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Shape-memory and self-healing properties of sustainable cellulosic nanofibers-based hybrid materials for novel applications

Review

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In the era of smart and sustainable technology driven by naturally occurring materials, various nanocellulose-based materials play a crucial role. Shape memory behaviour and self-healing capabilities of nanocelluloses are emerging as focal points in numerous research domains. Nanocellulose and its derivatives such as cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), are currently in the limelight due to their excellent shape-memory and self-healing properties, making them suitable for multifunctional devices. In this regard, CNF, as a cutting-edge material, has spurred researchers to explore its potential in developing contemporary multifunctional and personalized health devices. Therefore, a timely and comprehensive review is essential to gain deep insights into the effectiveness of shape-memory and self-healing capabilities of CNF for multifunctional devices. Herein, we first provide a brief introduction to all nanocellulose materials. This review also depicts recent advancements and

Abbreviations: AA, Acrylic acid; AESO, Acrylated epoxidized soybean oil; AM, Additive Manufacturing; BNC, Bacterial nanocellulose; CA, Citric Acid; CAN, Covalent adaptable network; CMC, Carboxymethyl cellulose; CNC, Cellulose nanocrystals; CNF, Cellulose nanofibril; CNT, Carbon nanotube; D-A, Diels-Alder; DCNF, Dicarboxylic cellulose nanofiber; DES, Deep eutectic solvent; DIW, Direct ink writing; DLP, Digital light processing; DMSO, Dimethyl sulfoxide; ECH, Electro-conductive hydrogel; ECO, Epoxy castor oil; FFF, Fused Filament Fabrication; FDM, Fused deposition modelling; GF, Gauge factor; GNP, Graphene nanoplatelets; HIPE, High internal phase emulsions; HPC, Hydroxypropyl cellulose; LC, Liquid crystalline; LIG, Lignin; MWCNTs, Multiwalled carbon nanotubes; NIR, Near-infrared; NVP, N-vinyl-2-pyrrolidone; PAA, Polyacrylic acid; PAM, Polyacrylamide; PBS, Poly(butylene succinate); PBAT, Polybutylene adipate terephthalate; PCL, Polycaprolactone; PCLA, Poly(ε-caprolactone-co-lactide); PDA, Poly(dopamine); PDES, Poly deep eutectic solvent; PDMS, Poly(dimethylsiloxane); PEG, Polyethylene glycol; PHB, Polyhydroxybutyrate; PIPS, Photopolymerization-induced phase separation; PLA, Polylactic acid; PNIPAM, Poly(N-isopropyl acrylamide); PVA, Poly(vinyl alcohol); SBS, Styrene-butadiene-styrene; SDGs, Sustainable Development Goals; SEM, Scanning electron microscope; SLA, Stereolithography; SME, Shape-memory effect; SMM, Shape-memory materials; SMP, Shape-memory polymer; TEMPO, 2,2,6,6-tetramethylpiperidine-N-oxyl; TENG, Triboelectric nanogenerators; TOCNF, Tempo-oxidized cellulose nanofibers; UN, United Nations; UV, Ultraviolet; VAC, Vinasse activated carbon.

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breakthroughs in the large and effective synthesis of CNF-based hybrid materials. Next, focusing on their self-healing and shape-memory performance, this review sheds new light on the advanced applications of CNF materials. Finally, perspectives on the current challenges and opportunities in this field are summarized for future researchers to gain an in-depth understanding of CNF-based smart and sustainable materials.

1 Introduction

As society progresses into the intelligent era driven by rapid advancements in science and technology, self-healing and shape-memory materials are at the forefront of research and innovation. Self-healing materials offer immediate repair in case of damage, thus ensuring safety, energy efficiency, and reduced environmental impact of synthetic materials, while also extending their service life [1]. Meanwhile, shape-memory materials possess the ability to sense external environmental stimuli, analyse them, and respond accordingly, endowing them stimuli-response properties. The functionalities of shape-memory materials, such as ease of shaping, rapid recovery, and large deformation, are becoming increasingly important in engineering research [2]. Some pioneering studies have shown that the integration of shape-memory properties with self-healing capabilities holds promise for achieving innovative functionalities in various sectors, including biomedical, aerospace, and flexible electronics [3]. Contemporary technology often relies on toxic and non-biodegradable materials, resulting in significant waste generation at the end of their lifespan [4,5]. More importantly, the compelling interest and escalating demands for non-biobased materials, alongside technological advancements, have highlighted the critical issues of plastic and electronic waste (e-waste), which pose significant environmental risks [6].

Consumers are estimated to discard around 50 million tons of e-waste annually, a figure projected to double by 2050. Most of this e-waste either ends up in landfills or is illegally exported to several developing countries, with only around 17% recycled through waste management systems [7]. The widespread use of synthetic plastics raises significant environmental concerns and hinders efforts to achieve net-zero carbon dioxide (CO_2) emissions by 2050, in line with the United Nations (UN) Sustainable Development Goals (SDGs) [8]. Hence, it is imperative to seek alternatives from naturally available materials as promising solutions to address these challenges [9,10]. In this regard, producing high-performance and functional materials by using sustainable and renewable resources has attracted extensive attention [11,12]. This is driven by various technical considerations, including the significant consumption of fossil-based petrochemical resources and the pressing need to discover innovative and sustainable materials and manufacturing technologies with zero or near-zero emissions [13].

"Sustainability" is defined as maximizing the capacity of a current system while minimizing its harmful effects on society, the environment, and the economy [14,15]. Specifically, sustainability involves striving to reduce both the impact of plastic consumption and overall energy consumption [16]. Therefore, sustainability indirectly promotes the use of plant-based sources such as biomass, agricultural waste, or the synthetic production of plastics known as bio-based plastics. Sustainability can be sustained over a long period by effectively utilizing these natural resources and integrating them into our lives [17,18]. Moreover, these bio-based materials address end-of-life disposal waste issues and significantly reduce the carbon footprint due to their closed carbon cycle as demonstrated in Fig. 1 [19-21]. It is worth highlighting that the use of bio-based materials or degradable materials is in line with the various UN SDGs such as SDG 3, SDG 12 to SDG 15. Modern sustainable biomaterials are in high demand and are not limited to functionalized vegetable oils, such as acrylated epoxidized soybean oil (AESO), acrylated canola epoxidized linseed oil and sunflower oil. Among all-natural bio-based materials, polysaccharides are promising eco-friendly materials for green electronics applications [22]. Polysaccharides comprise a diverse class of biomaterials, including cellulose, hemicellulose, and lignin (LIG), which are derived from some of the most abundant natural resources on the planet [23,24]. These polysaccharides exhibit intriguing characteristics such as lightweight, high flexibility, low cost, biodegradability, and biocompatibility, aligning well with the core principles of green chemistry [25].

Biomass-derived materials such as cellulose, starch, chitosan, chitin, collagen, gelatin and alginate have low carbon footprints and multifunctional properties crucial for sustainability [26]. In particular, cellulose holds significant potential in addressing environmental challenges due to its biodegradability and tannable properties [27,28]. Cellulose, widely recognized as nature's most abundant biopolymer, consists of linear polymers of anhydro-D-glucose units linked together via β-1,4-glycosidic linkage [29,30]. Hydrogen bonds form between three hydroxyl (OH) groups of anhydro-glucose, resulting in different intermolecular and intramolecular forces-based cellulosic structures [31,32]. Cellulose nanomaterials, including cellulose nanofibers (CNFs), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC), are promising green materials with excellent mechanical and physical properties, contributing to a sustainable circular economy [33-35].

To recapitulate, the extensive utilization of smart and self-healing materials (referring to Fig. 2) derived from naturally available resources for smart and flexible devices in ever-growing industries appears inevitable [36,37]. Hence, there is a critical need to advance towards sustainable materials possessing both shape-memory and self-healing properties [38,39]. These properties will not only prevent deformation but also play a crucial role in imparting smart functionalities [40]. It is noteworthy to mention that in the pursuit of developing smart and sustainable devices from naturally available materials, cellulose has emerged as a promising and highly attractive building block [41]. This is due to its renewability, abundant availability, appealing mechanical strength, and striking functional characteristics [42-44]. Smart and sustainable electronic devices are expected to fully align with

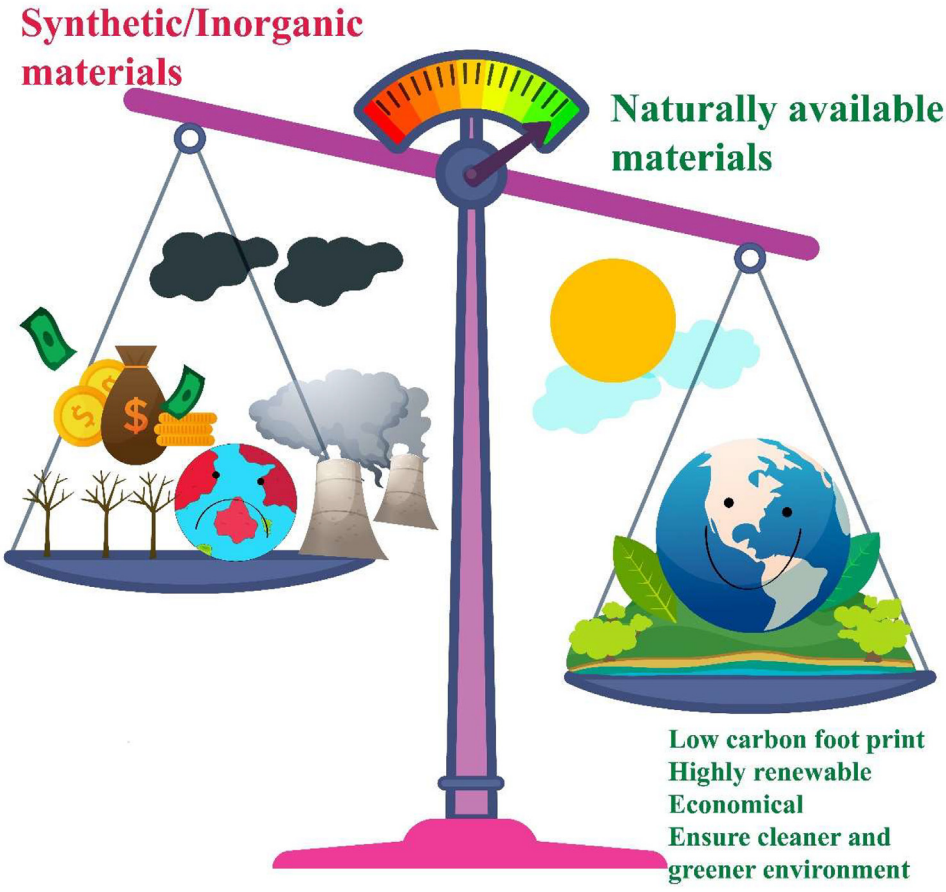

Fig. 1

The promising role of naturally available materials with regard to environmental concerns.

the SDGs outlined in the UN's Agenda 2030. Recently, numerous studies have focused on developing smart and sustainable materials using CNFs and CNCs, which have demonstrated improved shape-memory and self-healing performance [45]. Unsurprisingly, CNFs, being a degradable and eco-friendly material, exhibit exceptional mechanical properties, intrinsic flexibility, high aspect ratio, outstanding optical transparency, low density, and a smooth and reactive surface, positioning them at the forefront of smart and flexible product development [46-49]. The use of CNF-based sustainable devices finds extensive applications in various exciting fields such as energy [50], smart sensing packaging [51], water-oil separation [52], and personalized health devices. These personalized health devices enable selective, fast, and on-site decentralized monitoring of patient health conditions with portable systems, facilitating diagnosis, rapid decision-making, and medical interventions [53,54].

1.1 Review methodology

In the past five years, several review articles have highlighted the importance of nanocellulose across various fields. However, only a few of them have summarized the wider potentials of cellulose in additive manufacturing (AM) [59,60] and discussed its smart features [61-63]. Recently, Khalid et al. [64], in a review of the latest developments of CNC-based materials for sustainable applications, dedicated significant attention to nanocellulose. However, this review focused solely on the state-of-the-art 3D printing of CNC-based nanocellulose. Thus, current literature lacks a comprehensive study of the self-healing and shape-memory features of all major nanocellulose materials, with a specific focus on CNFs. Therefore, this review aims to comprehensively present the advancements and critical challenges in introducing nanocellulose materials, particularly focusing on their role in achieving multifunctionalities in terms of self-healing and shape-memory features and summarizing their unprecedented application prospects in various fields. Research gaps and promising future areas are critically discussed to provide deeper insights into the development of smart and sustainable nanocellulose materials.

Table 1 summarizes our main theme, ideas, keywords, relevant search engines and how the current review is planned. Remarkable and rapid progress has been observed in the last five years, as shown in Fig. 3. To date, most review papers on naturally available materials fall into the following categories:

- Shape-memory behaviour of smart materials
- Self-healing performance of naturally available materials
- 3D printing of naturally cellulosic materials
- Exploring the role of stimuli-responsive biomaterials
- Mainstream 3D printing methods for smart materials
- Smart functionalities for cutting-edge applications

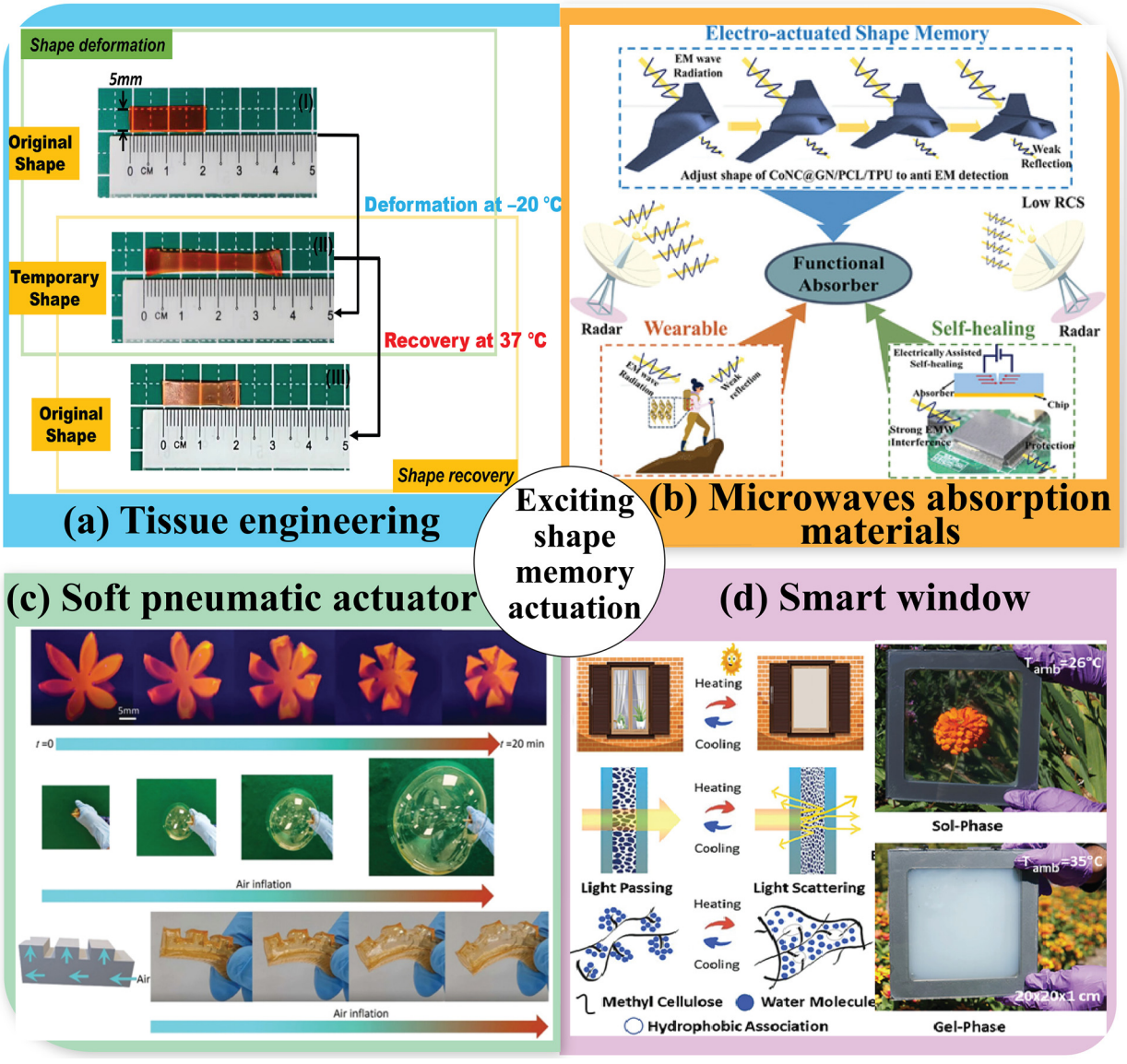

Fig. 2

Overview of various shape memory behaviour triggered from naturally available/biomaterials for intriguing engineering applications such as (a) Thermo-responsiveness of dyed poly(ethylene glycol) (PEG) 4000 polylactic acid (PLA)1500 multiblock copolymer film for esophageal stent applications recorded using a digital camera (adapted from Ref. [55] copyright 2024 Elsevier Ltd.); (b) Demonstration of highlighted characteristics such as ultra-thin (2.3 mm), ultra-light (4 wt.%) and broadband (6.21 GHz) of a multifunctional broadband shape-memory microwaves absorption of CoNC@graphene nanosheets (GN)/PCL/TPU-based materials (adapted from Ref. [56] copyright 2022 Wiley-VCH GmbH); (c) Shape-memory behaviour of AAC–Fe^{3+} hydrogels such as water-responsive flower with gradual closure petals after soaking it in deionized water and their applications as a soft pneumatic actuator with excellent self-healing efficiency (88%) (adapted from Ref. [57] under a Creative Commons Attribution License 4.0 (CC BY)); (d) Demonstration of a thermo-responsive smart window involved light scattering activated by temperature change before phase change at 26°C and after phase change at 35°C (adapted from Ref. [58] under a Creative Commons Attribution License 4.0 (CC BY-NC)).

2 Overview of synthesis techniques

Several manufacturing techniques have been reported in the literature for synthesizing nanocellulose-based hybrid materials, including melt compounding (mechanical mixing), solvent casting (solvent mixing), in-situ polymerization, and picking emulsion. The nanocellulose content in the polymer matrix significantly affects the resulting viscosity of the synthesized nanocomposites. Higher concentrations of nanocellulose lead to increased viscosity of the polymer matrix. This section briefly introduces the most adopted synthesis approaches.

2.1 Melt compounding (mechanical mixing)

The synthesis of CNF-based nanocomposites through the melt compounding process is the most convenient method, requiring minimal resources and chemical consumables. In this process, the polymer matrix is heated close to its melting point, and CNFs are mechanically mixed using conventional extruders, injection molding equipment or mechanical mixers. The shearing force is crucial in achieving homogeneous dispersion of CNFs within the polymer matrix. The prime advantage of this approach is its ease and simplicity, making it the most widely adopted process

Table 1

Summary of literature search for the current review article.

