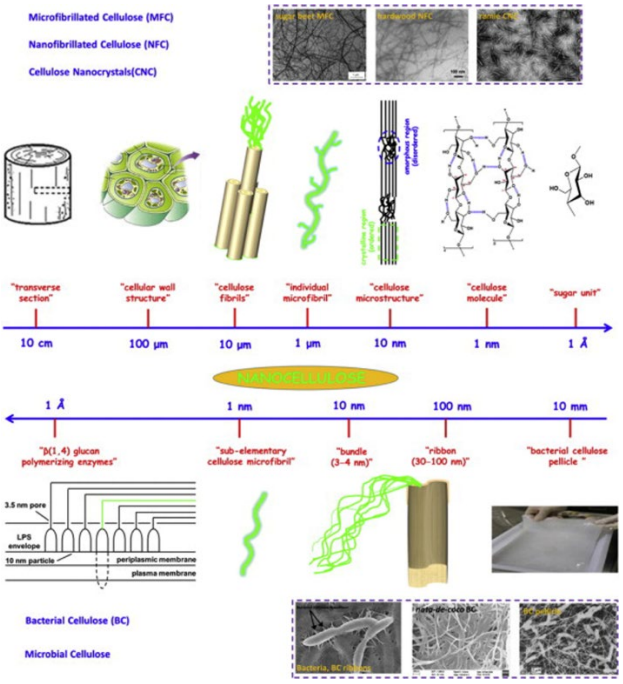


Figure 4: Structural hierarchy and dimensional scale of cellulose and nanocellulose materials – the transition from plant-derived cellulose fibrils to MFC, CNF, and CNC; the lower panel shows BNC formation, from enzymatic polymerization to fibril assembly and pellicle formation[44]

The ability of nanocellulose to interact via hydrogen bonding, electrostatic forces, or covalent linkages makes it particularly relevant for the design of DN hydrogels, which require synergistic combinations of rigid and flexible components to achieve high toughness and resilience.[17,40,41]

***Cellulose nanocrystals (CNCs)***

CNCs are nanoscale rod-like particles obtained by selectively removing the amorphous regions of cellulose, thereby preserving the highly ordered crystalline domains. They are typically produced via acid hydrolysis, most commonly with sulfuric, hydrochloric, or phosphoric acids. This treatment disrupts the less ordered regions of the polymer chain, leaving behind rigid crystalline fragments. Sulfuric acid introduces surface sulfate ester groups, which increase colloidal stability in aqueous suspensions, but simultaneously reduce the thermal resistance of the material.[46,47] By comparison, hydrochloric acid yields CNCs with fewer surface charges, offering better thermal stability, but poorer dispersion behavior.[48] Although less frequently applied, enzymatic hydrolysis provides a milder and environmentally friendlier route, yielding CNCs with high biocompatibility and without residual acidic functionalities, albeit with lower efficiency and longer processing times.[49]

Structurally, CNCs are characterized by diameters in the range of 5–20 nm and lengths typically between 100 and 500 nm, depending on the cellulose source and hydrolysis conditions.[50] Their high crystallinity (60–90%) translates into remarkable stiffness, with an axial elastic modulus on the order of 100-150 GPa, comparable to high-strength engineering materials.[51] The surface of CNCs is dominated by hydroxyl groups, which provide opportunities for chemical modification, as well as by additional functional groups introduced during processing. Such versatility makes CNCs not only stable in colloidal systems, but also highly adaptable to different polymer matrices.[44] In hydrogel design, CNCs play a dual role. On the one hand, their rigid morphology and high aspect ratio provide mechanical reinforcement, enhancing the stiffness, elasticity, and toughness of the gel network. On the other hand, their reactive surface functionalities allow them to act as crosslinking nodes within the polymer matrix, either through hydrogen bonding or via covalent and ionic interactions when chemically modified (*e.g.*, TEMPO oxidation or carboxylation).[52] CNC suspensions also exhibit shear-thinning and gel-like behavior, a rheological feature particularly useful for injectable hydrogel formulations.[53] In DN hydrogels, CNCs often serve as reinforcing agents for the brittle first network, enhancing fracture resistance and dissipating stress under deformation. Importantly, their renewable origin, biocompatibility, and degradability make CNC-based hydrogels highly attractive for applications ranging from wound dressings and drug delivery to tissue engineering and regenerative medicine.[54,55]

***Cellulose nanofibers (CNF)***

CNFs, also known as nanofibrillated cellulose, are long and flexible fibrils with diameters typically below 100 nm and lengths extending into the micrometer range. They contain both crystalline and amorphous regions and are typically isolated through mechanical fibrillation processes, such as homogenization, grinding, or ultrasonication, often assisted by enzymatic or oxidative pretreatments to reduce energy consumption

In contrast to CNCs, CNFs retain both crystalline and amorphous regions, which impart a unique balance of rigidity and flexibility.[50] CNFs are generally obtained by mechanical fibrillation, using high-pressure homogenization, microfluidization, grinding, or ultrasonication. Because these methods are energy-intensive, various pretreatments (*e.g.*, enzymatic hydrolysis, TEMPO-mediated oxidation, or carboxymethylation) are often employed to weaken interfibrillar hydrogen bonds and facilitate fibrillation.[30,56,57] The characteristic of CNFs lies in their ability to form entangled, percolating networks through hydrogen bonding and physical entanglement. This property enables them to generate highly hydrated, mechanically stable structures, even at low solid content.[58] Their fibrillar morphology provides flexibility and toughness, while their large surface area and abundance of hydroxyl groups enable strong interactions with polymer matrices and facile chemical modification. In hydrogel systems, CNFs serve as structural scaffolds, reinforcing the polymer matrix and significantly improving elasticity, resilience, and water retention. CNF-based hydrogels display shear-thinning rheology, making them suitable for injectable and 3D-printing applications.[40] Moreover, in DN hydrogels, CNFs can act as the ductile, energy-dissipating component of the second network,

complementing a brittle first network and thereby enhancing fracture resistance and toughness.[59]

***Bacterial nanocellulose (BNC)***

BNC is produced extracellularly by acetic acid bacteria *Komagataeibacter xylinus*. BNC has ultrafine fibrils (10–100 nm in diameter), which further organize into a three-dimensional reticulated network.[60] The biosynthetic process occurs under mild fermentation conditions and can be tuned by culture medium composition, pH, or agitation to control fibril orientation and network architecture.[61] Unlike plant-derived nanocellulose, BNC is obtained with exceptionally high purity, being free of lignin and hemicelluloses. Its intrinsic structure is a hydrogel-like nanofibrillar matrix with high porosity, a large surface area, and an outstanding capacity to retain water (up to 99%). The fibrils are flexible yet mechanically robust, yielding membranes and networks with high tensile strength and durability.[62] Moreover, the nanoscale organization of BNC facilitates nutrient transport and provides a biomimetic environment for cell adhesion and proliferation.[63]

BNC is unique among nanocellulose types in that it naturally forms stable hydrogels without the need for additional processing. Its hydrated fibrillar network serves as an effective structural scaffold, offering both mechanical reinforcement and high swelling capacity. These features explain its widespread use in wound dressings, artificial skin, and tissue engineering scaffolds.[64] In DN hydrogels, BNC can function either as a reinforcing backbone for the brittle first network or as a template for in situ polymerization of a second ductile network, thereby enhancing toughness and fracture resistance.[65] The ability to biosynthesize BNC in predefined shapes (membranes, tubes, and 3D constructs) further broadens its applicability in advanced hydrogel systems.

**Surface modification of nanocellulose**

Pristine nanocellulose interacts mainly through hydrogen bonding, which limits its compatibility with many synthetic polymers and restricts control over hydrogel performance. Chemical surface modifications provide a way to tailor nanocellulose for specific interactions, improving dispersion, interfacial adhesion, and functionality. Such modifications are essential when designing hydrogels with controlled mechanical strength, swelling, and stimuli-responsiveness, particularly in DN hydrogels, where synergy between rigid and ductile components is critical.[40,66] One of the most widely applied strategies for functionalizing nanocellulose is TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) oxidation, which selectively converts primary hydroxyl groups at the C6 position of cellulose into carboxyl groups.[35] This reaction introduces negative charges on the fibril surface, enhancing water dispersibility and colloidal stability, enabling ionic crosslinking with divalent or trivalent cations ($Ca^{2+}$, $Fe^{3+}$), which strengthens hydrogel matrices, and promoting electrostatic interactions with cationic polymers, such as chitosan.[67]

In hydrogel design, TEMPO-oxidized nanocellulose often acts as an active crosslinking element, creating ionic or covalent bridges within polymer networks and increasing structural integrity without compromising water content. Another way to functionalize nanocellulose is acetylation. By acetylation the hydroxyl groups are replaced with acetyl substituents, decreasing polarity and hydrogen bonding capacity. As a result, nanocellulose becomes more compatible with hydrophobic or amphiphilic polymers, enabling the formation of hybrid hydrogels with tailored swelling and mechanical behavior.[68] By reducing excessive hydrophilicity, acetylated nanocellulose also improves the dimensional stability of hydrogels in aqueous environments, an advantage in biomedical devices or packaging applications. Furthermore, through "grafting from" (initiating polymerization directly from the cellulose surface) or "grafting onto" (attaching pre-formed polymers), nanocellulose can be functionalized with synthetic or natural polymers. This strategy allows the introduction of responsive moieties, such as poly(N-isopropylacrylamide) (PNIPAM) for thermoresponsive hydrogels, acrylic acid derivatives for pH-responsive swelling, or bioactive polymers (*e.g.*, peptides, polysaccharides) for tissue engineering.[69] Grafted nanocellulose thus provides not only improved compatibility with polymer matrices, but also multifunctionality, transforming hydrogels into smart materials capable of adapting to environmental or physiological stimuli.

Surface modification critically determines how nanocellulose interacts with surrounding polymer matrices. Carboxylate nanocellulose, typically obtained via TEMPO oxidation, provides abundant ionic sites that promote crosslinking and considerably increase hydrogel stiffness and fracture resistance. Acetylated nanocellulose reduces surface polarity, improving miscibility with hydrophobic polymers, while imparting

greater dimensional stability and more controlled swelling. By contrast, polymer-grafted nanocellulose enables the integration of responsive or bioactive functionalities, opening routes toward drug delivery platforms, engineered tissues, and advanced biofabrication strategies. In double-network hydrogels, surface-modified nanocellulose acts as a versatile element, reinforcing the brittle first network through strong ionic or covalent bonds, while in the flexible second network, it contributes ductility and energy dissipation. This dual capacity makes nanocellulose a cornerstone for next-generation DN hydrogels.[15]

Concluding, we can say that the nanocellulose constitutes one of the most versatile families of bio-based nanomaterials, yet its effective translation into hydrogel systems is not without challenges. While CNCs provide rigidity, high crystallinity, and charged surfaces that reinforce and stabilize networks, their intrinsic brittleness and limited flexibility can constrain performance in dynamic environments. CNFs, with their entangled fibrillar morphology, excel in imparting elasticity and resilience, but their high viscosity and energy-intensive production may complicate large-scale processing. BNC, uniquely biosynthesized as a pure, hydrogel-like network, offers superior biocompatibility and structural mimicry of extracellular matrices; however, its production remains costly and sensitive to culture conditions, which hinders widespread application. Surface functionalization by TEMPO oxidation, acetylation, or polymer grafting, undoubtedly expands the integration of nanocellulose into diverse polymer matrices and enables the creation of stimuli-responsive hydrogels. Nevertheless, chemical modification introduces trade-offs, such as potential cytotoxicity of residual reagents or reduced biodegradability, which must be carefully addressed. In the framework of DN hydrogels, nanocellulose demonstrates remarkable duality: oxidized or grafted forms reinforce the brittle first network through strong ionic or covalent linkages, while unmodified or ductile fibrils dissipate stress within the second network. The challenge lies in balancing these contributions to avoid compromising swelling, permeability, or long-term stability. Overall, the structural diversity and surface adaptability of nanocellulose position it as a compelling platform for next-generation hydrogels. However, realizing its full potential in tissue engineering, regenerative medicine, drug delivery, and sustainable materials will require not only optimization of functionalization strategies, but also advances in scalable production and a deeper understanding of long-term biological interactions.