Literature searching criteria	
The focus of the publication period	Last eight years from 2016 to 2024 (till April 30)
Date of search	March 2024
Search Engines	Scopus, Wiley, Emerald, Sage, Nature, ASME, MDPI, Springer, Taylor and Francis, Science, American Chemical Society, Royal Society of Chemistry databases
Search keywords	Nanocellulose, cellulose nanofibers, shape-memory, self-healing
Publication type	Original research articles and the latest state-of-the-art reviews on similar topics
Scope	Physical properties of extracted CNFs, natural sources of CNFs, synthesis routes for CNFs self-healing and shape-memory function, stimuli mechanism, crosslinking, novel design, and emerging applications

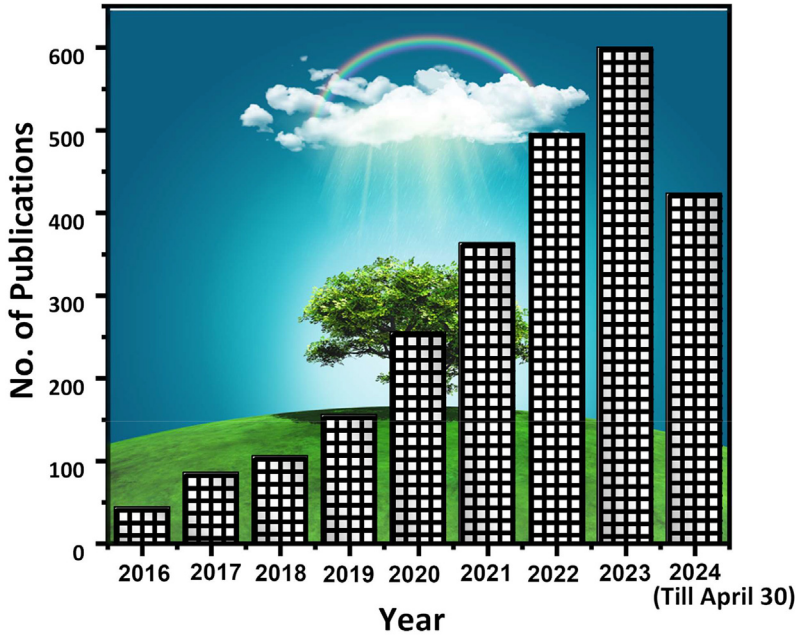

Fig. 3

The number of publications trend from the Scopus database and is based on the keywords "nanocellulose + self-healing" and "nanocellulose + shape-memory behaviour".

in both research and industry. However, several challenges are associated with this technique, particularly the tendency of CNFs to aggregate, especially when dried due to high surface area, which hinders the homogenous dispersion [65].

2.2 Solvent casting (solvent mixing)

The solvent casting technique is commonly used to produce CNF nanocomposite films [66]. In this process, polymers are dissolved in a chemical solvent (e.g., chloroform, dichloromethane, toluene, etc.), and CNFs are added subsequently with continuous stirring to produce mixed suspensions. Finally, the solvents are removed via heating and continuous stirring to achieve homogenous dispersions. After solvent removal, the mixture is produced in film form to eliminate any residual solvent [67]. Recently, Wang et al. [68] prepared high-performance ionic soft actuators using carboxylated CNF, ionic liquid, and polyvinyl alcohol (PVA) using the casting drying method. The developed actuator demonstrated remarkable actuation behaviour including such as long working ability (95% maintain for 2.5 h), large bending strain of 0.41% (peak-to-peak displacement of 13.6 mm), as a promising candidate for next-generation soft robots, artificial muscles, and human-robot interactions.

2.3 In-situ polymerization

In-situ polymerization involves the synthesis of insoluble composites through the polymerization of a reactive monomer in the presence of a catalyst. This process is executed by carefully controlling the reaction temperature and duration. To achieve this, monomers or prepolymers can be uniformly mixed with fillers in an appropriate solvent, where the monomers or prepolymers are soluble, while the resulting polymers of the monomers are insoluble [69]. The introduction of the monomer into the reaction system occurs after the catalyst has been absorbed on the surface of the nanofiller. The reaction initiates with monomer pre-polymerization, followed by the polymerization of prepolymers. As the process unfolds, the prepolymer gradually deposits on the core's surface, increasing its size [70].

2.4 Pickering emulsion

Pickering emulsion process is a versatile technique used to produce nanocomposites by utilizing solid nanoparticles as stabilizers at the oil-water interface [71]. In this method, solid particles, often nanomaterials, are dispersed in an aqueous phase, and a nonpolar liquid, typically containing a polymer precursor, is emulsified within this aqueous phase. The solid particles adsorb at the oil-water interface, forming a stable Pickering emulsion. The emulsion can then be further processed to solidify the polymer, forming nanocomposite materials [72]. One key advantage of the Pickering emulsion process is achieving high stability without traditional surfactants. The method also allows for excellent control over the distribution of nanoparticles within the emulsion, facilitating the production of nanocomposites with tailored properties [73]. However, careful optimization of process parameters is required to ensure optimal stability and homogeneity, and scalability considerations should be considered for industrial applications. Recently, Zhou et al. [74] developed Pickering emulsions stabilized novel konjac glucomannan-based highly antibacterial films loaded with thyme essential oil through bacterial CNF/Ag nanoparticles. Results show that tangerines treated with thyme essential oil through bacterial CNF/Ag nanoparticles exhibited excellent fresh-keeping properties and have application in the preservation of fruits and vegetables.

2.5 3D printing

3D printing is an emerging technology that deposits material in a layer-by-layer manner using computer-aided design software [75]. This technology offers unique advantages in producing complex structures with high efficiency and low cost [76]. It has been extensively utilized to print plant-derived sustainable structures for a variety of applications, particularly, biomedical and biotechnology [77]. Combining 3D printing technology with nanocellulose, such as CNF-based inks, provides an appealing pathway for fabricating sustainable structures in many research areas, especially amid prevailing environmental and economic concerns [78-80]. Nanocellulose-based materials are mainly printed through extrusion-based AM and stereolithography (SLA). Material extrusion methods include fused deposition modelling (FDM) [81] and direct ink writing (DIW) [82]. In FDM, materials are typically in filament form, which is melted and extruded through a hot nozzle [83]. In contrast, DIW involves extruding viscoelastic ink material through a deposition nozzle to fabricate a 3D structure layer-by-layer. Once extruded, the ink solidifies over time to form the desired structures [84]. CNF-based inks are particularly well-suited for 3D printing, thanks to their excellent rheological properties including strong shear-thinning properties and high zero-shear viscosity. These inks can act as effective rheological modifiers, ensuring optimal viscoelastic properties for extrusion-based printing [85].

Despite significant efforts being made in the 3D printing of nanocelluloses, a major challenge is the static nature of the printed structure, which limits their widespread use. Therefore, disruptive manufacturing technologies like 4D printing are anticipated to enable more efficient and dynamic customization of printed structures. These printed structures, in addition to their complex shapes, exhibit captivating features, including self-assembly, self-deformation, self-repair, and other functions by pre-setting their deformation scheme, enabling on-demand highly personalized structures [86]. Unlike traditional printed parts, 4D-printed components are dynamic and capable of movement within their structures [87]. Shape-memory materials, which include polymers, ceramics, and metals, are crucial in achieving these dynamic properties, with shape-memory polymers (SMPs) [88] being particularly promising for adaptable applications [89-91]. The development of lightweight and biocompatible materials, such as cellulose-based hydrogels, as well as nanocellulose including CNC and CNF [92], offer tailored and adaptable solutions for producing sophisticated geometric structural designs in novel green devices used in biomedical [93], soft robotics [94], and other applications [95]. Additionally, the electroconductive properties of cellulose-based ink can be enhanced by incorporating various nanoparticles such as graphene, carbon nanotubes (CNTs), and iron oxide particles [96-98]. However, only limited studies have discussed the 4D printing of naturally available materials [99-101]. A brief comparison between various synthesis techniques for fabricating CNC and CNF-based hybrid materials for achieving their smart functionalities is discussed in Table 2 along with their pros and cons.

3 Nanocellulose

Nanocellulose, a hydrophilic nanofiller, offers exceptional performance (referring to Fig. 4) due to its extensive chemical-modification capacity, stemming from its large surface area and unravelling physical, chemical, and mechanical properties [119,120]. Recognized as a feasible and sustainable alternative for environmental issues, nanocellulose boasts unique properties such as nontoxicity, biodegradability, high aspect ratio, surface reactivity, and high specific modulus [121-123], making it suitable for a wide range of applications. These applications include catalysis, energy storage devices [124], textiles [125], regenerative medicine, tissue engineering scaffolds [126], surface coatings [127-129], paper production, drug delivery [130], food packaging [131], and membranes [132]. Nanocellulose is typically extracted from cellulose fibers, a naturally available plant source [133-135], which contain both ordered (crystalline) and disordered (amorphous) regions of chain molecules (Fig. 5). Each type of nanocellulose, including CNC, CNF, and BNC, needs various methods of isolation and mechanical or chemical treatments, which also determine their distinct properties [136-138]. These processes typically include ultrasonic technique, high-pressure homogenization [139], cryocrushing [140], micro-fluidization [141], grinding [142], 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)-mediated oxidation [143], and biological treatment [144], like enzyme-assisted hydrolysis [145,146]. Among them, sulfuric acid hydrolysis with ultrasonication is commonly used to produce nanocellulose, resulting in highly negatively charged suspensions with significant colloidal stability [147]. Nanocellulose is also used as a filler in various synthetic and biopolymers, including polyester, rubber, polyurethane, polyolefin, epoxy resin, PLA, PCL and other polymer matrices [148]. Other treatments, such as urethanization, silylation, and polymer grafting, are sometimes required to improve the

Table 2

Overview of recent manufacturing techniques for nanocelluloses.

Manufacturing technique	Advantages	Disadvantages	Ref.
Melt Compounding	• Scalability • Cost-effective • Processing speed • Wide range of polymers • Energy efficiency	• Thermal stability • Limited control over CNF distribution and orientation • Potential agglomeration • Polymer degradation	[102-104]
Solvent Casting	• Homogenous CNF dispersion • Flexibility in material selection • Suitable for high aspect ratio CNFs • Low processing temperature • Control over CNF orientation	• Solvent handling • Energy-intensive solvent removal • Potential polymer-solvent interactions • Limited scalability • Difficulty in higher CNF contents	[105-107]
In-Situ Polymerization	• Improved CNF dispersion • Strong interfacial adhesion • High CNF concentrations • Simplified processing • Reduced agglomeration	• Complex reaction control • Polymer degradation • Limited scalability • Complex process optimization • Longer processing times	[108-110]
Pickering Emulsion	• High stability • Control over CNF distribution • Versatility • Reduced agglomeration • Potential for green chemistry	• Complex process optimization • Limited to certain polymers • Scale-up challenges • Energy-intensive • Potential for particle sedimentation	[111-114]
3D Printing	• Meticulous surface finishing with superior accuracy • Convenience in building large structures. • Application of a series of materials • Simple setup • Low cost • Easy enhancement in multiple properties	• Minimum feature size limited by nozzle diameter and material properties. • Limited resolution • Difficulties in Ink preparation • Post-processing is needed to remove moisture. • The rough or grainy appearance	[115-118]

mechanical properties of hydrophilic nanocellulose, which tends to aggregate within hydrophobic matrices such as PLA [137,149,150].

3.1 Cellulose nanocrystals

CNCs, also known as cellulose nanowhiskers (CNWs) or nanocrystalline cellulose (NCC), are stiff and spindle-shaped crystalline nanomaterials with high aspect ratios and crystallinity ranging from 54% to 88% [156-159]. CNCs are mainly produced from abundant biomaterials extracted from various resources using acid hydrolysis, which removes the amorphous regions of cellulose while crystalline regions remain intact [160,161]. CNCs also hold excellent mechanical properties such as stiffness (10–100 GPa) and strength (300–6000 MPa), making them suitable for sustainable composite development [162-165]. In recent years, CNCs have found extensive use in 3D printing, often combined with renewable biopolymers such as hydrogels, PLA, PVA, and PCL at concentrations ranging from 0.1% to 10% [166-169]. However, CNCs often require surface modification before use due to their hydrophilic nature [170].

Numerous studies have reported on the use of pristine CNCs in photocurable resins for vat photopolymerization techniques like SLA and DLP, and as a nanofiller in liquid monomer mixtures for other printing processes [171-173]. For instance, Latif et al. [174] produced extrusion paste using high-concentration CNC (~25.94 wt.%) cross-linked with citric acid (CA) contents, as depicted in Fig. 6. The results indicated that the CNC/CA-based 3D-printed structures exhibited excellent flexural strength, particularly when the paste contained CNC:CA: CNF in a ratio of 20:2:1.

3.2 Bacterial nanocellulose

Nanocellulose synthesized by bacteria was first proposed in the 1990s by Watanabe et al. [175]. It is a biopolymer with a highly crystalline linear glucose polymer and has a wide range of properties, as depicted in Fig. 7A, such as purity, conformability, highly porous nature, water-holding capacity, and high thermal and mechanical stability. BNC can also cross-linked with other components to tune its properties and enhance its bio-functionality, owing to the abundant hydroxyl groups in its structure [176]. It is mainly synthesized by the bacterium *Gluconacetobacter xylinus* (also named *Acetobacter xylinus*), as well as some other bacteria species such as *Agrobacterium tumefaciens, Gluconacetobacter, Rhizobium spp.*, and *Gram-positive Sarcina ventriculi* [177]. However, the broader economic significance of the BNC is still dependent on breakthrough developments in production technology [178]. BNC also has many tissue-like properties, such as biocompatibility, shapeability, and water retention capabilities, which pave the way for various biomedical

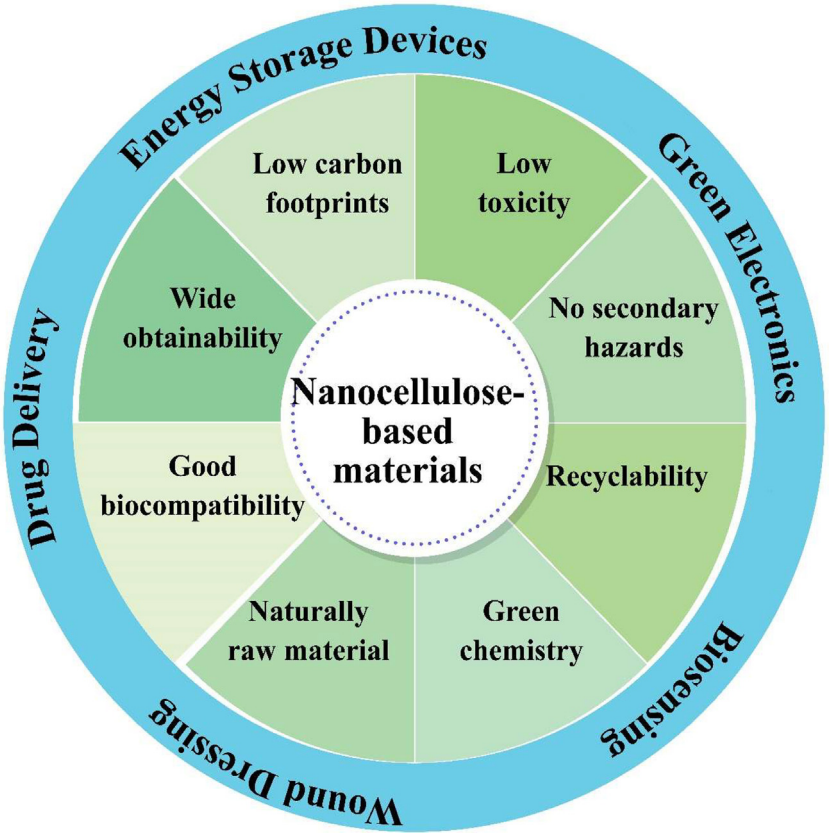

Fig. 4

Nanocellulose materials with satisfying properties for exciting biomedical applications (Figure drawn with the help of Ref. [151]).

applications such as wound healing and tissue regeneration [179]. Abdollahi et al. [180] recently prepared BNC membranes having excellent repellency properties from *Gluconacetobacter hansenii* bacteria cultured in Hestrin–Schramm (HS) medium for three weeks. The BNC membranes were flash-frozen with liquid nitrogen and then freeze-dried to achieve highly porous structures and mechanical properties.

3.3 Cellulose nanofibers

Different terms are associated with the different cellulose states. As per the Technical Association of the Pulp and Paper Industry (TAPPI), the four most used forms of cellulose, also highlighted in Fig. 7B, are described as cellulose microcrystalline (CMC) produced by hydrolyzing cellulose with a diluted mineral acid having spherical or rod-like particles. Next microfibrils of cellulose (CMF) are obtained from purified cellulose pulp with multiple aggregates due to large mechanical refinement, which typically ranges from 500 to 2000 nm in length and 20 to 100 nm in width [181]. Generally speaking, CMF serves as a broad category for cellulose nanofibrils (CNFs), also named nano-fibrillated cellulose (NFC) nanofibers, cellulose nanofibers, and aggregates of fibrils [182]. CNF is a type of nanocellulose with a width of 5–30 nm, a length of less than 1000 nm, and an aspect ratio greater than 50. CNF is composed of semicrystalline structures with a mixture of both amorphous regions and crystalline regions and is typically manufactured using various mechanical processes [183].

CNFs are usually long, wide, and flexible nanofibers entangled in a network structure and extracted from abundant available vegetal or bacterial cellulose sources [184-187]. Despite the myriad of advantages in the controlled synthesis of nanocellulose, current synthesis procedures for the CNF usually need long reaction times and harsh conditions. Effective CNF fabrication involves mechanically defibrillating cellulose pulp using high-pressure homogenizers, disc ultra-refiners, or high-pressure microfluidizers. [188]. Table 3 provides dimensions of various extracted CNF materials from different natural resources. CNF can also improve the mechanical properties of other biopolymers, such as PLA, due to its higher crystallinity and fewer defects [189]. Recently, Cai et al. [190] showed that tannic acid-reinforced CNF composites can be exploited as all-water-based high-performance wood adhesives. Latif et al. [191] studied a facile technique for producing extrusion paste using CNC and CNF for 3D printing, yielding highly concentrated CNC/CNF paste with excellent mechanical properties as depicted in Fig. 8. Table 4 offers a brief comparison of various nano-cellulosic materials.