## PREPARATION STRATEGIES OF DN HYDROGELS USING NANOCELLULOSE

### CNF-enhanced DN hydrogels of polyvinyl and alcohol polyacrylamide

Polyvinyl alcohol (PVA) and polyacrylamide (PAM) are two of the most researched and easily accessible systems that offer double hydrogel networks. When considered separately, PVA has outstanding biocompatibility and degradability, but poor mechanical qualities, whereas PAM is easy to mold and chemically stable, but frequently brittle due to its excessively dense polymer network. Ou *et al*. created a DN hydrogel using a PAM polymer network and a PVA freeze-thaw crystalline network to overcome the mechanical drawbacks of single component hydrogels.[70] This hydrogel demonstrated exceptional elongation (380%) and tensile stress (890 kPa). When CNF were integrated into a PAM polymer network as a reinforcing agent, a composite hydrogel with mechanical properties 2.6 times higher than those of the initial sample, reaching 54 kPa,[71] was achieved. Similarly, introducing CNF into a PVA polymer network to form hydrogels through repeated freezing and thawing significantly improved their properties due to the formation of an extended network of hydrogen bonds between the hydroxyl groups of the PVA and the CNF. While the elongation at break dropped to 200%, it was discovered that the tensile stress rose in proportion to the CNF content and the number of freeze-thaw cycles. However, the tensile strength improved significantly up to 840 kPa.[72] Thus, CNFs are highly effective hydrogel reinforcement materials because they have outstanding overall qualities and can interact with the matrix material to enhance the hydrogel's qualities. Inspired by the aforementioned strategies for improving hydrogels through multiple networks and hydrogen bonds, Li *et al*.[73] designed and synthesized a high-performance multi-network composite conductive hydrogel based on PAM and PVA dual network hydrogels, but also introduced stearyl methacrylate (SMA) and CNF as reinforcing agents to achieve excellent comprehensive properties. The first network was constructed using AAm and SMA polymeric monomers via thermal polymerization, using ammonium persulfate (APS) as a thermal initiator and crosslinker *N,N′*-

methylenebis(acrylamide) (MBA) – Figure 5. The crosslinking in the first network was further enhanced by hydrophobic interactions. The second polymeric network was formed from PVA and CNF through hydrogen bonds between the OH groups in both polymers. CNF was previously dispersed into a micellar solution composed by sodium chloride (0.8 mol/L) and sodium dodecyl sulfate (SDS) (7 wt%). The intricacy of the crosslinked structure was increased by the CNF fibers' involvement in the creation of the freeze-thaw network, as well as their entanglement with the polymer network. The exceptional durability of the CNF served as a "rope" that securely joined the composite hydrogel's chemical and physical networks. By successfully enhancing the hydrogel's energy dissipation network and mechanical properties, this design was able to achieve remarkable toughness (5.41 MJ/m$^3$), superior fatigue resistance, and a tensile strength of 1.82 MPa.[73] Additionally, the hydrogel's high electrical conductivity (535 mS/m) due to the presence of NaCl within the hydrophobic micelles allowed it to respond quickly to activities involving human-computer interaction and real-time human motion monitoring.[73]

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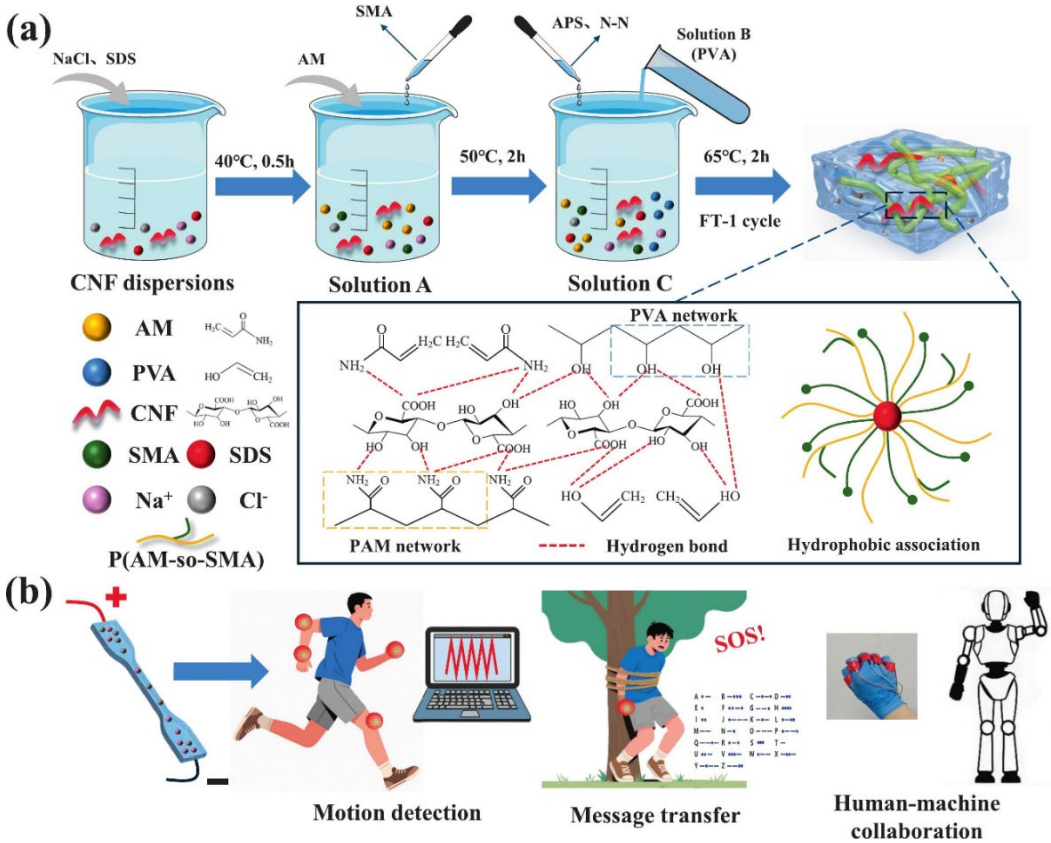


Figure 5: Schematic diagram of the synthesis of a DN hydrogel: (a) detailed process of hydrogel preparation, highlighting possible hydrogen or hydrophobic interactions, which enhance the DN crosslinking process; (b) conceptual framework for illustrating the potential capabilities of hydrogels, as well as potential applications in motion sensing, message transfer, and human-machine cooperation[73]