4 Synthesis of cellulose nanofibers

The synthesis of CNFs can be broadly categorized into two main methods. The first method involves the use of intensive shear forces to break the van der Waals interactions and hydrogen bonds between the original cellulose fibers [207]. The second method entails the isolation of CNFs from various raw pulps

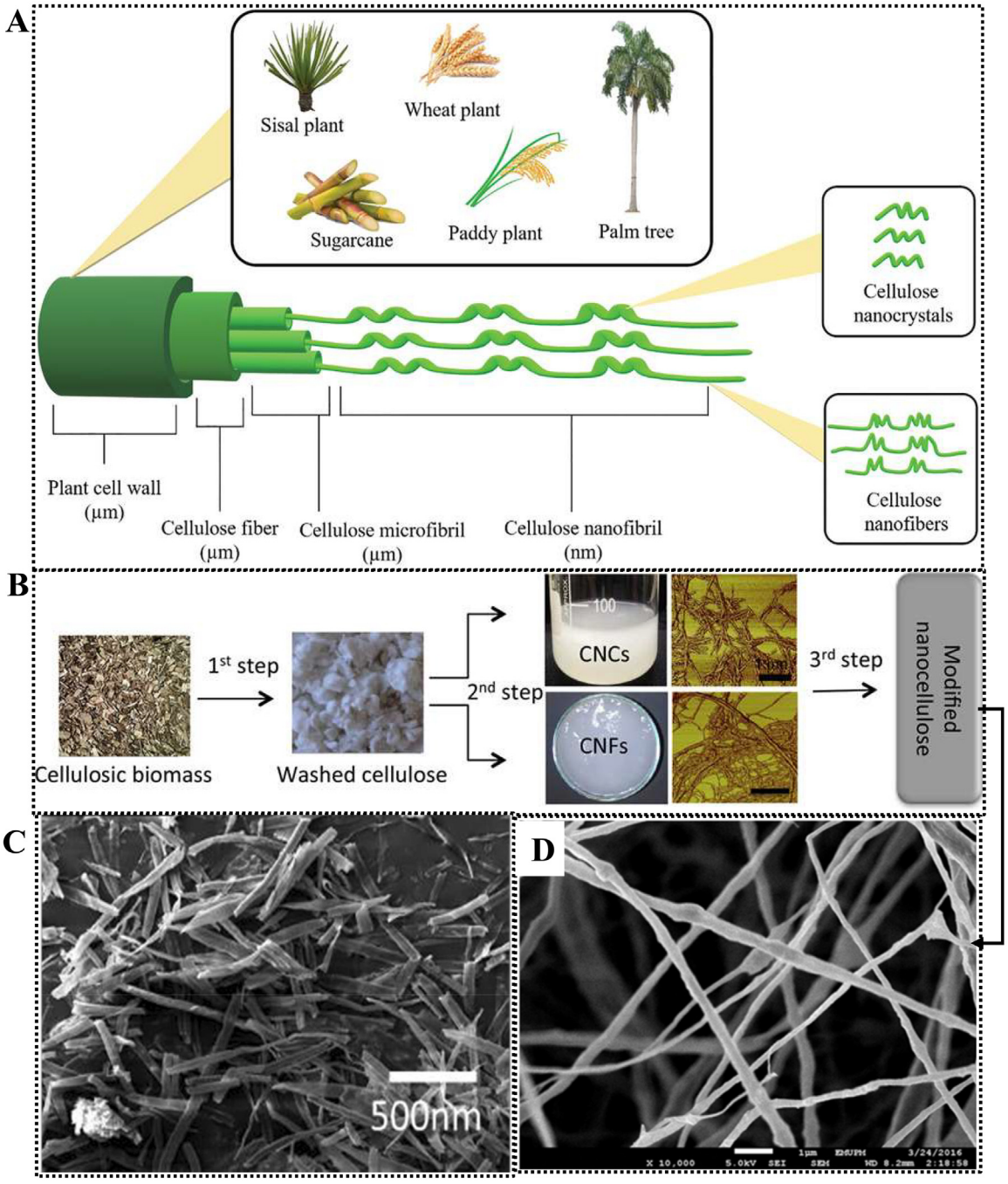

Fig. 5

A) Nanostructure of cellulose extracted from plants in the form of cellulose CNC and CNF (adapted from Ref. [152] copyright 2021 Wiley-VCH GmbH), B) Three main steps are involved in the isolation and modification of nanocellulose; step one involves extracting cellulose from cellulosic biomass; step two involves isolating CNC and CNF; step three involves using enzymes to modify/functionalize the isolated nanocellulose (adapted from Ref. [153] copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim), C) Scanning Electron Microscopic (SEM) images of CNC particles with 84.91% crystallinity obtained via acid hydrolysis (adapted from Ref. [154] under a Creative Commons Attribution License 4.0 (CC BY-NC)), D) The SEM micrographs of CNF through ultrasonication (10,000x magnification) (adapted from Ref. [155] under a Creative Commons Attribution License 3.0 (CC BY)).

using chemical pretreatment, followed by traditional mechanical methods such as homogenization, grinding, and ultrasonication processes [208,209]. The ultrasonic process is used to separate the nanofibrils from the remaining purified nanofibers. Additionally, relatively new mechanical methods, such as thin screw extrusion, steam explosion, subcritical water hydrolysis, and cryo-crushing, are employed to achieve CNFs with superior physical and chemical properties [210-212].

4.1 Pretreatment

The role of various pretreatments is highly promising in the effective synthesis of CNFs, including deep eutectic solvent

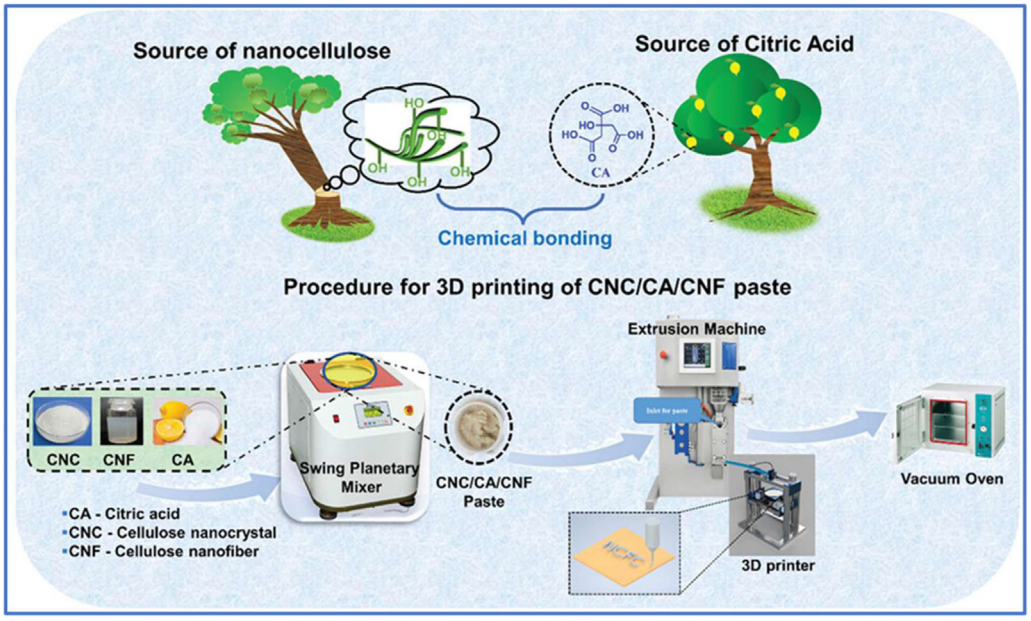

Fig. 6

Schematic diagram explaining the procedure for 3D printing of CNC/CA-based 3D structures (adapted from Ref. [174] copyright 2022 Wiley-VCH GmbH).

Table 3

Dimensions of CNF from various natural resources.

Natural resources	Type of Nanocellulose	Nanocellulose dimensions from various sources		Ref.
		Crystallinity (%)	Diameter (nm)	
Wood derived	CNF	85.3	6.6 ± 1.9	[193]
Sugar beet pulp	CNF	62.3	22	[194]
Coconut residues	CNF	29.20-76.70	70-120	[195]
Sugarcane bagasse	CNF	61.1	6-100	[196]
Banana peel/bract	CNF	75.8	73-89	[197]
Alfa fibers	CNF	-	5-12	[198]
Pine sawdust	CNF	66.1	5-40	[199]
Allium cepa L. Skin Biowaste Food Residues	CNF	-	10.61	[200]

Table 4

Comparison of various nanocelluloses.

Types	Commonly employed source	Extraction Procedure	Dimensions	Properties	Commonly employed Applications	Ref.
CNC	Tunicin cotton, bark of mulberry, and wood.	Acid Hydrolysis	Length =100–3000 nm, Diameter = 3–50	Longer length and high crystallinity	• Biosensors • Energy Storage • Food industry	[162,201,202]
CNF	High plants such as potato and sugar beet	Mechanical synthesis	length = several mm 5 nm < d < 60 nm	Network structured nano-scaled fibers and high crystallinity	• Food industry • Biomedical sector	[164,203,204]
BNC	*Gram negative bacteria*	Bacterial synthesis	20 nm < diameter < 100 nm	High aspect ratio	• Wound healing • Biomedical applications	[205,206]

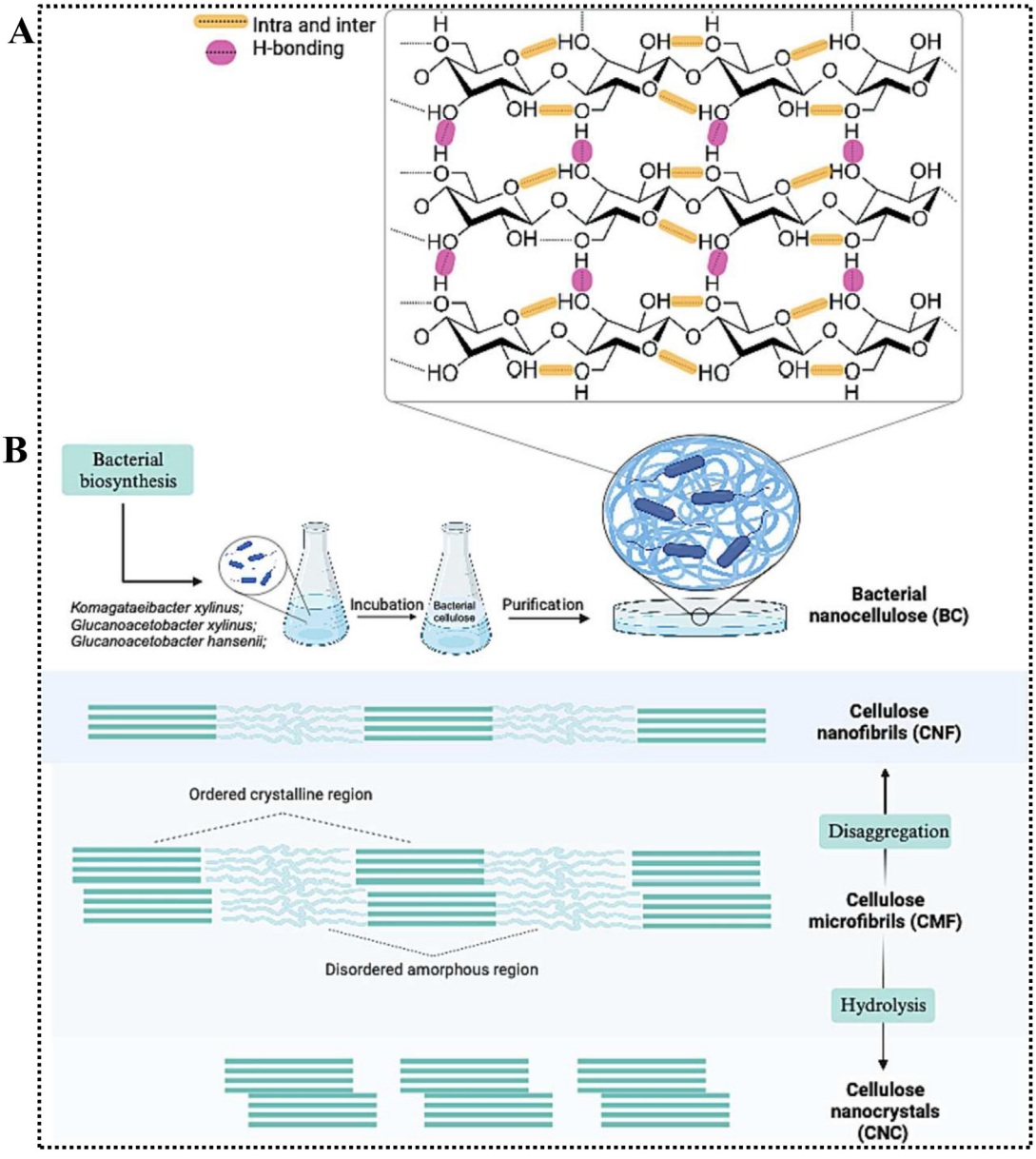

Fig. 7

A) Chemical structure of nanocellulose, pink spheres of hydrogen bonding revealing typical segments for surface modifications, B) nanocellulose featuring the structure-properties relationship characteristic of four nanocellulose obtaining methods (A, B are adapted from Ref. [192] copyright 2024 Elsevier B.V.).

(DES) pretreatment, solvent-assisted, ionic solution, enzymatic pretreatment, and TEMPO etc. These pretreatment processes, combined with numerous mechanical methods, enhance swelling capacity and hydration while lowering the overall energy requirement. Generally, oxidation and ionic solutions are adopted for CNF to improve their chemical and thermal stabilities and to reduce their vapor pressure. Through oxidation, various negatively charged groups, including carboxyl and carboxymethyl, can be incorporated into cellulose, particularly with methods like TEMPO, carboxymethylation, cationization, and other oxidation processes.

4.1.1 TEMPO oxidized CNF

As early as 2006, Isogai et al. first reported an effective process for obtaining individualized CNFs from native wood cellulose fibers by TEMPO-mediated oxidation in aqueous conditions [213]. Since then, TEMPO-mediated oxidation has garnered significant attention for various raw cellulosic pulp materials, leading to the synthesis of TEMPO-oxidized cellulose nanofibers (TOCNFs) that are now commercially available. TEMPO is water-soluble and contains stable nitroxyl radicals. During the TEMPO-oxidized reaction, the C_6-hydroxyl groups on cellulose surfaces are selectively oxidized into C_6-carboxyl groups by

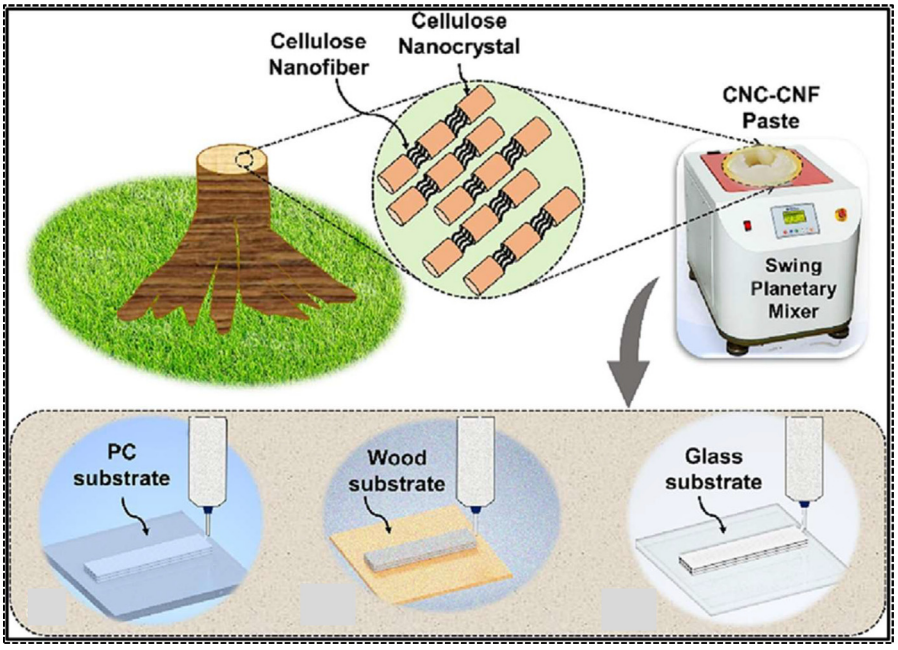

Fig. 8

3D printing process for highly concentrated CNC/CNF-based structures (adaptedfrom Ref. [191] copyright 2023 Elsevier Ltd.).

hypobromous acid (HBrO) or hypochlorous acid (HClO) under mild conditions, forming aldehyde and carboxyl groups. These deprotonated carboxyl groups (-COO^-) negatively charge the fiber surface, weakening the van der Waals interaction and hydrogen bonding between fibers [214]. Typically, TOCNFs have an average carboxylate content of 1.7 mmol/g, especially when derived from wood. They exhibit excellent crystallinity (65–95%), widths of 3–5 nm, large aspect ratios (>50), excellent zeta potential in aqueous solution (-75 mV), preserved highly natural crystalline nanostructure, impressive tensile strength (200–300 MPa), and dispersion as individual nanofibrils in water [215]. Li et al. [216] employed TEMPO-oxidized CNFs as phenyl propylene ketone ether nanofillers for both hydrophobic PCL and hydrophilic PVA-based composite films using the hydrosetting method. The resulting composite films obtained from sustainable materials can be utilized for applications in the field of ultraviolet (UV)-shielding, providing almost 100% UV shielding.

4.2 Mechanically treatments

Mechanical treatments can directly extract CNFs from wood fibers using various methods, including high-pressure homogenization, ultrasonication, ball milling, and microjet homogenization, as summarized in Fig. 9. In ultrasonication, CNFs are obtained through the cavitation effect generated by high-intensity ultrasonic waves, which disrupt the internal structure of cellulose fibers. Recently, Wang et al. [217] utilized a twin screw extruder to produce PP-based NFC nanocomposites and observed improved NFC dispersion within the PP matrix when the screw speed was varied from 200 to 1000 RPM. An increased screw speed resulted in higher shearing force, leading to improved NFC dispersion. Likewise, Rahmi et al. [218] developed CNF from mechanically isolated lignocellulosic oil palm empty fruit bunches to demonstrate the potential application as a particle stabilizer for Pickering emulsion. Insight of this study demonstrated an ultrafine grinding-ultrasonication combination process was employed for obtaining high-quality CNF having a degree of crystallinity of 66.75%, diameter of 54.80 ± 0.85 nm and a potential zeta value of -40.77 ± 1.05 mV. Ultrasonication was performed for 30-60 minutes under 20 kHz frequency and an amplitude of 80%. Moreover, CNF 0.5% (w/v) was optimized as oil and water emulsion particle stabilizer with a combination of ultra turrax homogenization at 9,500 RPM and ultrasonication produced 7.78 ± 0.71 μm emulsion droplets.

4.2.1 High pressure homogenization

High-pressure and microjet homogenization are used to convert microfibers into nanofibers, achieving high-quality CNFs under a microfluidizer or homogenizing machine. These high-pressure and high-speed machines induce turbulence effects based on cavitation and shear hysteresis. However, such processes have some negative effects, such as clogging, the need for long fibers as the raw material and high energy consumption.