Recently, an innovative application of CNF was reported in the fabrication of DN hydrogels composed of PVA and PAM. In this system, CNF acted not only as a nanoscale reinforcing component, but also as an effective physical crosslinker, promoting interfacial interactions between the two polymer networks. The incorporation of CNF significantly enhanced the mechanical integrity and toughness of the DN hydrogel by dissipating energy under deformation, while maintaining high flexibility and water retention. Moreover, the hierarchical structure introduced by CNF improved load transfer between PVA and PAM chains, leading to a synergistic strengthening effect that surpassed that of conventional DN hydrogels. In this instance, the authors used the distinctive mechanical and morphological characteristics of CNF by employing it as a "glue" or "bridge" to join the two polymers in question, creating amazing triple-layered networks where CNF is always in the centre of the polymer network building.[74] In this context, CNF act as a highly effective reinforcing agent due to their high aspect ratio, large surface area, and abundance of hydroxyl groups. The hydroxyl functionalities on the CNF surface readily interact with the hydroxyl groups of PVA, facilitating the formation of a dense network of hydrogen bonds. These interactions not only strengthen the intermolecular associations within the PVA matrix, but also serve as additional physical crosslinking sites, thereby enhancing the overall structural integrity of the polymer network. As a result, the incorporation of CNF promotes improved load transfer, restricts polymer chain mobility, and contributes to the development of a more robust, mechanically reinforced, and dimensionally stable composite structure.[75] The hydrogel has a "triple network-interconnected" energy dissipation mechanism thanks to the excellent functioning CNF fibers, which firmly join the double networks as a third network. Thus, even after a single freeze-thaw, the composite hydrogels continue to show substantially improved mechanical characteristics (1.41 MPa) and strength (6.73 $MJ/m^3$) in comparison to the documented multiple freeze-thaw cycles of PVA-based hydrogels.[70,72] Additionally, the addition of $Zn^{2+}$ causes coordination bonds to form with the carboxyl groups of CNF,[75] strengthening the interlocking of many networks and giving the composite hydrogel superior electrical conductivity and antibacterial qualities. Additionally, the composite hydrogel has outstanding responsiveness (108 ms) and sensitivity (GF = 8.74). Such CNF-reinforced DN systems represent a promising strategy for designing next-generation soft materials with applications in flexible electronics, biomedical scaffolds, and stimuli-responsive devices.

The versatility of the polymer pair, PVA and PAM, which are primarily used to form DN hydrogels, has allowed researchers to design increasingly complex structural systems (by adding other components) in an effort to give the synthesized hydrogels new, remarkable properties like improved conductivity or operability in extremely high or low temperatures (antifreezing properties, for example). It was recently revealed that the authors employed a 3:1 molar ratio of water and DMF as a DN network building medium. This is because DMF is known to significantly improve the hydrogel's antifreezing and moisturizing qualities.[76] In order to improve crosslinking through hydrogen bonds, the first polymer system made from PVA was submerged in a solvent combination that included nanocellulose (0.1%) as reinforcing agent. Tannic acid, AAm (which will supply the secondary polymer network of PAM through radical polymerization), and KCl were added to the solution after the PVA had been dissolved. While KCl is added to improve the hydrogel's electrical conductivity, tannic acid and CNF will both help by forming hydrogen bonds through intercalation between the two polymer structures.[76] It is noteworthy that this dual-network ionic organic hydrogel has a steady resistance temperature coefficient (TCR of 0.455 °C), good electrical conductivity (3.63 S/m), ultrahigh sensitivity (GF up to 18.74), and outstanding tensile qualities (603%, 0.26 MPa).

CNF has been involved in the design of magnetic DN networks, which are constructed on the PVA/PAM, because of the remarkable capacity of the PVA/PAM polymer combination to self-assemble and readily form a double cross-linked network. In this new approach, a multinetwork structure has been constructed using a combination of flexible chain polymers, including PVA, PAM, and PNIPAM (Fig. 6). By forming more hydrogen bonds, the use of TEMPO-oxidized CNFs as a nanofiber reinforcing agent resulted in a significant improvement to guarantee a high mechanical strength.[77] A salting out process was used to further increase the cross-linking density in order to improve the dissipation of energy provided from external sources and achieve a higher mechanical

strength. While the magnetically responsive layer demonstrated a high magnetization (6.1 emu/g) and a good tensile strength (0.47 MPa), the temperature responsive layer that was developed had a high tensile strength (1.97 MPa).[77] This hydrogel system exemplifies the versatility of DN design, where the synergistic combination of PVA and PAM provides a mechanically robust, yet highly flexible matrix. The incorporation of CNF introduces additional levels of structural hierarchy, intermolecular interactions, and functional tunability. Moreover, the surface chemistry and high aspect ratio of CNF enable the integration of further functionalities, such as ionic conductivity, improved water retention, and responsiveness to external stimuli (pH, temperature, or ionic strength). As a result, what begins as a model DN hydrogel system is transformed into a multifunctional material platform with emergent properties that extend its potential applications to areas such as flexible electronics, soft actuators, and biointerfaces.[77]