Recently, Yao et al. [220] prepared CNF films using high-pressure homogenization and vacuum filtration processes from commercial microcrystalline cellulose (MCC), as highlighted in Fig. 10. They demonstrated that increasing homogenization pressure (1000 bar) and number of cycles (15 cycles) improved various characteristics of the CNF films, such as dispersion stability of CNF suspensions, aspect ratio (87.8), hydrophilicity, air barrier property (4.8 μm/Pa·s), mechanical properties (tensile strength of 67 MPa), and zeta potential (– 23.9 mV). Overall, this study offered an interesting approach for producing highly effective and eco-friendly CNF films with exceptional performance, rendering them attractive for biodegradable packaging applications.

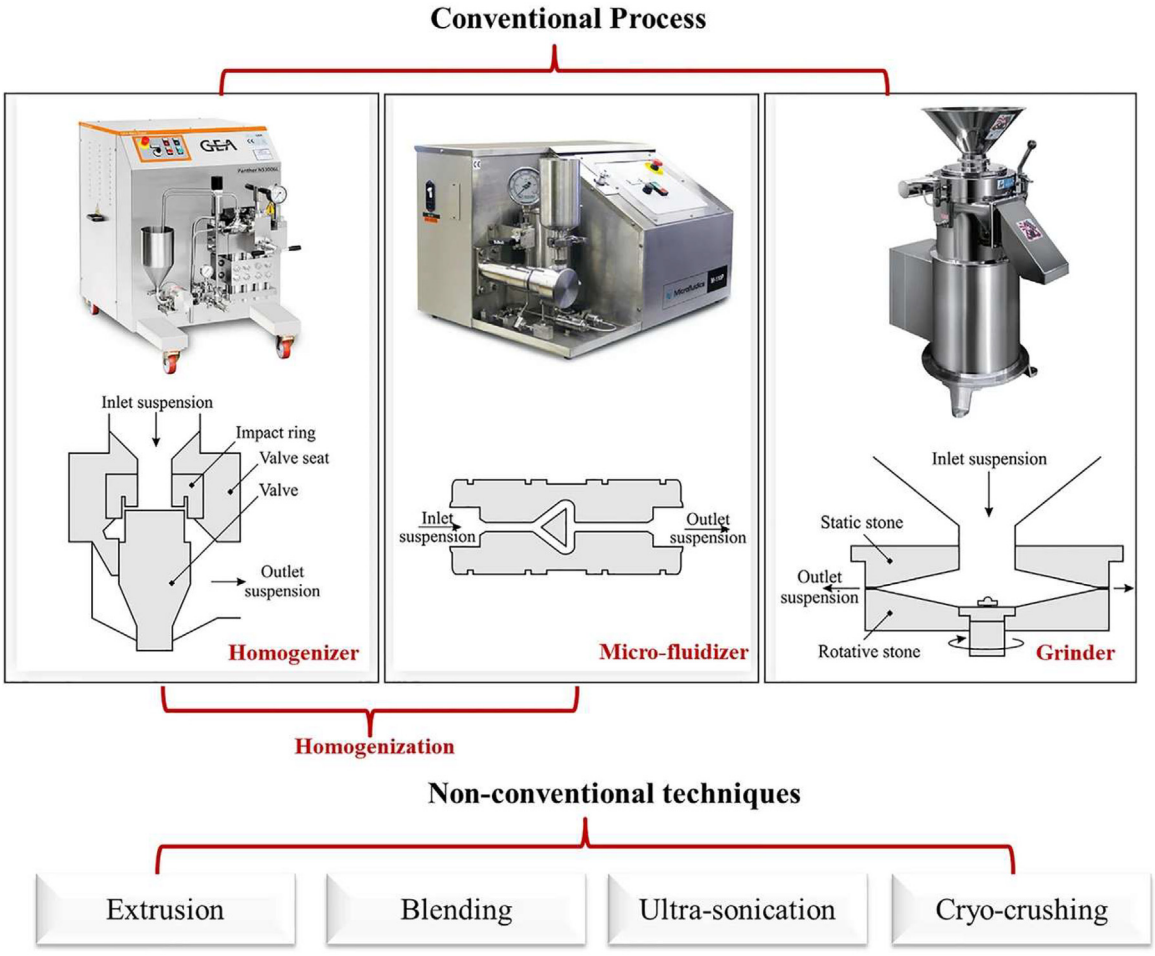

Fig. 9

Overview of various mechanical processes for CNF production [219] (photographs were adapted through www.niro-soavi.com, www.microfluidicscorp.com, and www.masuko.com).

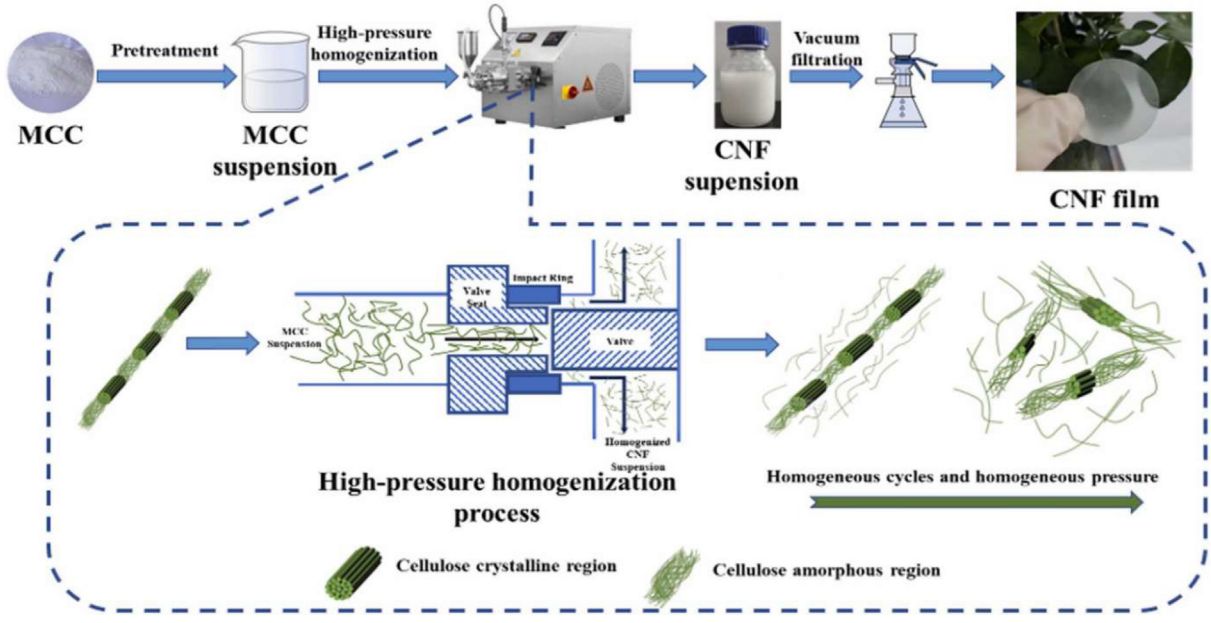

Fig. 10

The process for preparing CNFs and CNF films (adapted from Ref. [220] copyright 2023 Elsevier B.V.).

4.2.2 Grinding

The grinding process involves moveable and fixed discs where cellulose materials are fed to obtain large and smooth CNFs with high efficiency, low-energy requirements, and reduced susceptibility to clogging. However, CNFs obtained from the grinding process may have poor physical strength, damage the fiber structure, exhibit low crystallinity, and lower thermal stability at times [221]. Supian et al. [222] extracted CNF from empty fruit bunch for developing high-end products through novel nano-grinding treatment. Moreover, the cellulose produced was wet grounded using a Fritsch Pulverisette 7 nano-grinder at 722 rpm with 5% (w/v) fibers to water ratio for developing high-quality CNF at 30 min of grinding time. Also, the chemical compositions of the CNF remain unaffected through the proposed nano-grinding treatment as revealed by spectroscopy comparison between the cellulose and the CNF and the thermal stability of the cellulose and CNF was the same as demonstrated by thermal analysis. Similarly, Costa et al. [223] isolated CNF from sweet sorghum bagasse using a nano-grinding treatment in combination with a chemical process. It has been shown that cellulose fibers were fibrillated with six various distances of gap in a grinder (from zero position): -10; -30; -50; -70; -90; and -110 µm with 5 passes in each gap using this ultrafine grinder. Furthermore, micro images revealed an impressive diameter of 22.4 nm for the proposed CNF with excellent crystallinity of 57.25% using a proposed ultrafine grinder (110 µm).

4.2.3 Ball milling

In ball milling, celluloses are crushed between the balls inside a hollow cylinder container. This process generates a strong shear force that breaks the hydrogen bonds and van der Waals interaction forces between cellulose molecules, leading to the individual separation of cellulose fibers [224]. Ulaganathan et al. [225] prepared CNF suspension through ball milling and CNF/PVA film prepared using mixing and mechanical stirring. The reported results showed that ball milling was performed in the planetary ball mill at 300 rpm for 0.5 to 8 hours. After that cellulose slurry was repetitively washed with distilled water and centrifuged at 12000 rpm for 0.5 to 3 hours. Besides this ball milling ensures better interaction of CNFs with PVA polymer lattice by uncovering more hydroxyl bunches on the surface for potential application in food packaging. Likewise, Nassrullah et al. [226] studied the effect of adding CNFs to zeolite Y in a wet ball milling process. As demonstrated by the experiment the mixture was ball milled using an E_{max} ball mill (Retsch, Germany) at a speed of 1000 rpm for 30 min at 20–22°C. This work proved that the adsorption capacity of ball-milled particles for methylene blue significantly improved to 29.26 mg/g from 10.66 mg/g for the pristine Zeolite. Thus, CNF is highly effective in protecting zeolite Y particles and possibly other micro particles during ball milling.

5 Characteristics of smart CNFs and their hybrids

Here, in the section below, some noteworthy characteristics of CNFs are summarized.

5.1 Self-healing behaviour

As discussed above, cellulosic materials exhibit excellent physiochemical properties, including high flexibility and self-repairability in the case of damage (self-healing behaviour) [227]. Self-healing can be explained based on four criteria: localization, temporality, mobility, and mechanisms. Localization refers to the size of the damage that needs to be repaired. Temporality refers to the time-dependent nature of the self–healing process. These two criteria are indirectly linked; the ease or challenge of achieving temporality depends on the size of the damage (localization). Next is mobility, which refers to the ability of polymer chains or repair agents to move into the damaged area. This criterion is closely related to temporality. It is important to note that if there are more crosslinking points, the system is more restricted, and repairability may be challenging or may not occur [228]. Lastly, the mechanism (referring to Fig. 11) is crucial and is typically achieved through chemical reactions of pre-embedded healing agents in micro-containers, referred to as extrinsic self-healing, or dynamic reversible bonds in polymer networks, referred to as intrinsic self-healing, or maybe combinations of both (extrinsic and intrinsic) [229].

5.1.1 Intrinsic self-healing

Reversible chemical reactions involving dynamic covalent and non-covalent bonding in SMPs allow the topological network structure to undergo rearrangement, particularly under stimuli such as light, temperature, and humidity, as presented in Fig. 12. This enables materials to achieve intrinsic self-healing ability without the need for additional reagents. Borate ester bonds, imine bonds, disulfide bonds, acyl hydrazone bonds, Ru-Se coordination, and Diels-Alder (D-A) bonds are regarded as the main class of reversible covalent bonds, while, metal coordination bonds, hydrogen bonds, electrostatic interactions, ionic interactions, etc are considered as reversible non-covalent bonds [231]. The dissociation and association processes are considered the main mechanisms for realizing intrinsic self-healing processes [232]. In contrast, extrinsic self-healing depends on an external healing agent that can be confined within the elastomeric matrix using capsules or vascular networks. Intrinsic self-healing ability is achieved via the reversible D-A and retro-D-A reactions at higher temperatures, as well as non-covalent bonding with lower binding energy. This allows for highly efficient self-healing in SMPs, which can respond to external stimuli and induce automatic repair [233]. Self-healing behaviour from naturally available materials can be employed in various applications, including biomedical monitoring with intelligent drug delivery systems, structural safety, and tissue regeneration for wound healing, as summarized in Fig. 13.

5.1.2 Self-healing from naturally available materials

The self-healing feature is a fascinating phenomenon for many applications [235]. Integrating novel devices such as soft electronics and soft robotics (thoroughly discussed in the subsequent section) with the self-healing ability of materials will allow researchers to achieve noteworthy characteristics of these devices, including reliability and durability (automatically repair damages) [236-238]. Recently, Wei et al. [239] studied

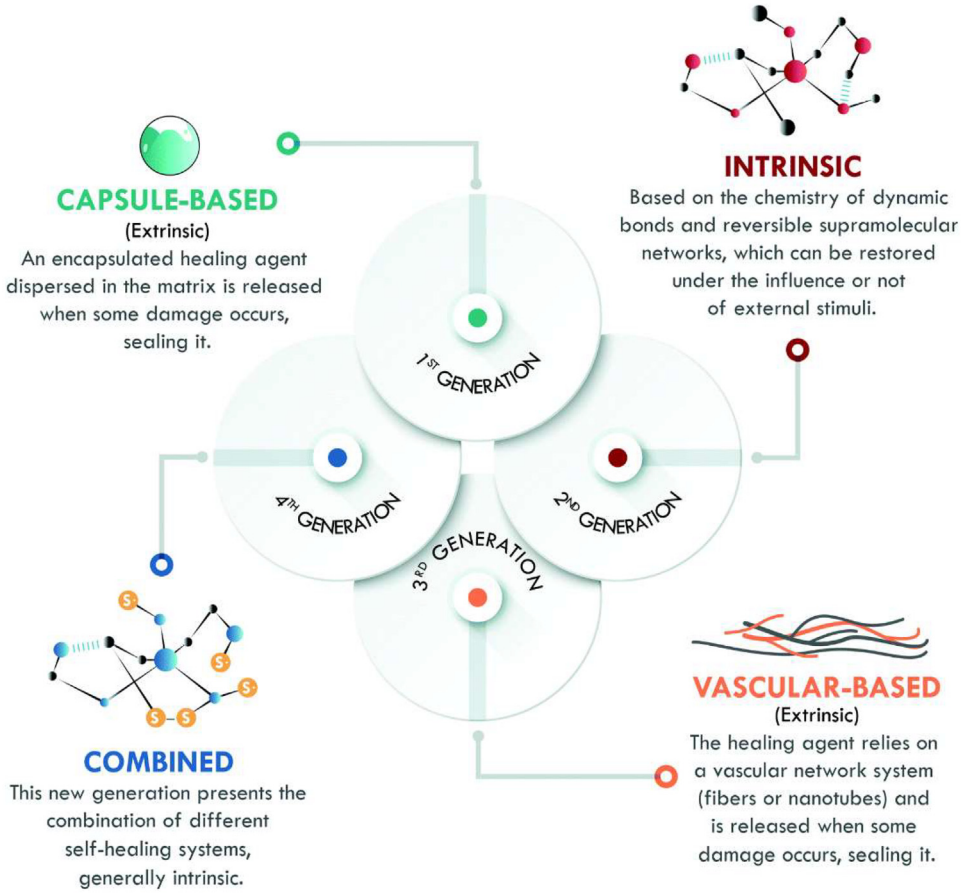

Fig. 11

Fourth generation of self-healing materials as per the healing mechanism involved (adapted from Ref. [230] under a Creative Commons Attribution License 3.0 (CC BY-NC)).

MXene/polyacrylic acid (PAA) and CNF alkaline treated, exhibiting printability and self-healing characteristics. These developed biocompatible conductive hydrogels displayed excellent properties such as self-healing (within 1s), sensitivity (gauge factor (GF) of 2.16), adhesion, recognition, and distinction, as presented in Fig. 14A. Thus, proposed CNF-based intelligent hydrogels are promising materials for many emerging applications, such as wearable multifunctional sensors, including vocal sensing, strain sensing, signature detection, and Morse code transmission. Zhou et al. [240] investigated CNC/fluorinated polyacrylate containing coumarin for achieving good oleophobicity, surface repair performance and hydrophobicity. Reported results showed that photo-responsive CNC demonstrated self-healing behaviour when the developed emulsion was coated on a fabric surface.

Wu et al. [241] studied novel poly(acrylic acid (AA)-N-vinyl-2-pyrrolidone (NVP))/carboxy methyl cellulose (CMC)-based hydrogels for printing ink. Insights of this study revealed that the printed hydrogels demonstrated excellent mechanical properties and self-healing characteristics, such as healed stress at 81% and healed strain at 91%, as illustrated in Fig. 14B. Various objects like manipulators were successfully customized using these novel hydrogels by photocurable 3D printing, having high toughness and complex structures and capable of performing a wide range of functions. Thus, developed 3D-printed high-performance hydrogels are promising materials such as flexible wearable sensors. Likewise, Wang et al. [242] fabricated CNF/poly deep eutectic solvent (PDES)-based conductive elastomers through DIW-based 3D printing. Therein maleic acid/choline chloride (MA/ChCl) was used for nanofibrillation and chemical modification of cellulose in the deep eutectic solvent (DES) systems. Results showed that 3D-printed CNF/PDES under UV light were used for signal detection and transmissions, as presented in Fig. 14C and were also suitable for monitoring human body motions through flexible sensors with excellent stability and sensitivity in the field of flexible sensing. Likewise, Juan et al. [243] produced highly self-healable CNF hydrogels and shape-memory cryogels from chitosan functionalized with an aldehyde group and synthesized as the crosslinker. Insights of this study showed that the proposed CNF hydrogels demonstrated high self-healing efficiency (~100%), as presented in Fig. 14D, and the cryogels (nanocellulose/chitosan 1:6) possessed thermally induced shape-memory properties.