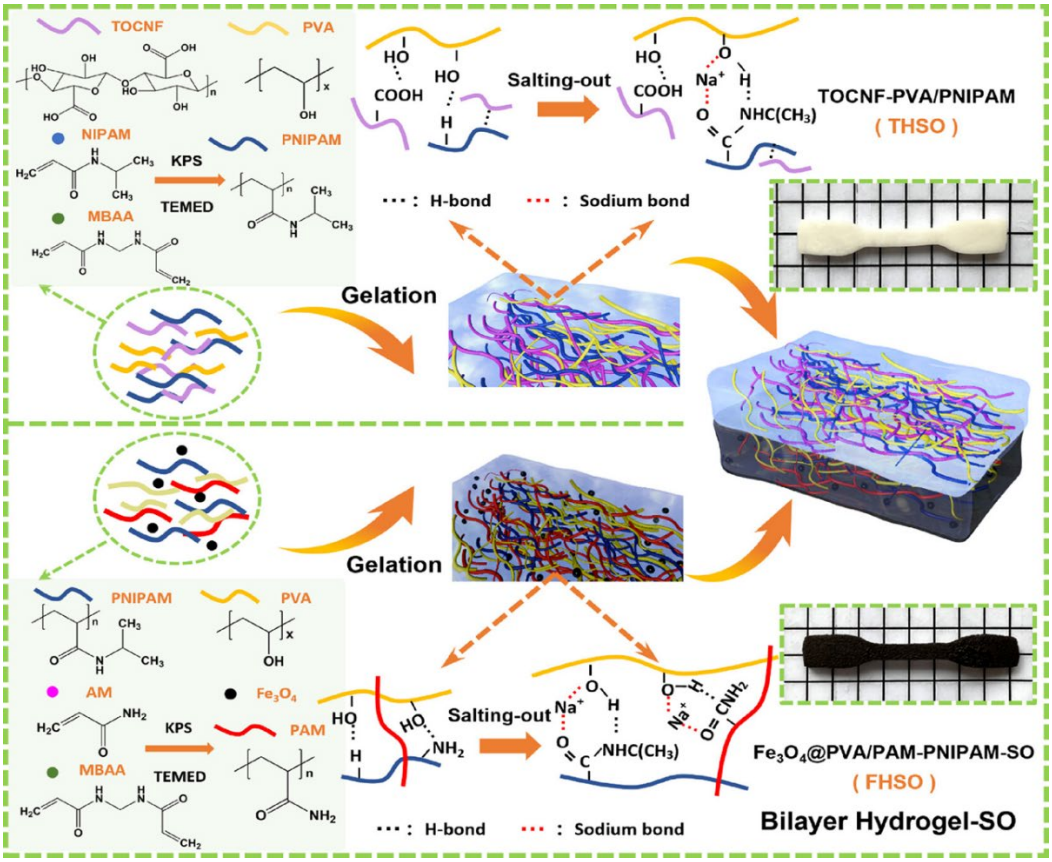


Figure 6: Design of the bilayer hydrogel structure, consisting of PNIPAM, PVA, and PAM, TEMPO-oxidized CNF (TOCNF); radical polymerization of acrylamide (AM) with the participation of N,N′-methylenebis(acrylamide) (MBAA), potassium persulfate (KPS) initiator, tetramethylethylene diamine (TEMED, 99%) catalyst is also illustrated[77]

**CNF functionalized with photopolymerizable groups**

A flexible but challenging technique for adjusting the reactivity of the carboxyl groups on the surface of cellulose nanofibrils and increasing their potential applications is functionalization. By inserting polymerizable moieties, such as allyl or (meth)acrylate groups, the surface of CNFs can be endowed with sites capable of undergoing free-radical or photoinitiated polymerization, hence permitting their covalent integration into crosslinked polymer networks or copolymer matrices. In addition to improving CNFs' interfacial compatibility with synthetic polymers, this alteration makes it possible to create hybrid nanocomposites with adjustable mechanical, thermal, and response characteristics. To prevent aggregation, loss of fibrillar morphology, or over-substitution, which could jeopardize the intrinsic hydrogen-bonding network and mechanical reinforcement capabilities of CNFs, a controlled and uniform grafting of these functional groups necessitates meticulous reaction condition optimization. In this regard, a highly flexible DN

was designed and synthesized. The first network of the DN uses CNF with attached allyl groups and gelatin with grafted methacrylic groups. The first network's allylated nanocellulose and methacrylated gelatin form entanglements of chains anchored by hydrogen bonds with poly(acrylic acid) chains in the polymerizable deep eutectic solvent (PDES), constituted by the introduction of a hydrogen bond acceptor, namely choline chloride (ChCl), which forms the second network[78] (Fig. 7). An optimized elastomer with this special structure has great toughness (12.82 MJ/m$^3$) and mechanical strength (5.23 MPa). While PDES offers stability over a broad temperature range (−20 °C to 70 °C) and relative humidity range (25–75%), along with antimicrobial properties, dynamic hydrogen bonding and chain entanglement work in concert to provide high resilience (~80%) and excellent fatigue resistance (~89.5% strength retention). Furthermore, the dual-network elastomer's dual-network energy dissipation processes provide superior impact and abrasion resistance. The addition of aldehyde groups, which have the primary benefit of being readily employed in combination processes with the amino groups of different partner species, so creating Schiff bases is another ingenious strategy that expands the area of application of CNF (Fig. 7 (b)).

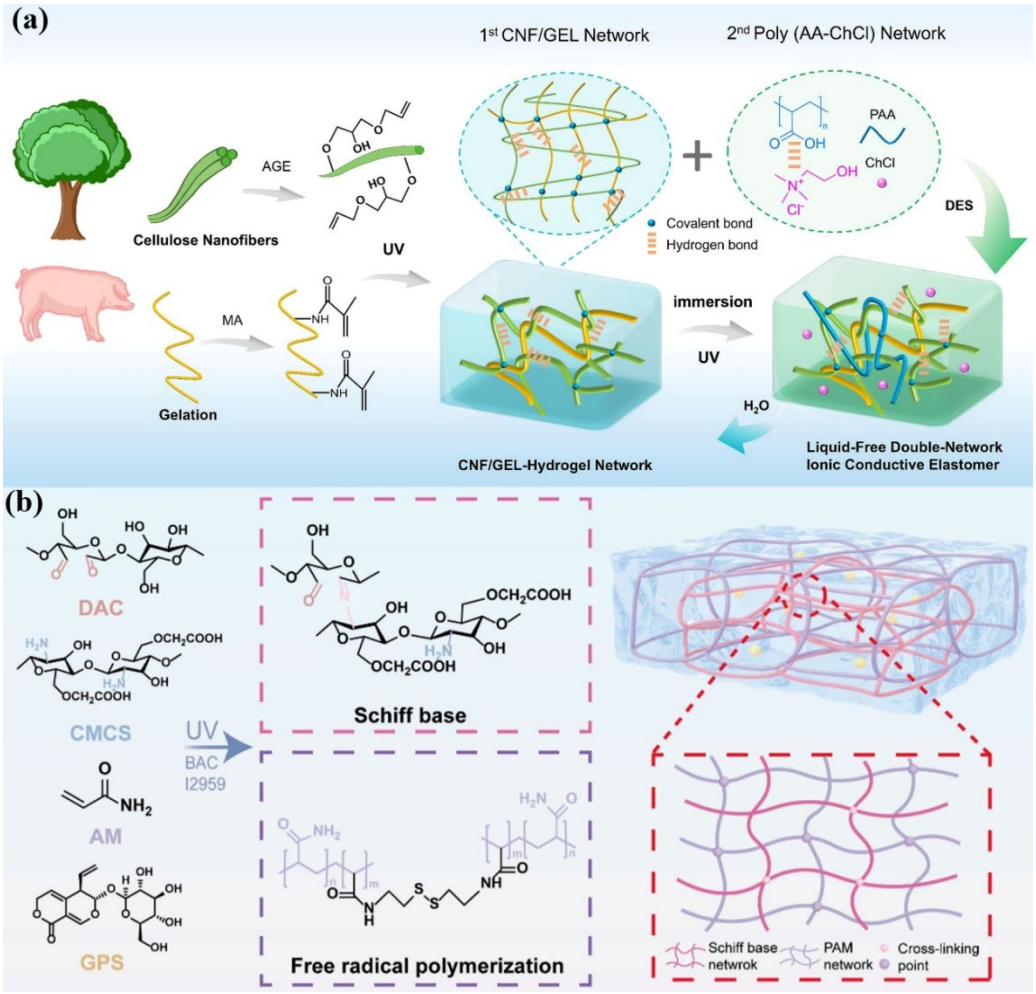


Figure 7: Structural design of the elastomeric DN network: (a) Scheme showing the synthesis process, molecular structure and possible interactions within the elastomer consisting of allylated CNF and methacrylated gelatin as the first network and polyacrylic acid in PDES as the second network;[78] (b) Schematic production of the DN hydrogel made up of carboxymethyl chitosan (CMCS) and CNF with aldehyde groups (DAC), while the second network is made up of PAM, which is the product of acrylamide (AA) polymerization. Notably, gentiopicroside (GPS), a naturally occurring secoiridoid glycoside, was added to the hydrogel due to its anti-inflammatory properties[79]

Dai and co-workers employed cellulose nanofibers that were selectively oxidized with sodium periodate to introduce aldehyde functionalities, yielding dialdehyde cellulose (DAC).[79] This modification exploits the well-established ability of periodate to cleave vicinal diols within the cellulose backbone, thereby generating highly reactive aldehyde groups without compromising the fibrous nanostructure. The presence of these aldehyde groups is particularly advantageous, as they can rapidly form covalent imine (Schiff base) linkages through reversible condensation reactions with primary amines under mild, aqueous conditions, without requiring catalysts or harsh processing environments. To harness this reactivity for the design of a dynamic polymeric network, the authors introduced carboxymethyl chitosan (CMCS), a water-soluble derivative of chitosan that not only provides abundant amino groups for Schiff base formation, but also enhances solubility and chemical versatility compared to native chitosan. Through the combination of DAC and CMCS, the first polymer network stabilized by reversible Schiff base linkages was constructed, imparting the system with self-healing and stimuli-responsive properties arising from the dynamic covalent nature of the crosslinks. The second polymer network in the DN hydrogel assembly was composed of PAM, synthesized via free-radical polymerization of AM monomers, which provided mechanical robustness and flexibility to the matrix.[79] To further endow the system with bioactive functionality, gentiopicroside (GPS), a natural secoiridoid glycoside derived from *Gentiana* species, was incorporated into the hydrogel network. GPS was selected due to its well-documented pharmacological properties, particularly its potent anti-inflammatory activity, which plays a pivotal role in modulating the wound microenvironment. By attenuating excessive inflammatory responses and promoting a balanced immune regulation, GPS contributes to accelerated skin tissue regeneration, reduced scar formation, and improved overall wound healing outcomes. The resulting hydrogel's extraordinary mechanical qualities, such as its tensile strength (>400 kPa), stretchability (>1400%), toughness (>2900 kJ/m$^3$), and high self-adhesion to skin (2.7 kPa), were made possible by the clever design and preparation process of this double cross-linked network. It also greatly accelerated wound healing and showed outstanding biocompatibility.

## MECHANISMS BY WHICH CELLULOSE ENHANCES DN PERFORMANCE

The reinforcement of DN hydrogels by nanocellulose results from a complex interplay between structural integration and interfacial interactions. The fundamental synergy of DN hydrogels – combining a brittle, highly crosslinked first network with a ductile, energy-dissipating second network – is well established. However, nanocellulose incorporation introduces additional reinforcing pathways that merit closer examination. These include physical entanglement, stress transfer, chemical crosslinking, and energy dissipation, whose relative contributions depend strongly on nanocellulose type, surface chemistry, and dispersion quality – parameters often insufficiently documented in the literature.[15,17,59] Physical entanglement is most prominent in the case of CNFs. Their extended length and flexibility enable the formation of percolated, hydrogen-bonded fibrillar scaffolds that reinforce hydrogel matrices. This mechanism is often mentioned as the primary reason for improved toughness.[80] Nevertheless, the same property introduces practical limitations: CNF suspensions exhibit high viscosity, which complicates homogeneous dispersion during hydrogel synthesis and raises concerns regarding reproducibility and scalability. Stress transfer is primarily mediated by CNCs. Acting as rigid nanoscale fillers, CNCs redistribute mechanical loads from flexible polymer chains to stiff crystalline domains, thereby delaying crack initiation and propagation.[45] Their efficiency, however, is highly sensitive to surface chemistry. Sulfated CNCs disperse well in aqueous environments but compromise thermal stability, whereas hydrochloric-acid-derived CNCs are thermally more stable but prone to aggregation. This trade-off underscores the need for systematic studies correlating CNC surface states with macroscopic hydrogel properties. A further mechanism is chemical crosslinking, which becomes accessible through surface modification strategies, such as TEMPO-mediated oxidation. By introducing carboxyl groups or other reactive moieties, nanocelluloses can act as ionic or covalent anchors that stabilize brittle networks.[67] Although effective, such modifications often involve complex chemistries, residual reagents, and increased cost, all of which limit practical application. Excessive crosslinking may also reduce swelling capacity, thereby diminishing one of the intrinsic advantages of hydrogels in

biomedical applications. Nanocellulose also contributes to energy dissipation by providing sacrificial bonds – hydrogen, ionic, or fibrillar pull-out – that absorb mechanical energy and enhance fatigue resistance.[81]

Quantifying the exact contribution of these reversible interactions relative to the sacrificial fracture of the first network remains a challenge, leaving much of the optimization of nanocellulose–DN hydrogel systems empirical rather than predictive. Beyond mechanics, nanocellulose offers functional enhancements, such as drug-loading capacity, improved biocompatibility, and stimuli-responsive behaviour.[66] While these attributes are promising, they are often demonstrated under idealized laboratory conditions. Long-term stability, cytocompatibility *in vivo*, and reproducibility at scale remain underexplored and represent critical hurdles to real-world translation. Taken together, nanocellulose improves DN hydrogels through a constellation of reinforcing mechanisms and functional pathways. Yet, the field must now progress from proof-of-concept demonstrations toward systematic evaluations and standardization, with attention to morphology–property correlations, surface modification effects, and scalability. Only by addressing these challenges can nanocellulose evolve from a promising additive to a cornerstone in the rational design of next-generation DN hydrogels.