Conductive nanocellulose hydrogels offer multifunctional platforms for diverse applications in wearable electronic devices, character recognition management and artificial intelligence

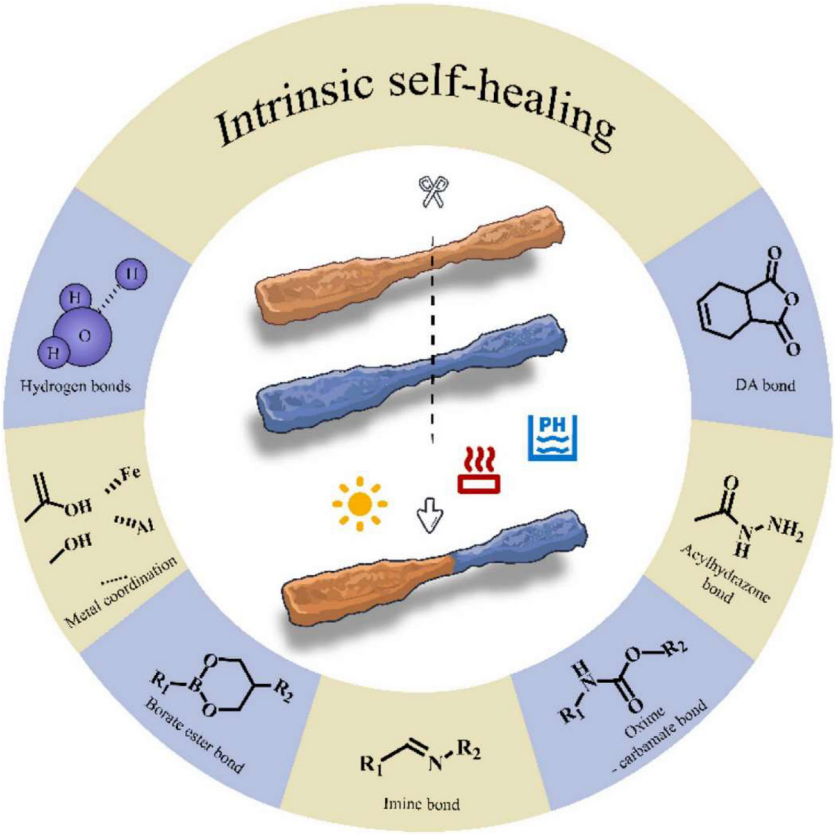

Fig. 12

Reversible dynamic bonds of intrinsic self-healing materials (adapted from Ref. [232] copyright 2023 Elsevier B.V.).

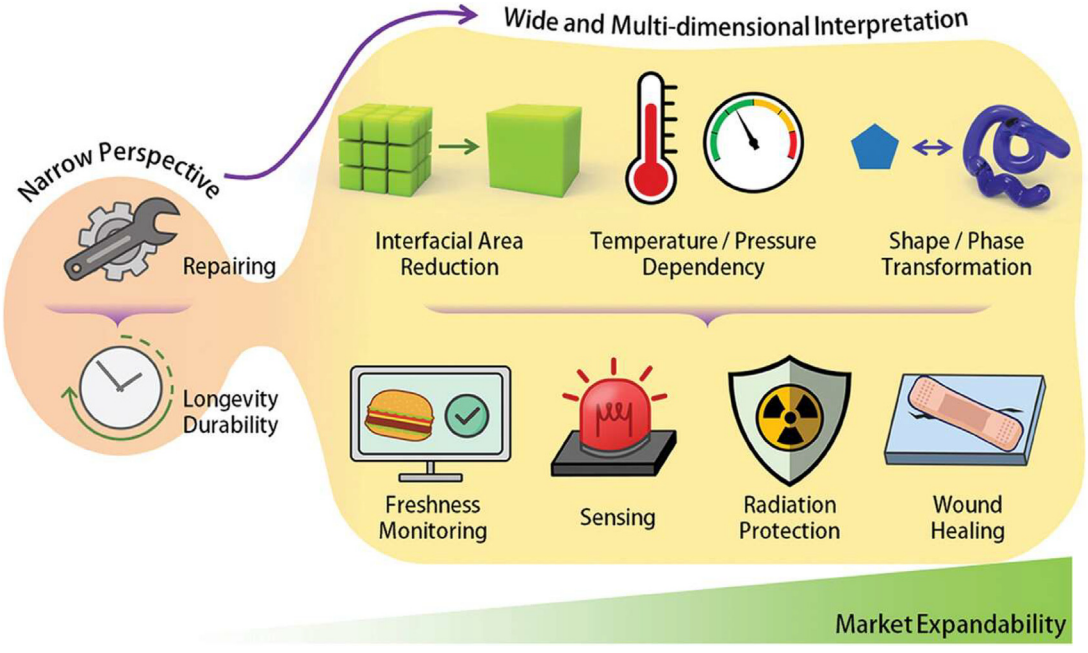

Fig. 13

Market expandability by application diversification based on multi-dimensional interpretation of self-healing behaviour (adapted from Ref. [234] under a Creative Commons Attribution License 4.0 (CC BY))

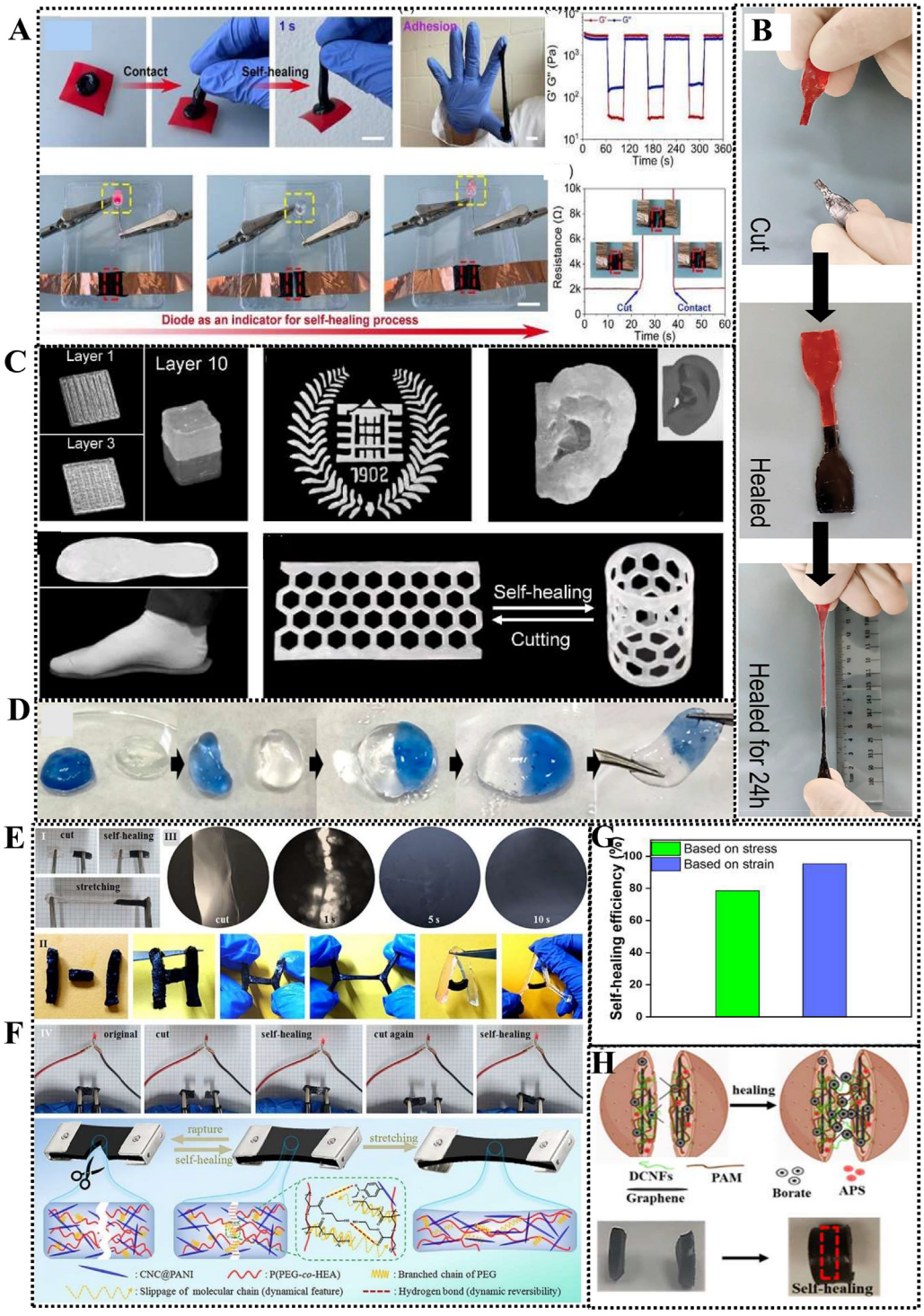

Fig. 14

A) Images of developed Ca-PAA-CNF-MXene hydrogel fast self-healing capability, and adhesivity cyclic strain sweeps of a prepared hydrogel. Self-healing behaviour of Ca-PAA-CNF-MXene hydrogels with a diode used as an indicator, and monitoring resistance change (in real-time)(adapted from Ref. [239] under a Creative Commons Attribution License 4.0 (CC BY)); B) Various characteristics and functions of CMC-based hydrogels such as self-healing process (adapted from Ref. [241] copyright 2021 Wiley-VCH GmbH); C) Images of layer-by-layer printing of cubes, 3D printed emblem of Nanjing Forestry University, ear model, and real-size shoe pad, a planar mesh shape changed into a 3D tubular through self-healing after 3D printing (adapted from Ref. [242] copyright 2022 Elsevier B.V.); D) Representation of self-healing behaviour such as cutting of two circular samples into semicircles and then placed together for 0.5 h followed by stretching of the healed sample by a pair of tweezers (adapted from Ref. [243] copyright 2022 American Chemical Society); (E) Images of self-healing property of CHP-0 hydrogel and CHP-1.5 hydrogel, self-healing process and change of diode brightness during cut-off and repair, (F) Demonstartion of self-healing mechanism of hydrogel in the cutting-healing process (E,F are adapted from Ref. [244] copyright 2024 Elsevier Ltd.); G-H) Self-healed PAM/DCNF/4B hydrogels (G) self- healing recovery of the hydrogel base on stress and strain (H) self-heling mechanism (G,H are adapted from Ref. [245] under a Creative Commons Attribution License 4.0 (CC BY)).

devices. Recently, Wang et al. [244] showed that free-radical polymerization of skeleton hydroxyethyl acrylate (HEA) and PEG methacrylate with polyaniline-coated cellulose nanocrystal (CNC@PANI) hydrogels were the best for strain sensing applications. This CNC@PANI hydrogel is highly enriched with multifunctionalities such as self-adhesive, high stretchable, self-healing, (95.04 % after 60 s), as presented in Fig. 14E and Fig. 14F. It also exhibited high strain sensitivity (GF = 1.68), low detection limit (0.5 % strain), and fast response time (96 ms) making it capable of operating in harsh environments for accurate handwritten numeral recognition.

Abouzeid et al. [245] achieved various multifunctional properties, such as excellent conductivity, self-healing, and strength, using dicarboxylic cellulose nanofiber (DCNFs)/PAM hydrogels. The addition of borax into DCNFs provided a superabsorbent feature to the DCNF/PAM hydrogels. Moreover, this hydrogel possessed high cycling stability (stable after 1000 compression cycles with 50% strain), highly sensitive response (GF= 1.36) in the strain ranges from 10 to 80% and superior compressive strength (132 kPa), as presented in Fig. 14G and Fig. 14H. Thus, the proposed hydrogel provides an idea for the realisation of functional CNF-based materials for human-machine interfaces for detecting various human (mechanical) motions accurately and reliably.

Abuallah and Okay [246] studied 4D-printed behaviour of poly(acrylic acid)-based hydrogels using a SLA technique in which water used as a stimuli medium. The shape-memory and self-healing characteristics of printed hydrogels were observed due to a reversible strong-to-weak gel transition temperature and melting and crystallization of the hydrophobic hexadecyl acrylate C16A domains, as presented in Fig. 15A, Fig. 15B and Fig. 15C. Furthermore, the 4D behaviour of printed hydrogel can be controlled near the body temperature by adjusting the molar ratio of the monomers. Xiao et al.[247] designed highly electro-conductive hydrogel (ECH) by incorporating CNC grafted phenylboronic acid (CNCs-ABA) and multiwalled carbon nanotubes (MWCNTs) into PVA. Insights of this study showed high healing efficiency (97.1%) as presented in Fig. 15D exhibited within 2 min relying on ultra photothermal effect of MWCNTs and reversible micro-crystallization with excellent conductivity 3.8×10^{-2} S/m attributed to the synergistic effect of MWCNTs and NaOH. Furthermore, a remarkable shape recovery (82.1%), and fixity ratio (78.2%), as presented in Fig. 15E, owing to pH-induced dynamic borate was also observed. Thus, all these characteristics of ECH hydrogel are widely attracted for strain sensing applications for monitoring human motion with fast resistance response to applied strain with remarkable biocompatibility.

5.2 Shape-memory behaviour

Emerging smart materials offer rational solutions for creating dynamically designed structures that can change their structures, colours, properties, or functions [248]. These dynamic features of printed structures are captivating for their active utilizations in soft robotics and biomimetic applications [249-251]. The effective utilization and importance of nanocellulose materials, due to their response to stimuli in various environments, are promising for achieving multiple shape-morphing behaviours for widespread applications in stretchable soft sensors and smart displays [252]. Self-folding, twisting, and bending are widely demonstrated as unique shape-memory behaviours of nanocellulosic printed structures [253-255]. For example, Tahouni et al. [256] proposed a co-design technique for 4D printing of hygromorphic structures through FFF. Two elements were incorporated into FFF: cellulose-filled filaments with different hygro-responsiveness, stiffness, and mesoscale structuring. Filaments were developed by compounding cellulose powder within two matrix polymers with low and high stiffness and mass ratios of 0–30%. Results showed that 4D-printed structures fully transformed into various shapes and could repeat their complete cycle, particularly at 35–90% relative humidity conditions. These conditions are similar to the daily and seasonal weather cycles. Furthermore, Mohan et al. [257] improved the shape-responsive performance of cellulose structures by adding a small percentage (0.5–2.0 wt%) of graphene nanoplatelet (GNP). These smart cellulosic structures demonstrated excellent shape-memory behaviour by reversible folding into cube and flat sheets under hydration and dehydration processes.

Shape-memory materials (SMMs) derived from nanocellulose, often referred to as sensitive or "smart" hydrogels, possess adjustable swelling and shrinking features. Nie et al. [258] achieved various superior properties such as flexibility, shape-memory properties, and recyclability of methyl-nadic-anhydride-modified ethyl cellulose (NEC)/epoxy castor oil (ECO) supramolecular composite films using supramolecular recombination and epoxy ring-opening esterification. Results demonstrated that incorporating ECO, transesterification catalyst, hydrogen bonds and reversible ester bonds significantly improved the shape-memory behaviour of NEC/ECO composite films. Ren et al. [259] examined infrared light-responsive PLA composites with 3 wt.% of LIG through 3D printing. The study revealed that printed structures demonstrated excellent shape-memory behaviour and photothermal effects under near-infrared laser irradiation. Additionally, these structures exhibited satisfactory mechanical and rheological properties. This proposed approach is expected to be promising for fabricating ideal actuator components for various applications. Müller et al. [260] investigated complex polyurethane acrylate structures reinforced with up to 15 wt% CNC using DIW printing. When the printed materials were exposed to visible light, Azobenzene photochromes grafted onto CNC surfaces showed a shape-memory behaviour, with 30%–50% reversible softening upon exposure to visible light. Additionally, the 3D complex structures responded to environmental stimuli through phototunable energy absorption. Therefore, printed structures reinforced by CNC show promise in areas where dynamic responses to environmental changes are required. It has been nearly a century since Olander Sweden first reported in 1932, the discovery of a new type of shape-memory material as gold–cadmium alloys. These alloys, when deformed, exhibited the ability to automatically revert to their original shape upon heating to a certain temperature [261]. In the 1940s, Vernon introduced the concept of "elastic memory" and in 1950, Charles discovered shape-memory behaviours such as shape recovery and fixation in a chemically cross-linked polyethylene under specific environmental stimuli [262].

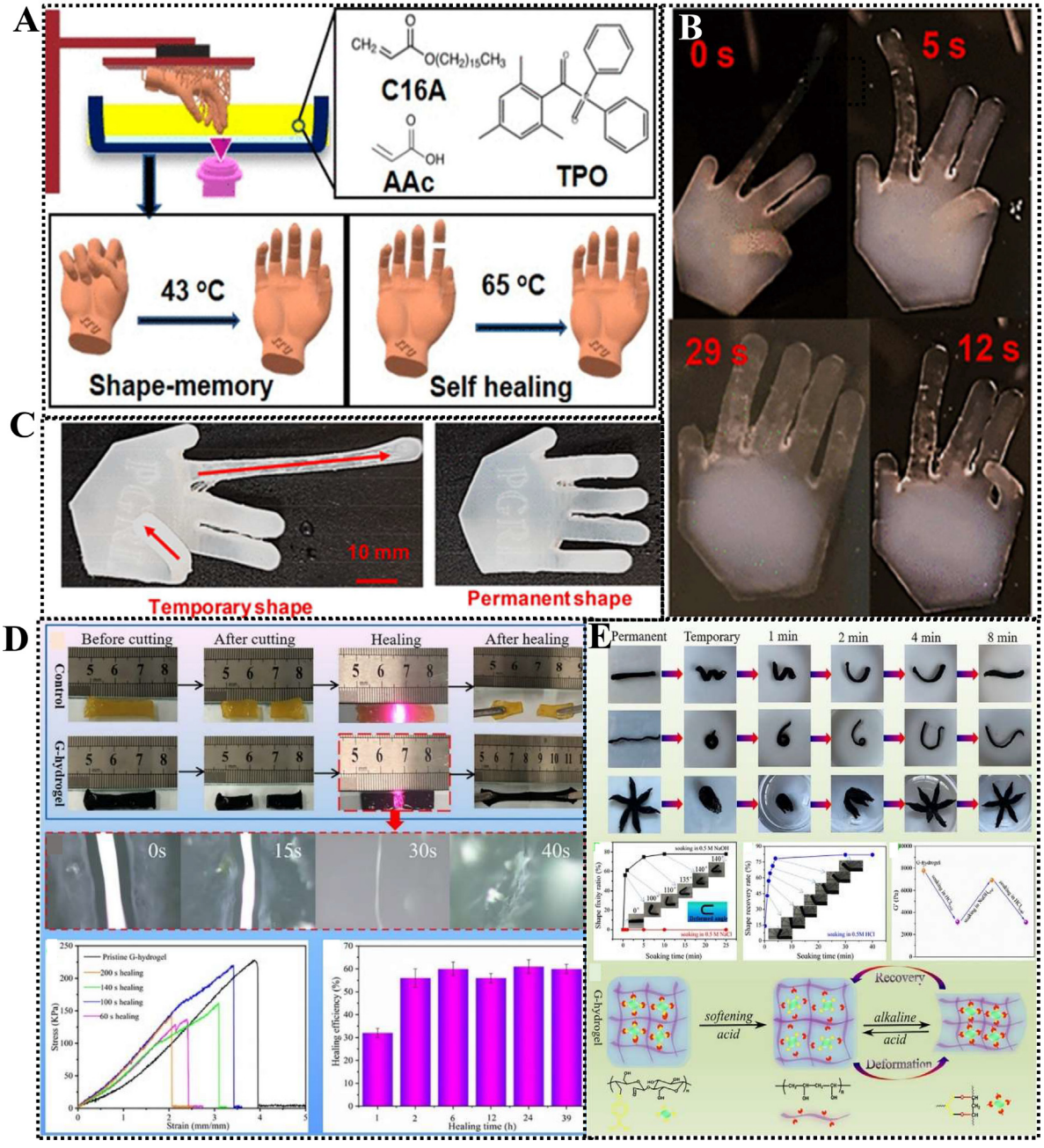

Fig. 15

A) Schematic diagram depicting shape-memory and self-healing characteristics of printed hand, B) Temporary and permanent shapes of a printed robotic hand, C) Shape-recovery behaviour in water at 43°C (A, B and C are adapted from Ref. [246] under a Creative Commons Attribution License 4.0 (CC BY)); D) Demonstration of healing mechanism and their healing efficiency under near-infrared (NIR) illumination, E) Images illustrating shape-memory process of hydrogel and their performance evaluation such as shape fixity ratios (Rf) curve and shape recovery ratios (Rr) curve under various soaking time in alkaline solution (D,E are adapted from Ref. [247] copyright 2020 Elsevier B.V.).