**Sacrificial/brittle network**

The idea of a sacrificial or brittle network is fundamental to energy dissipation and overall mechanical performance in many tough, multi-network polymeric systems. Usually made up of a rigid, highly crosslinked, or physically stiff component, this network is intended to fail under stress in a controlled manner. In cellulose-based systems, the intrinsic stiffness of cellulose fibers, fibrils, or nanocellulose can provide this first network. When mechanical load, such as tension, compression, or shear, is applied, the brittle network fractures, effectively absorbing a significant portion of the applied energy. This sacrificial fracture stops serious cracks from propagating through the material, which would otherwise cause sudden failure. While the brittle network breaks locally, the more ductile or elastic secondary network remains intact, maintaining the material's overall structural integrity. This secondary network can accommodate large deformations, allowing the material to stretch, bend, or compress without completely disintegrating. The synergy between the sacrificial, cellulose-based network and the flexible secondary network produces materials that are both strong and tough. Due to its high aspect ratio, excellent mechanical stiffness, and surface functionality, nanocellulose is particularly well-suited for forming this brittle network. Its nanoscale dimensions allow for homogeneous distribution within a matrix, which optimizes energy dissipation and prevents stress concentration points. Furthermore, nanocellulose has the capacity to establish hydrogen-bonded or physically entangled networks, offering a controllable equilibrium between fragility and fracture energy. Adjusting the concentration, aspect ratio, or degree of aggregation of cellulose allows one to fine-tune the mechanical response of the sacrificial network for specific applications in hydrogels, composites, or hybrid polymer systems.

**Reinforcement and load transfer**

The highly crystalline, rod- or ribbon-like nanostructures known as CNFs and CNCs have remarkable mechanical qualities, such as a high tensile strength and a Young's modulus between 100 and 200 GPa. These nanocellulose components serve as stiff reinforcing fillers when added to a hydrogel or softer polymeric matrix. Two complimentary mechanisms – efficient load transfer and intrinsic reinforcement – give rise to the mechanical enhancement. In terms of intrinsic reinforcement, the inherently high stiffness of CNFs/CNCs contributes directly to the composite’s overall modulus and strength. Their high aspect ratio allows them to form an interconnected network or percolating structure within the softer matrix, which resists deformation under applied stress. This network effectively bears part of the load, reducing strain on the softer matrix. As regards the load transfer mechanism, through robust interfacial interactions, the stress applied to the composite is effectively transferred from the softer matrix to the stiff nanocellulose. Van der Waals forces, hydrogen bonds, and even covalent crosslinking in chemically modified systems are examples of these interactions. By reducing localized strain in the softer network, effective load transfer increases the material's resilience to mechanical failure under compressive, cyclic, and tensile loading scenarios. Elastic modulus, cyclic fatigue resistance, compressive strength, and tensile strength are all generally significantly increased by the use of

CNFs/CNCs. Because the nanocellulose network restricts deformation under compressive loads, the reinforced matrix may withstand greater stress before breaking because of the stiff nanocellulose backbone. Up to the percolation threshold, the composite's total stiffness rises in direct proportion to the amount of nanocellulose present. Because stress is distributed more evenly and the nanocellulose network inhibits the onset and spread of cracks, repeated loading results in less permanent deformation. Features of nanocellulose, such as aspect ratio, crystallinity, surface chemistry, and dispersion quality within the matrix, have a significant impact on the reinforcing effect. While aggregation or inadequate interfacial bonding can lower reinforcing efficiency, optimal nanofibril alignment can further improve directional mechanical characteristics.

**Crosslinking interactions**

A wide variety of functional groups, mostly hydroxyl (-OH), carboxyl (-COOH), aldehyde (-CHO), and occasionally amine ($-NH_2$) groups, depending on chemical modification, are present in cellulose derivatives and operate as crosslinking active sites. These functional groups give cellulose-based materials a flexible platform to adjust their mechanical, thermal, and chemical properties by facilitating the creation of both covalent and non-covalent crosslinks.

The polymer network can be stabilized by covalent bonds, which are powerful, long-lasting interactions. For example, cellulose's hydroxyl groups can react with glutaraldehyde, epichlorohydrin, or diisocyanates to create urethane, acetal, or ether bonds, respectively. Carbodiimide-mediated amide bond formation with amine-containing compounds is facilitated by carboxyl groups. These covalent crosslinks improve the hydrogel or film's mechanical strength, stiffness, and chemical resistance, which qualify it for long-term or load-bearing uses.

On the other hand, reversible and dynamic, non-covalent interactions include van der Waals forces, ionic interactions, and hydrogen bonds. In order to provide structural cohesion and flexibility, hydrogen bonds can develop between the hydroxyl groups of neighboring cellulose chains or between cellulose and other polar molecules. If cellulose derivatives are altered to contain charged groups, such as carboxymethyl cellulose (which is negatively charged) interacting with multivalent cations (like $Ca^{2+}$) to produce physical crosslinks, ionic interactions may take place. Self-healing qualities, shape restitution following mechanical deformation, and sensitivity to environmental stimuli like pH, temperature, or ionic strength are all attributed to these reversible non-covalent interactions.

Covalent and non-covalent interactions combine to form dual-crosslinked networks in a variety of sophisticated cellulose-based materials. While non-covalent contacts add dynamic behavior, durability, and adaptability, covalent connections offer long-term stability. This combination is especially useful in drug delivery systems, hydrogels, and flexible electronics, where self-healing and mechanical resilience are essential.

**Architectural effects**

The micro- and nanostructural architecture of cellulose-based materials has a significant impact on their mechanical and functional characteristics. This includes elements that affect the material's performance in diverse ways, including its porosity, hierarchical reinforcement, templated mineralization, and fiber alignment.

Mechanical characteristics like stiffness, strength, and toughness are greatly impacted by the orientation of cellulose fibers at the micro- and nanoscale. Similar to how wood or tendons work, aligned fibers tend to increase directional strength, enabling the material to resist force along the alignment axis. In contrast to aligned systems, random or isotropic fiber orientations offer a more uniform distribution of stress, but typically have a lower total stiffness.

Templated mineralization is the process of carefully applying minerals, such as silica and calcium phosphate, to cellulose fibers. As biotemplates, the fibers direct the nucleation and development of inorganic crystals in a spatially ordered fashion. By precisely controlling the size, shape, and orientation of mineral deposits, such templating improves their mechanical qualities and functional behavior.