Stimuli-responsive materials, also termed smart materials, are designed to respond to one or more environmental stimuli. SMMs fall into this category and demonstrate the shape-memory effect (SME) [263]. The past two decades have witnessed tremendous growth in the understanding and utilization of shape-memory behaviour, particularly in soft materials such as SMPs, which are an important class of smart materials [264]. SMPs can be deformed into a temporary shape and later recover to their original shapes. They also exhibit quasi-plastic deformation under various external stimuli such as temperature, NIR light [265], electricity, magnetism [266], pH, chemical reagent, pressure, humidity, acoustic wave or combinations thereof. The type of SMP that has only one temporary shape perfectly describes the "one-way SME" of smart materials. Thanks to substantial efforts from researchers in developing more advanced SMPs, it is now entirely possible to achieve two-way SME (exhibiting two temporary shapes), three-

way SME (displaying three temporary shapes), and multiple-way SME beyond the simplest one-way SME. The two-way SME in SMPs is reversible and is triggered by external stress or internal stress developed by the skeleton phase during the cooling process and melting shrinkage of the crystallization region during the heating process, governed by two phenomena: melting-induced contraction and crystallization-induced elongation [267,268]. SMPs can be classified as thermosetting, and thermoplastic based on the crosslinking methods of the fixed phase. The reversible switch and stable polymer network of SMPs are the main features of the polymers that contribute to their SME [269-271]. The reversible switch is formed by crystalline-to-amorphous transitions, reversible chemical crosslinking, glass transitions, anisotropy/isotropy conversion, or supramolecular structure association/dissociation, giving rise to fixing temporary shapes [272-274]. Whereas the stable polymer network is composed of crystalline phase, molecular entanglement, chemical crosslinking, or interpenetrating network, determining the permanent shape of the polymer [275,276].

It is important to mention here that achieving multiple SMEs is possible due to several switching domains with narrow thermal transitions, particularly for thermally induced SMPs, or one switching domain in a SMP with a large thermal transition by incorporating various separate glass/melting transitions in the system with several polymeric functionalities [277-279]. Thus, multiple SMEs have more complex actuations and complicated requirements compared to two-way and three-way SMEs [280,281]. They are usually possible for bilayer polymers, copolymers, and polymer blends with well-defined and unique glass and melting transitions as switching elements [282]. As highlighted in Fig. 16A, a typical shape-memory process for an SMP begins with heating the temperature up to the transition temperature (T_{trans}) acting as an external force to mechanically deform and immobilize the SMP into the temporary shape. Subsequently, fixation of temporary shape occurs during cooling. This temporary shape only exists if the stimulus is maintained. Then, the SMP is able to recover to its original shape upon release of the stored energy of deformation during shape fixing while the temperature is increased up to T_{trans} [283]. As discussed earlier, dynamic covalent bonding in SMPs can be selectively and reversibly broken and later rejoined under temperature, catalyst, and light radiation, thereby realizing dynamic equilibrium under non-equilibrium conditions, as highlighted in Fig. 16B. These dynamic covalent bonds form a covalent adaptable network (CAN), vitrimer or thermoadapt polymer in reversible covalently crosslinked polymer networks. Thus, they are useful for preserving self-healing capability, SME, and reconfigurability [284].

5.2.1 *Programmed SMP materials*

Multiple SMEs allow SMPs to switch into various shapes under the stimulus, along with the relevant shape programming process, which comprises a set of independent and repeatable operation processes [287]. Therefore, a profound and in-depth understanding of the programmable shape recovery process can pave the way for many exciting opportunities with advanced properties [288]. As summarized by Yang et al. [285], the programming processes are mainly cold, hot and warm, as presented in Fig. 17A, and are dependent on the temperature range in which the shape programming is done. The temperature lower than T_{trans}, at which the temporary shape is fixed, is referred to as the shape-fixing temperature. Next is the shape-recovery temperature, which usually aligns with the shape-deforming temperature, at which the polymer chains regain mobility, and the material starts to revert to its original shape [289,290].

The ratio between the deformation after and before removing the external load during shape programming is termed as the shape-fixation ratio. The ratio between the recovered shape and the maximum deformation is referred to as the shape-recovery ratio. Lastly, the time duration needed for a SMP to regain its maximum possible recovery back to its original, permanent shape is represented as the shape-recovery time [271].

The shape programming processes involve activating polymer chains triggered by external stimuli, followed by deformation under load [291]. Subsequently, the stimulus is removed to fix the shape under the load, and then the load is removed to realize shape programming [292,293]. Thus, SMPs are deformed to the targeted temporary shape under sets of repeatedly programming procedures, typically at higher temperatures (greater than T_g), followed by fixation of the kinetically trapped state(s) upon cooling [294]. For instance, Guo et al. [295] combined both irreversible and reversible shape morphing processes to undergo shape-programming via the SME and subsequent reversible actuation of the programmed shape, as highlighted in Fig. 17. Insight of this study revealed that the proposed technique of combining reversible photo-actuation, (re)programmable shape, and environmental adaptability opens the door for novel applications such as responsive materials-based actuators. Interestingly, combining programming and stimulating smart materials is an exciting avenue that could bring shape-memory phenomena into new and exciting applications [296].

5.2.2 *Bio-based SMP*

Research on SMPs is generally classified into several areas: tuning molecular structures to meet new applications, exploring smoother and faster stimulation mechanisms tailored to specific applications, designing new molecular structures for 3D printing systems, and realizing the importance of more sustainable SMP materials with exciting multiple-way SME [297]. Currently, most SMPs are derived from non-renewable sources, raising significant environmental concerns. Therefore, bio-based SMPs (bio-SMPs) offer potential alternatives and feasible solutions. Bio-SMPs are typically plant oils, LIG derivatives, itaconic acid, vanillin PLA, polyhydroxyalkanoates and poly(butylene succinate) (PBS), as well as vegetable oils such as castor, linseed and soybean oils [298,299].

It is important to highlight that, in addition to their excellent shape-memory properties resulting from a unique combination of biobased building blocks and dynamic covalent chemistry, bio-SMPs offer ease of deformability, tunable T_{trans}, and excellent biodegradability. These properties make them particularly suitable for applications in wearable electronics and personalized health devices. Bio-SMPs benefit from water and temperature-based stimuli, which are widely praised by the scientific community

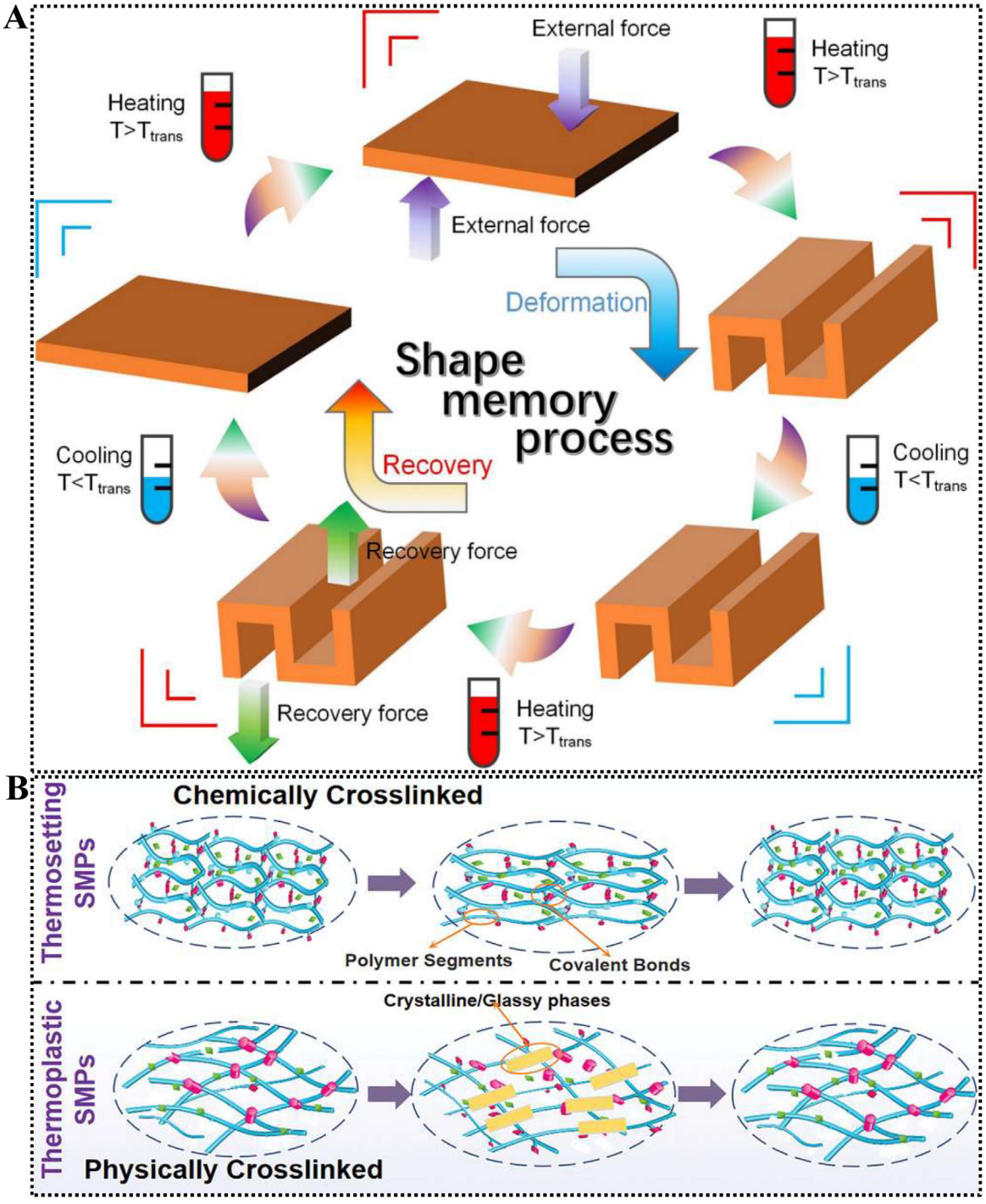

Fig. 16

A) Shape-memory process illustration for typical SMPs such as shape deformation above T_{trans}, shape fixation below T_{trans} and shape recovery above T_{trans} (adapted from Ref. [285] copyright 2023 Elsevier Ltd.]); B) Representation of shape-memory mechanism for both thermoset and thermoplastic SMPs (adapted from Ref. [286] copyright 2023 Wiley-VCH GmbH).

owing to some noteworthy advantages, compatibility with naturally biological materials, shape-memory behaviour that can easily monitored and controlled through the swelling and shrinkage for water-triggered bio-SMPs. Water-induced shape-memory function for nanocelluloses is particularly significant as it supports the development of multifunctional structures. Water-responsiveness is typically evaluated through bend-recovery test as well as the swelling effect which can release the internal stress and lead towards its recovery. Swelling decreases the relaxation time of polymer chains fully relaxed by the plasticizing effects of water molecules for the upcoming next generation of biomedical applications [300].

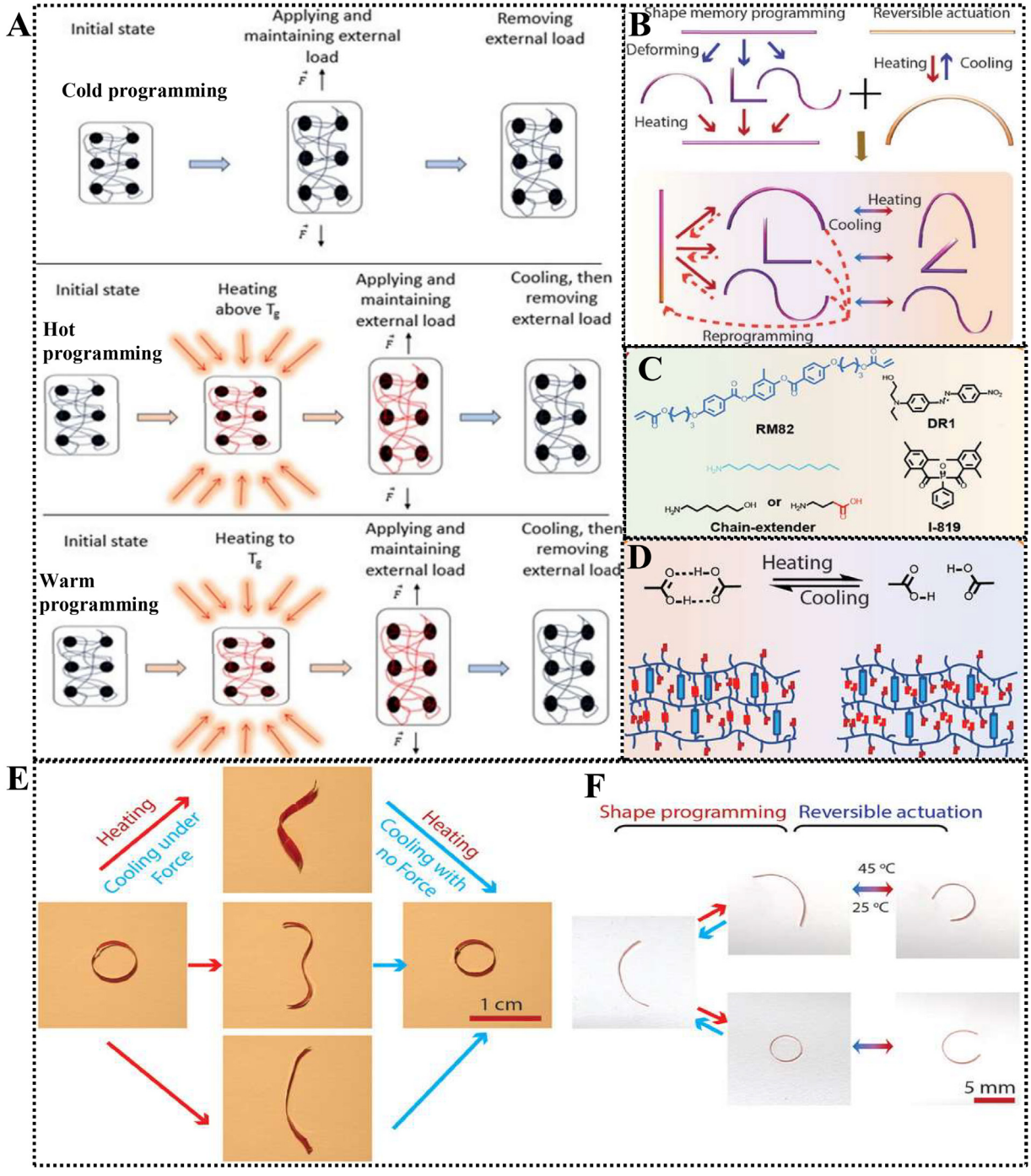

Fig. 17

A) Schematic representation of different programming of SMPs (adapted from Ref. [271] copyright 2024 Elsevier Ltd.); B) Schematic depiction of shape-memory programming combined with reversible actuation, C) The chemical structures of the materials used, D) The shape-memory programming depends on hydrogen bond breaking and reforming upon heating and cooling, respectively, E) Representation of shape-memory programming and reversible actuation ((B-E) are adapted from Ref. [295] under a Creative Commons Attribution License 4.0 (CC BY)).

On the other hand, most nanocellulose hydrogels are temperature-sensitive inherently where higher temperatures demonstrate disfavouring motif formation and accelerating its dissociation [301]. Recently, Garemark et al. [302] studied shape-memory function of bio-aerogels having the composition same as native wood fabricated through a one-step treatment of native wood (containing nanofibril networks) using an ionic liquid mixture of [MTBD]+[MMP]−/dimethyl sulfoxide (DMSO). Results showed that developed bio-aerogels exhibited strong shape-memory behaviour upon submerging into the water as these aerogels returned to their original shape in a repeated manner, as presented in Fig. 18A, Fig. 18B and Fig. 18C. These results

Fig. 18

A) Schematic diagram illustrating the hierarchy of natural wood and the one-step treatment to form highly malleable wood hydrogels (on the left side) and an aesthetic freeze-dried hydrogel aerogel like natural wood (On the right-hand side), B) Images of wood, twisted, its dry shape, shape-memory performance, and reshaped structure, C) Wrapped wood hydrogel around a glass cylinder and aerogel of helical shape, large wood hydrogel veneer, deformed state, and consequent dry hydrogel, with U-bend against fiber direction (A, B and C are adapted from Ref. [302] under a Creative Commons Attribution License 4.0 (CC BY)); D) Illustration of the thermal-activated shape-memory performance of the ionogel molded in a flower shape (dyed in red, top panel) and a strip (bottom panel) while green arrows illustrate the recovery process while orange arrows indicate the programming process (adapted from Ref. [303] under a Creative Commons Attribution License 4.0 (CC BY-ND)); E) Comparison of the shape-memory behaviour of developed films in an oven set at 82°C pure PVA (on the left side of each figure) and the PVA/10% CNCs depicting the faster shape recovery behaviour of PVA/CNC nanocomposites (on the right side of each figure) (from folded to straight shape) (adapted from Ref. [304] copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); F) Demonstration of SMEs of vanillin methacrylate and C13 methacrylate including hot-pressed flat sample, fixed shape #1; arrows are drawn on the edge of the sample to show the concave and later the sample was heated at ~70°C and deformed and after ~5 min cooled, after heating "Fixed" sample #1 was recovered with a heat gun in less than 1 min, the shape "Fixed" shape #2 was changed to concave up while applying a load for 3 h by heating the samples to 125°C, After heating "Fixed" shape#2 with concave up was recovered with a heat gun in less than 1 min (deformed and fixed shapes were stable at for at least 48 h room temperature) (adapted from Ref. [305] copyright 2023 American Chemical Society); G) Proposed mechanism for multi-stimuli responsive shape-memory (adapted from Ref. [306] copyright 2024 American Chemical Society).

successfully shed light on simple, sustainable, and biobased shape-memory aerogels which can open the door for many engineering applications from renewable resources. Shan et al. [303] reported shape-memory and self-healing performances of ionogels from UV-assisted DIW printing technique by mixing nanocrystalline celluloses into ionic liquid. The insights of this study showed that developed ionogel exhibited superior mechanical properties such as toughness (~34 kJ m^{-2}), Young's modulus (~44 MPa), and stretchability (~870% strain) and offered as multifunctional platforms for high-performance soft grippers, and temperature sensors bestowed with excellent shape-memory behaviour, as presented in Fig. 18D, and self-healing ability.