In order to combine stiffness, toughness, and flexibility, nature frequently uses hierarchical structures, which are arrangements across several length scales. Fiber bundles at the nanoscale, microscale networks, and macroscale designs are all possible in cellulose-based composites, with each scale working in concert to increase load-bearing capacity and dissipate energy. By imitating natural composites like bone or nacre, hierarchical reinforcement enables materials to improve durability and withstand the spread of cracks.

Mechanical, transport, and functional qualities are greatly influenced by the quantity, size, and connectivity of pores. While excessive or uncontrolled porosity may jeopardize mechanical integrity, managed porosity can improve flexibility, decrease density, or create channels for fluid transmission.

Composite structures resembling natural nacre are produced by depositing mineral particles, like calcium phosphate, onto cellulose fibers. These "brick-and-mortar" configurations allow the material to effectively distribute stresses while stiffening the network by spreading stiff mineral "bricks" within a flexible cellulose "mortar". Through crack deflection and energy dissipation via the organic matrix, this architecture not only increases stiffness, but also improves fracture resistance. These hybrid designs offer a highly effective stress management method by combining the benefits of toughness from the polymeric matrix and hardness from minerals.

**Control of swelling, bound vs free water**

One essential feature of hydrophilic polymer networks, such those made of cellulose-based materials is swelling. Extreme swelling can seriously impair the material's mechanical qualities, even though a certain amount of swelling can be advantageous for water absorption and diffusion. Over-swelling weakens the network by introducing internal stress and lowering the effective crosslink density, which increases the network's susceptibility to deformation or collapse.

There are two different types of water in polymer networks: bound and free. Through hydrogen bonds or other intermolecular interactions, bound water directly interacts with the polymer chains, preventing excessive expansion and promoting network stability. Free water, on the other hand, moves freely throughout the network and causes swelling, which can weaken mechanical strength. It behaves similarly to bulk water. Therefore, preserving structural integrity depends on managing the ratio of bound to free water. Networks of cellulose are essential to this regulation. Water is physically constrained by the thick, interwoven structure of cellulose strands, which restricts molecular mobility and lessens the production of free water. Furthermore, cellulose can be chemically modified by crosslinking or functionalizing hydroxyl groups, which further limits water accessibility and adjusts swelling behavior.

Cellulose-based networks are especially well-suited for applications where both hydration and structural integrity are crucial, such as drug delivery hydrogels, flexible electronics, or biomaterials, because they encourage bound water and restrict free water, which help maintain mechanical stability even in the case of high water content.

**Rheological and structural effects**

The incorporation of nanocellulose into hydrogel matrices has profound implications for rheological behavior and structural organization. Unlike conventional fillers, nanocellulose actively participates in network formation due to its high aspect ratio, surface chemistry, and ability to establish multiple non-covalent interactions with surrounding polymers.[41]

***Network entanglement and gelation kinetics***

CNFs, owing to their length and flexibility, readily form percolated entangled networks that act as structural backbones within hydrogels. These fibrillar scaffolds significantly influence gelation kinetics by lowering the critical gelation concentration and accelerating network formation.[82] In contrast, CNCs, with their rigid rod-like morphology, contribute less to entanglement, but can promote nucleation sites for crosslinking, thereby modulating gelation pathways. The balance between fibril entanglement and crystallite reinforcement ultimately dictates the microstructure of nanocellulose-reinforced hydrogels.

***Viscoelastic behavior improvement***

Nanocellulose enhances the viscoelastic response of hydrogels by providing additional reversible interaction sites. Rheological studies consistently show increases in storage modulus (G′) relative to loss modulus (G″) when nanocellulose is incorporated, reflecting a shift toward more elastic and solid-like behavior.[54] This improvement arises not only from physical entanglements and hydrogen bonding, but also from secondary relaxation mechanisms, such as ionic or covalent interactions in surface-modified nanocellulose. Importantly, these interactions act as sacrificial bonds that can reversibly break and reform, contributing to self-healing and enhanced resilience under cyclic loading.[83] While these rheological improvements are promising, several challenges remain. CNF-rich systems often display excessively high viscosities, complicating

processing and injectability. CNC suspensions, though less viscous, can aggregate without careful surface modification, leading to heterogeneity in gelation. Furthermore, most rheological evaluations are conducted under small-amplitude oscillatory shear, which may not fully capture performance under large deformations relevant to biomedical use. A more systematic correlation between nanocellulose morphology, surface chemistry, and macroscopic viscoelastic properties is necessary for rational design of advanced hydrogel systems.[44]

## CONCLUSION AND FUTURE RESEARCH DIRECTIONS

Cellulose and its derivatives have proven to be powerful components in the design of double-layered hydrogels, contributing to mechanical reinforcement, sacrificial energy dissipation, functional modifiability, and sustainability. Recent studies have shown that, when properly incorporated (in terms of cellulose form, crosslinking strategy, and network architecture), cellulose-based DN hydrogels can approach or even match the performance indicators of synthetic DN systems, including tensile strength, compressive modulus, toughness, and cyclic resistance. However, achieving the optimal balance of properties (strength vs. extensibility vs. swelling vs. biocompatibility), ensuring long-term stability, and increasing production remain open challenges. Future innovations in hierarchical design, green chemistry, advanced manufacturing, and *in vivo* validation will be essential to realizing the full potential of cellulose-based DN hydrogels in biomedical, environmental, and technological applications.

Given the current state of research on DN hydrogels, several promising directions and intriguing areas of research emerge. One of the biggest challenges is transitioning from synthetic polymers to networks entirely formed by sustainable polymers (based on cellulose or other polysaccharides), while achieving high mechanical performance. Recent work using crosslinking agents derived from vegetable oil is a good example. Another intriguing research area is to mineralize and reinforce hydrogels to enhance their mechanical properties by introducing inorganic components, such as calcium phosphate (CaP), hydroxyapatite templated by cellulose, or hierarchical architectures (*e.g.*, nanofibers, microfibril scaffolds) to mimic natural load-bearing tissues (*e.g.*, bone and cartilage). One high-impact research direction would be preparing stimuli-responsive or smart DN hydrogels. In this case, it would be useful to find cellulose derivatives that respond to pH, temperature, or ionic strength, as well as self-healing networks and dynamic or reversible crosslinks. Modern methods of material processing should be adapted for the fabrication of DN hydrogels. These methods include advanced fabrication techniques, such as 3D/4D printing of cellulose-based DN hydrogels, patterning, gradient structures, and bilayer/multilayer systems for biomimicry.

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