Similarly, Farina et al. [304] prepared a novel gas-switchable/responsive polymer using CNC-based poly(2-(*N, N*-diethylaminoethyl) methacrylate) (CNC-g-PDEAEMA-Py CNC-g-PDEAEMA-Py. Furthermore, two systems, the first PVA-CNC nanocomposite, were prepared by mixing water-soluble PVA with dispersed CNC upon CO_2 bubbling. Second, styrene-butadiene-styrene (SBS) triblock copolymer was dissolved to make SBS-CNC nanocomposite by transferring CNC into the toluene solution upon N_2 bubbling. Results showed that both systems demonstrated excellent shape-memory behaviour, as presented in Fig. 18E. Thus, the potential to be used further in emerging applications such as CO_2 switchable polymers.

Asempour et al. [305] explored SME of thermally reprocessable Schiff-base vitrimers made of copolymers of vanillin methacrylate, derived from LIG and vanilla, and C13 methacrylate, from vegetable oil, with 70% biobased carbon content. The results showed that temperature-triggered SME also presented in Fig. 18F incorporated vitrimer with two shape-programming cycles. Thus, proposed vanillin methacrylate and C13 methacrylate may open interesting avenues to support greener vitrimers for exciting applications in soft devices, with highly tunable functionalities. Guo et al. [306] studied the shape-memory performance of MXene/sodium carboxymethyl cellulose (CMC)/PVA as matrix-based composite films. Insights of this study showed that MXene nanosheet addition improved mechanical strength, solar–thermal conversion and impressive healing efficiency (85.7%) for the proposed composite film. Moreover, the developed composite films demonstrated outstanding shape-memory performance, as presented in Fig. 18G, to different stimuli such as heat, light, and water and the precise manipulation of the shape-memory behaviour can be modulated by adjusting the MXene content due to interfacial interactions. Thus, the MXene incorporation in this study opens opportunities in the design and development of multifunctional, multi-stimuli responsive shape-memory composites for various smart technologies.

5.2.3 Shape-memory performance of CNF-based materials

Ruiz et al. [307] reported the development of a low solid content (< 2 wt% CNF), covalently crosslinked CNF/poly(N-isopropyl acrylamide) (PNIPAM)/$CaCl_2$ hydrogel. This unique network approach improved the shape recovery and reswelling ability in which they were formed after different drying and rewetting cycles and can further be tuned by controlling the ionic strength of the surrounding medium, as presented in Fig. 19A. In another study, Maji et al. [308] prepared a novel bio-based thermo-responsive SMP containing surface acylated CNF and maleic anhydride grafted polystyrene-block-polyethylenebutylene-block-polystyrene-triblock copolymer (MA-g-SEBS). The developed SMP composite demonstrates high shape fixity (~94%) and excellent shape recovery performance (92%), as presented in Fig. 19B, under torsional strain due to stored elastic energy. This facile study contributed significantly toward multiple cell adhesion, cytocompatibility and biocompatibility properties for achieving various biomedical applications. Li et al. [309] studied shape-memory properties of TEMPO-oxidized CNF/polyacrylamide (PAM)/gelatin hydrogels using an in-situ free-radical polymerization approach. The double network was created by a physically cross-linked gelatin network and a chemically cross-linked PAM network. It was shown that the composite hydrogels demonstrated impressive thermo-induced shape-memory properties, as presented in Fig. 19C, owing to the thermoreversible nature of the gelatin network with superior mechanical characteristics such as high strength (>200 kPa), and high strain (>650%) obtained. This simple and facile strategy provides superior shape-memory behaviour hydrogel with improved mechanical strength for numerous engineering applications. Likewise, Prosvirnina et al. [310] achieved novel 3D printing ink using bacterial CNF functionalized with methacrylate groups in a polymerizable deep eutectic solvent (DES) for the realization of highly tuned shape-memory performance. Results showed that adding 12 wt% water improved its strength (11.9 MPa) and ultimate elongation (300%). Also, these CNF-based materials showed impressive shape-memory properties such as shape fixation 80% and recovery coefficients (95.8%), presented in Fig. 19D.

Wang et al. [311] fabricated CNFs/carbon nanotubes (CNTs)/vinasse activated carbon (VAC) composite material using simple vacuum filtration and freeze-drying process with a multi-layer hierarchical conductive structure. It was shown that CNT ensures fast transfer of electrons which is crucial for the loss of electromagnetic waves while VAC offers sufficient double-layer performance. Also, the proposed composite materials exhibited a certain shape and performance by incorporating a vitrimer polymer with a dynamic cross-linked network structure, as presented in Fig. 19E. Thus, the proposed practicable technique for sustainable CNF materials opens new avenues to support energy storage and intelligent EMI shielding applications.

Wang et al. [312] introduced a novel interpenetrating network hydrogel produced by chemically crosslinking between dialdehyde CNF/PVA with nitrogen-doped carbon quantum dots (CDs). The proposed hydrogel was fabricated by a one-step hydrothermal process. Insights of this study showed that developed fluorescent hydrogels demonstrate fluorescence recovery triggered by ascorbic acid and borax-triggered shape-memory with high stretchability (530 %), and excellent strength (0.96 MPa). Furthermore, different folding/assembling 2D fluorescent hydrogel sheets produced various complex 3D hydrogel geometries, as presented in Fig. 19F. These complex geometries further extended data encryption ability under the alternating treatment of Fe^{3+} solution and ascorbic acid solution for high-end applications in important security information encryption and protection. Ma et al. [313] designed

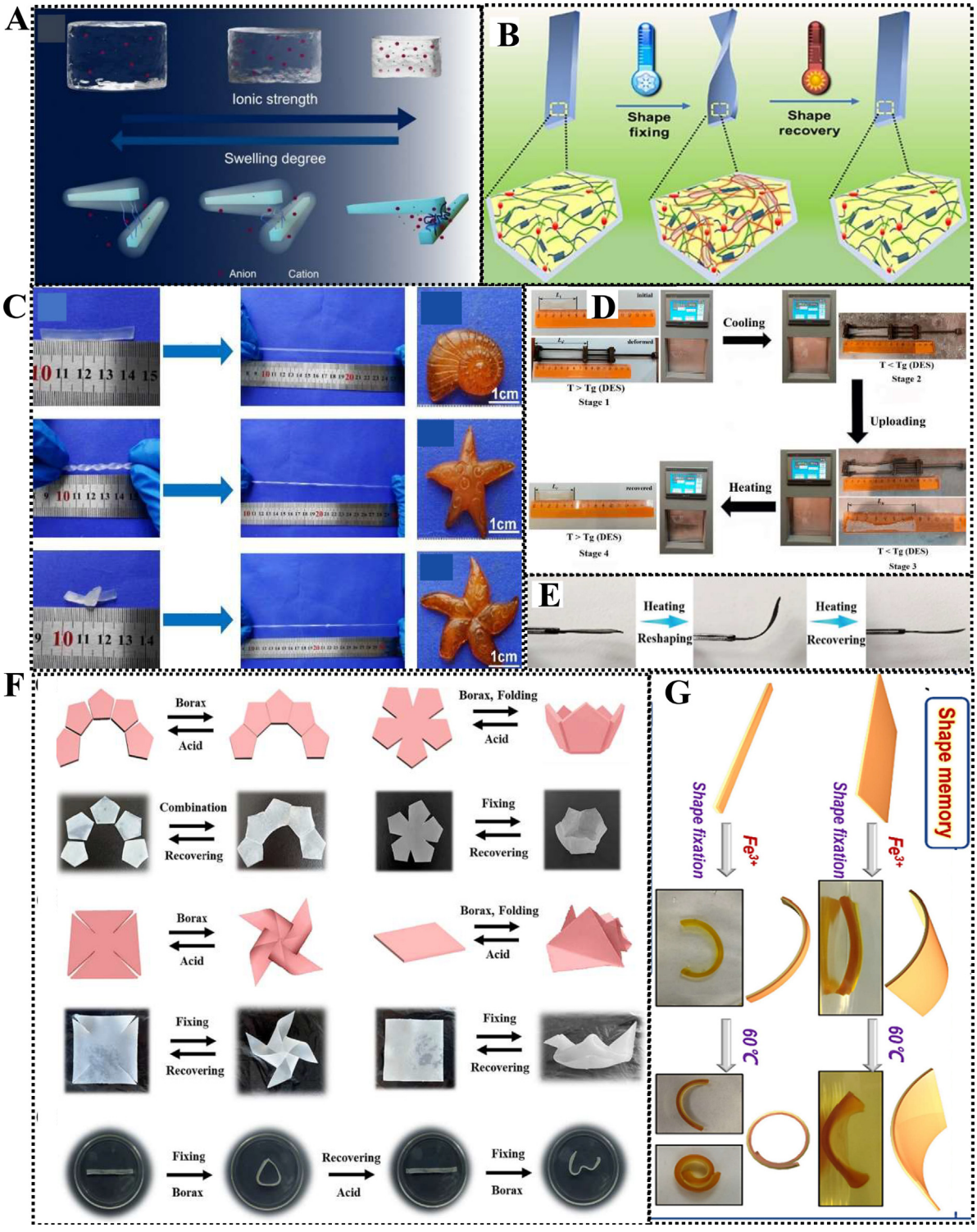

Fig. 19

A) Schematic and visual depiction of the swelling mechanism for the covalently crosslinked gels (adapted from Ref. [307] copyright 2023 Elsevier Ltd.); B) Schematic illustration of the orientation and domain formation of acylated CNF in MA-g-SEBS (adapted from Ref. [308] copyright 2024 American Chemical Society); C) Demonstration of tough and flexible, with the ability to withstand various high-level deformations for proposed composite hydrogels, the gels are also free shapeable into various complex shapes dyed with methyl orange) with wet TOCNF5/PAM/Gelatin10 hydrogels (adapted from Ref. [309] copyright 2017 Elsevier Ltd.); D) Scheme representation of cyclic thermomechanical tests in a static mode exhibiting shape-memory performance for the 3D printed model in the shape of a dog bone, obtained from modified CNF-0 dispersion (adapted from Ref. [310] under a Creative Commons Attribution License 4.0 (CC BY)); E) Shape-memory behaviour CNF/CNT/VAC composite material (adapted from Ref. [311] copyright 2023, Springer Nature); F) Various 3D PVA/DACNF hydrogel complex geometries and the cyclic test on their shape-memory performance such as pentagon splice, bowl-shaped hydrogel, pinwheel and crane-shaped hydrogel (adapted from Ref. [312] copyright 2023 Elsevier B.V.); G) 3D modelling and photos of rectangular bilayer hydrogel sheet and strip depicting the shape transformation process (adapted from Ref. [313] copyright 2024 Elsevier Ltd.).

a thermosensitive actuator based on TOCNF/PNIPAM layer and a non-responsive TOCNF/polyacrylamide (TOCNF/PAM) layer. Results showed that the TOCNF/PNIPAM hydrogel demonstrated superior mechanical properties such as high tensile strength (~24.0 kPa), high compressive strength (~89.2 kPa), and high elongation at break (~170.7 %). Moreover, the proposed bilayer PNIPAM/TOCNF/PAM hydrogel actuator exhibited excellent performance of shape-memory and temperature-driven performance, as presented in Fig. 19G, due to the incorporation of Fe^{3+}. This work opens opportunities for designing novel intelligent flexible soft robots.

Water-based stimuli affect the wet strength and shape-memory properties of cellulosic materials. Recently, Meng et al. [314] improved the water responsiveness of CA/CNF/PVA/LIG sustainable materials. They found that the amount of LIG and the ratio of CNF to PVA altered the crosslinked network structure of the CA/LIG/PVA/CNF membrane, as presented in Fig. 20A. These changes in microstructure affected the material's responsiveness to water. Furthermore, the water-induced shape-memory recovery rate reached 100% within 4 s, while the membrane maintained excellent mechanical properties. It exhibited the highest tensile strength (60 MPa) and tensile modulus (0.7 GPa) in its swollen state and had the ability to block ultraviolet radiation, with a transmittance value of less than 8% in the ultraviolet region (200–400 nm). This study provides valuable insights into the design of CA/LIG/PVA/CNF-based smart membranes. Furthermore, da Costa et al. [315] prepared various shape-changing CNF films that mimic plant responsiveness. The twisting of CNF film within the thickness was done by an asymmetrical expansion through a gradient of carboxylate groups. Moreover, the immersion of CNF film in various organic solvents such as ethanol, isopropanol, dimethyl sulfoxide (DMSO), cyclohexane, acetonitrile and water controlled its asymmetrical expansion and triggered its shape recovery performance, as presented in Fig. 20B. This study provides an environmentally friendly approach for designing biomimetic CNF-based composite films for building materials, soft robotics, and electronic applications.

6 Discussions

6.1 Applications

The hunt for innovative applications with the improved properties of the current nanocellulose-based materials is a driving force for research and development (R&D) across the world including different universities, research groups and commercial companies [316-318].

6.1.1 Wearable electronics

As smart technology advances, wearable electronics show promise for various biomedical applications, including precision diagnosis and treatment, personalized health monitoring, and electronic skins [319,320]. Naturally occurring materials enhance the design and use of intelligent, highly flexible, skin-compatible, adaptable, and mechanically/electrically transformative properties, outperforming traditional rigid materials [321]. In line with sustainability and environmental friendliness, cellulosic materials are now considered as building blocks for wearable electronics [322,323]. For instance, Shahbazi et al. [324] introduced thermo-responsive hierarchical macroporous structure by in-situ crosslinking of the CNC/CNF-stabilized Pickering-high internal phase emulsions (HIPEs) using an emerging hot-melt extrusion-based printing technique. These HIPE were labelled as PPH-2, PPH-4, PPH-6, PPH-8, and PPH-10, based on emulsion containing 0.2, 0.4, 0.6, 0.8, and 1.0 wt% CNF, respectively, to demonstrate the continuous phase of Pickering-HIPE during 3D printing. Insights from this study showed that these 4D printed structures with a high level of porosity demonstrated a significant shape-memory function upon selective heat stimuli, particularly by converting Pickering-HIPE to poly-Pickering-HIPE. Furthermore, these 4D structures were enriched with ultra self-recovery performance, as presented in Fig. 21**A,** and exhibited excellent mechanical strength. Overall, this novel work showcased the utility of remotely controllable 4D printing by heat activation for a highly interconnected open-cell porous structure which is biocompatible, sustainable in nature and best for soft robotics, and biofabrication applications. Likewise, Sang et al. [325] investigated the photo-responsive performance of the PAM matrix, 2,2,6,6-tetramethylpiperidin-1-yloxy-oxidized CNF reinforcement and polydopamine (PDA)-modified black phosphorus (BP) photosensitizer using free-radical polymerization method. The study revealed that oxidized CNF enhanced the homogeneous dispersion of BP@PDA nanosheets through hydrogen bonding interactions. Moreover, as a result of the synergistic effect of CNF and PDA, the conductive hydrogel demonstrated excellent mechanical properties, superior photoelectric response (referring to Fig. 21B), high cycling stability, impressive strain sensitivity (GF = 6.0), and pressure sensing capability (0.13 kPa^{-1}) for detecting human motion. Thus, combining these CNF/PDA hydrogels opens up an interesting avenue in the design of advanced sustainable materials for emerging wearable electronics applications.

Another novel work by Goyal et al. [101] demonstrated the shape-memory properties of novel alginate /PNIPAM reinforced with TEMPO-oxidized CNF hydrogels through DIW printing. These hydrogels possessed highly anisotropic thermo-responsive shape-morphing performance at and above 36°C, demonstrating novel shape-morphing functional architectures, as presented in Fig. 21C and Fig. 21D, with superior mechanical properties such as tensile strength (150 kPa), Young's modulus (6.77 MPa), and toughness (83 kJm^{-3}). This novel approach provides an idea for devising sustainable ink formulations for a plethora of biomedical applications including soft robotic devices and tissue engineering.

6.1.2 Smart and flexible displays

With the rapid progress in 3D-printed sophisticated smart structures, an enormous increase has been observed in soft electronics over their rigid counterparts [326]. Although many flexible electronics have been fabricated using conductive polymers and metals/semiconductors, their performance is not up to the mark. However, natural materials such as hydrogels [327] and nanocellulose materials have been intensively studied using 3D/4D printing for developing soft, flexible electronics due to their stretchable 3D polymeric network [328]. These soft and smart devices predominantly driven from nanocellulose materials can stretch in a broader range and conform to the

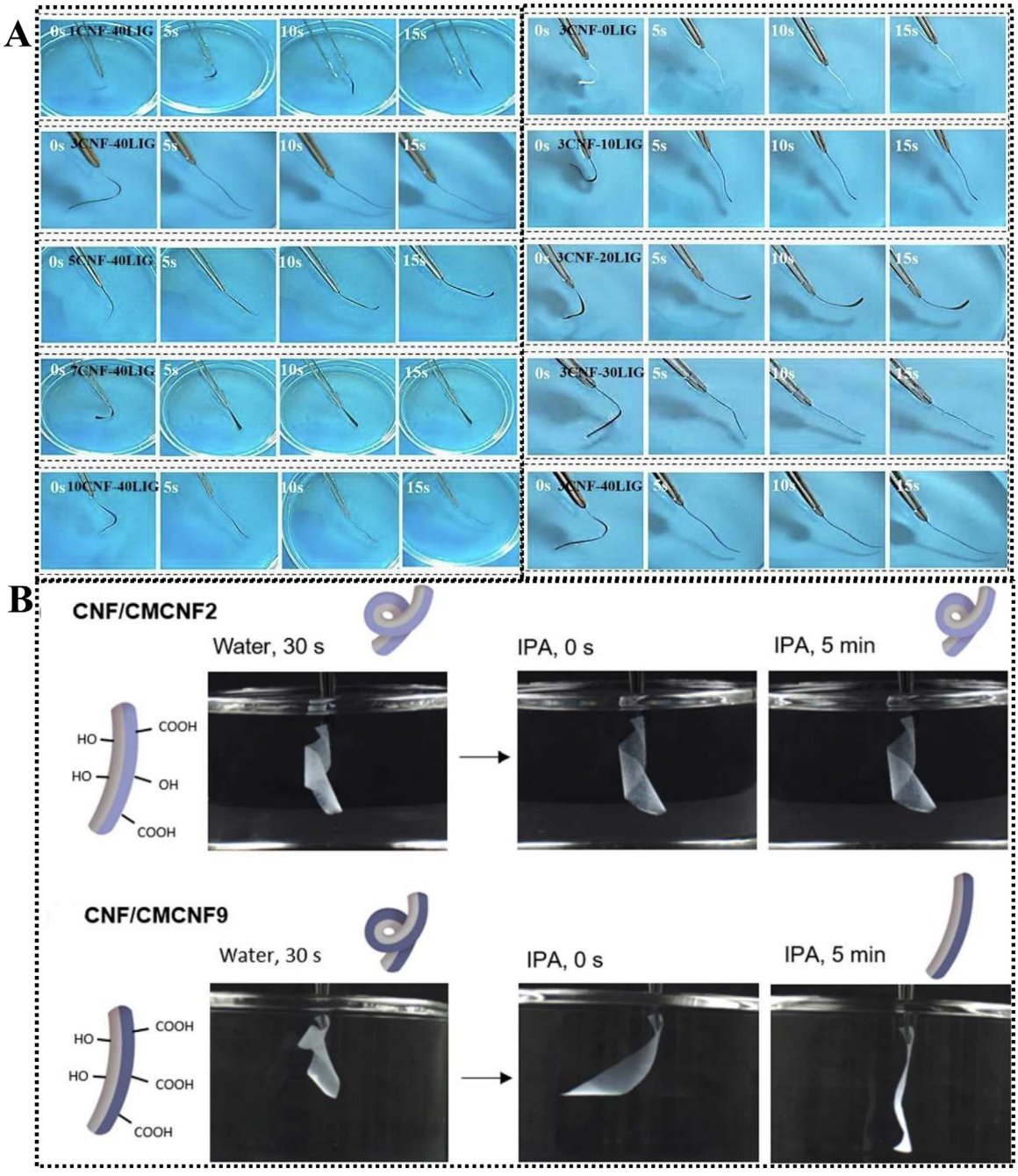

Fig. 20

A) Shape-memory performance and response time of a nanocomposite film with the change of content ratio of CNF to PVA and the amount of LIG added (adapted from Ref. [314] copyright 2022 Elsevier Ltd.); B) Images illustrating the twisting in water followed by the shape recovery test in isopropanol (IPA) of a CNF/carboxymethylated CNF2 and b CNF/carboxymethylated CNF9 bilayer films (adapted from Ref. [315] copyright 2023 Springer Nature B.V.).

corresponding change in their colours, shape, and functions, thus trying to solve an unresolved dilemma of high performance of smart electronics from sustainable materials. Smart and flexible devices typically contain a conductive material embedded within a stretchable polymer, and nanocellulose materials are potential additives. Moreover, it is predicted that the global market for flexible electronics will reach $44.8 billion by 2026, growing at a Compound Annual Growth Rate (CAGR) of 18.6%, up from $15.7 billion in 2020. This growth is only possible with the effective utilization of nanocelluloses [329]. Recently, Chen et al. [330] studied a novel chiral smart bionic skin film by assembling a smart nanodot based on the molecule on the CNC photonic crystal. The developed bio-skin film was sensitive to light and humidity-based stimuli and had multi-channel fluorescence emission. Furthermore, it triggers multiple intelligent signals due to supramolecular interactions. Thus, the developed film is

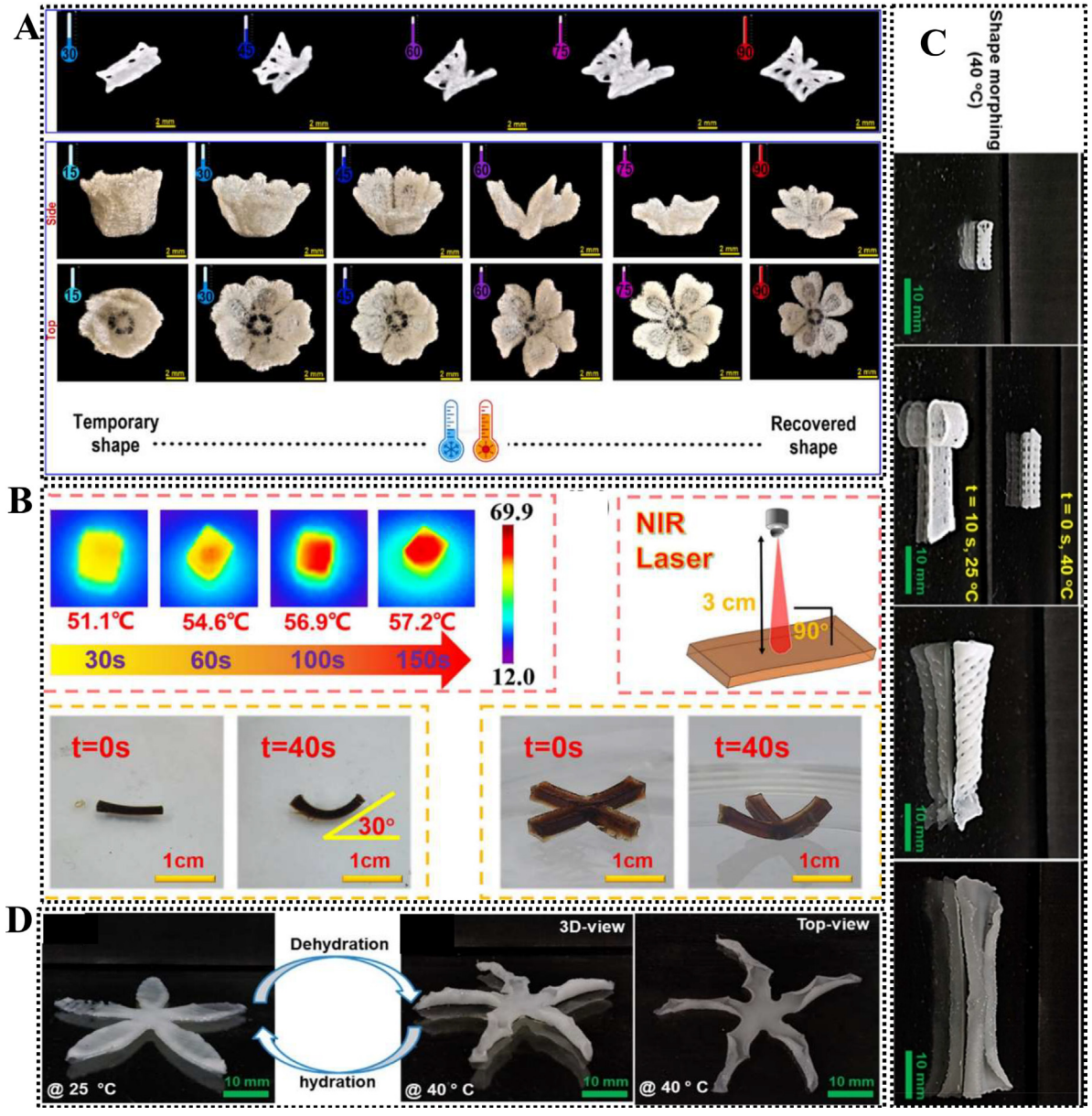

Fig. 21

A) 4D printed PPH-8 object demonstrating sequential shape-memory response as affected by temperature changes, the arbitrary transformation between permanent and temporary 3D shapes of printed "butterfly" on top and "flower with 5 petals" on the bottom and each shape monitors the temperature of the atmosphere through a thermometer graphic (adapted from Ref. [324] under a Creative Commons Attribution License 4.0 (CC BY)); B) BPTP-5 hydrogel infrared thermographic images under the power density of 1.5 W cm−2, and irradiated with a NIR light source, bending behaviour under NIR irradiation of BPTP-5 hydrogel including striped and cross-shaped (adapted from Ref. [325] copyright 2024 Elsevier Ltd.); C) Precise control over temperature-responsive shape-morphing curvatures of 4D printed bilayer architectures, D) Deployed to flat configuration upon hydration, temperature-responsive shape morphing (dehydration) attains the folded 4D petal shape (C,D are adapted from Ref. [101] copyright 2024 American Chemical Society).

similar to photonic crystal skin materials and has the potential to be used in various applications such as tissue engineering, bionic artificial skin materials, 3D printing materials, and optical devices. Incorporations of various nanoparticles in printing materials further improve precision and controlled deposition for embedded electronics, untethered and autonomous robotic functions. For example, Yoo et al. [331] developed novel soft actuators based on nanoporous TOCNFs/2D platinum ditelluride (PtTe2) layers under hydration/dehydration stimulant states. The results showed that vertically stacked TOCNF/2D PtTe2 actuators demonstrated excellent actuation characteristics, as highlighted in Fig. 22A, and are potential candidates for biomimetic devices and soft robotics.

4D printing is also indispensable as the printed structures realized novel functions such as spatial sensing for achieving large-scale and cost-effective fabrication methods, particularly in commercializing e-skins [332]. For instance, Wei et al. [333] used commercially available and biodegradable hydroxypropyl

Fig. 22

A) Illustration of shape-shifting behaviour and various 3D actuations, photos of lifting 0.451 g weight by U-shaped TOCNF/2D PtTe2/PI actuator at 10 V, globally connected six actuators 3D folding actuation before (top) and after (bottom), sequential 3D folding images, schematic diagram illustrating U-shaped TOCNF/2D PtTe2/PI actuator with selectively integrated TOCNF, 3D twisting actuation in projected view) (adapted from Ref. [331 under a Creative Commons Attribution License 4.0 (CC BY))]); B) 3D printed sample of 65 wt% HPC/ 0.1 wt% CNF/0.05 wt% CNT, encapsulated with polybutylene adipate terephthalate (PBAT) depicting colour change from green to purple, C) HPC/CNF/CNC-based materials showing their colour changing behaviour in response to different temperature stimuli, and the HPC-CNT-CNF display independently controlling the display of each segment under temperature response (B, C are adapted from Ref. [333] under a Creative Commons Attribution License 4.0 (CC BY)); D) 3D print of cross-linkable CNF: alginate composite inks and side-by-side comparison of Octopus figurine printed with 3% MFC + 3% alginate and 5% CNF 2:1 + 3% alginate composite inks can be used as anisotropic human muscle tissues to mimic native muscle function and structure (adapted from Ref. [336] copyright 2023 American Chemical Society); E) DIW printing of CNF/alginate/$CaCO_3$ for producing various structures such as tube, bucket, ear, and boat (adapted from Ref. [337] under a Creative Commons Attribution License 4.0 (CC BY)).

cellulose (HPC) as a matrix material and CNTs to develop a novel composite bioink for 3D printing. Moreover, to improve the rheological properties of bioink, a 0.4 wt% of CNF was also added. The results showed that developed novel HPC-CNT-CNF composite materials changed their colours in response to external stimuli, such as temperature and stress, as presented in Fig. 22B-Fig. 22C. Thus, multipurpose colour- HPC-CNT-CNF-based composite materials are promising for emerging green electronics by developing an eco-friendly visual intelligent device. Likewise, Balcerowski et al. [334] produced structurally coloured, periodically wrinkled, and non-iridescent HPC capable of responding under suppressed angular colour response through a DIW technique. The results showed that the planar texture of the cholesteric HPC induced periodic wrinkling deformation patterns at a high shear rate due to extrusion. Furthermore, the proposed 3D-printed technique has the potential to adapt to high-quality light filters and monochromators for many optical applications. Upadhyay and Ojha [335] investigated 4D printing technology for producing complex shapes in a simplified and controllable manner using covalent adaptable networks (CANs). CANs demonstrated excellent shape-shifting ability under various stimuli such as light, temperature or chemical stimuli. These CANs have excellent mechanical properties and self-welding ability and can adapt to any programmed shape under nominal stress due to dynamic covalent linkage, which develops room-temperature malleable CANs. Thus, the developed 4D-printed CANs can be employed in transparency and ambient conditions due to their self-healing ability and promising applications of scratch-resistant coatings on display items.

Recently, extensive efforts have been devoted to producing soft robotic actuation systems with biomimetic intelligence using naturally available materials. In this context, nanocellulose-based biomimetic soft actuators offer many vivid advantages, including high flexibility, high degree of freedom, bistable configurations, reconfigurability, adaptability to the living systems under sustainable or eco-friendly environment, and reusable or degradable options for these devices [338]. Moreover, these soft robotics can achieve fast and reversible shape change through short stimulation impulses and maintain various stable shapes without externally powered systems [339,340]. 3D printing for soft robotics proposed novel ways to improve its self-healing properties, ease of operation, on-demand and rapid fabrication, complexity in shapes, high-performance flexibility and stretchability, and controllable deformation for picking and releasing various toxic substances, or at those places where human interaction is not possible [341,342]. These properties are appealing for a wide range of applications, including soft electronics optoelectrical sensors, less invasive microsurgical tools, drug delivery, surgery, artificial organs, and biomimetic artificial organs.

6.1.3 Biomedical applications

Advances in various synthesis techniques for naturally available materials are leading to the emergence of tissue engineering applications, including bio-engineering scaffolds and personalized healthcare devices [343]. 3D printing technologies hold great promise for the biomedical sector because they can produce or mimic exact human-based parts and tissues (reffering to Fig. 22D and Fig. 22E) with higher accuracy [344]. Furthermore, its capability to develop on-demand and highly patient-specific conditions and treatments such as donner shortage, dental, blood vessels, ear, and nose with exact human compatibility is attractive and has garnered tremendous attention worldwide [345-347]. By 2030, wearable devices will be adopted globally by up to 65.6% of the population, initially 12.3% in 2020. Now, efforts are currently being made to develop various biomedical devices. For example, cellulose oxalate nanofibrils in hyaluronan-based hydrogels produced ideal shear-thinning bioinks with long-term stability for widespread tissue engineering applications. For instance, Phan et al. [348] investigated 3D printable hydrogel using poly(ε-caprolactone-co-lactide)-b-poly(ethylene glycol)-b-poly(ε-caprolactone-co-lactide (PCLA) and CNC. Results revealed that CNCs reinforced the PCLA copolymers' micelle network via inter-micellar bridges and controlled the release of biologics. Moreover, the 3D printing results exhibited that printed hydrogels had good injectability, high shape fidelity, formed stable 3D structures up to ten layers and have enormous prospects as a controlled release and breast cancer treatment applications.

For instance, Träger et al. [349] proposed a novel technique for free-standing multimaterial printing using cellulose oxalate nanofibrils in hyaluronan-based hydrogels. Results showed that printed structures have excellent biocompatibility, with viability of primary human dermal fibroblasts above 80% at 7th day after seeding. Thus, the proposed nanocellulose/ hydrogels are promising bioinks for fabricating complex geometries that can support cell growth. Similarly, Baniasadi et al. [350] used cellulose nanofibrils reinforced aloe vera bio-hydrogels for developing 3D geometries through the DIW technique. 3D-printed structures exhibited excellent wet stability and protected the shape from extensive shrinkage upon drying. These 3D structures, possessing bio, porous, and wet stability characteristics, show promise for biomedical applications. Oladapo et al. [351] studied CMC with cellulose fibers of high cellulose content to evaluate their microstructure, stability and shrinkage properties in 4D printing. 4D printing capability was observed due to changes in complex microstructure with time due to moisture, and results were excellent, particularly at 2.5% by mass of CMC. Now, CMC-based materials are effectively used in fast self-healing ionic hydrogels for a solid foundation for bionic skin and flexible sensor-based novel applications [352]. Radeke et al. [336] improved the dispersibility of cellulose fibrils through a solvent-controlled partial carboxymethylation for producing negatively charged CNF. This process enabled CNF to structurally match the size and dimensions of natural collagen fibers, making it suitable for use as 3D printing inks. The results demonstrated that this novel composite ink could be used for 3D printing cell-laden and cross-linkable structures. They showed how myotubes derived from human and murine skeletal myoblasts could be programmed into linear and complex nonlinear architectures on soft printed substrates with intermediate fiber contents. Thus, the proposed facile approach using CNF/gelatin/alginate inks can be employed to fabricate anisotropic human muscle tissues that effectively mimic native structure and function.

6.1.4 Other applications

Nanocellulose has excellent biocompatibility, thixotropic, photonic properties, high strength and Young's modulus with tunable self-assembly, which are essential for many applications such as functional papers, antibacterial coatings, optoelectronics, scaffolds [353], food packaging [354], biosensors, energy storage devices [355], pressure sensing [356], catalysis, environmental remediation, and electrochemically controlled separation [357,358]. Gauss and Pickering [359] recently used 20 wt.% of grafted CNF/PLA in FDM-based 3D printing for improving thermo-mechanical stability, particularly above 10 wt% grafter CNF. Tang et al. [360] studied novel liquid crystal (LC) templating-based vat photopolymerization printing for producing bioinspired porous structures. The printed structures showed hygro-responsive behaviour based on the photopolymerization-induced phase separation (PIPS) and liquid crystals electro-alignment. Furthermore, the printed structures have excellent shape control accuracy, fast dynamic response, and high reliability due to the templated LCs, which were programmable arranged nanofillers. The results showed that the proposed novel technique has promising applications in ultrafiltration membrane smart anticounterfeiting devices. Thus, novel stimuli-responsive fibers have tremendous potentials for use in anticounterfeiting applications and as next-generation smart textiles [361]. Broadly speaking underlying mechanisms of nanocellulose materials including CNFs have potential applications in optical materials, mechanical reinforcing, edible inks, and soft bioelectronics [362]. Particularly, CNF has provided an ideal platform that shows great promise as an attractive candidate for a wide variety of sensing applications [363].

The cellulose-based natural materials and their characteristics such as compatibility, stability, and degradability promote other applications like food processing, apparel architecture and interior and complex parts [364-366]. Furthermore, the main theme behind the 3D/4D-printed natural materials research efforts is pushing for lean and sustainable manufacturing; this is considered the most resource-efficient and eco-friendly way [367-369]. For instance, Cheng et al. [370] proposed an innovative universal microgel-directed suspended printing technique for developing different mesoporous aerogels using microgel matrix and Kevlar nanofiber as the primary printing ink material. Furthermore, other materials were also used, such as inorganic (MXene, silica, graphene), organic (alginate, cellulose, chitosan), and inorganic-organic (MXene/alginate, graphene/cellulose, silica/chitosan) for fabricating different forms of spatial 3D aerogel architectures**.** Zhang et al. [371] proposed a novel technique for developing a potential DIW using naturally PVA composite reinforced by PDA with PDA/CNCs. The results showed that PDA/CNC hybrid composites had excellent water resistance, thermal stability, and mechanical properties mainly due to ferric ions coordination cross-linking interactions.

It should be noted that the versatility of different applications of cellulose-based materials is driven mainly by their smart features. However, today's 3D printing should never be seen as a standalone process for developing high-end applications using cellulosic-based natural materials [372-374]. It is imperative to consider other smart manufacturing techniques for cellulose as an integral part of competing for new smart materials and ground-breaking applications. This is comprehensively summarized in Table 5, which considers multi-process systems or an integrated process involving multiple systems.

6.2 Challenges/limitations

It is paramount to progress towards new sustainable technologies that can reduce the use of fossil fuels and improve the efficiency of the generated and consumed energy. This review focuses on the importance of smart and sustainable manufacturing within cellulose-based materials. Synthetic materials generally employed have various ecological problems and have limited functionalities. We noticed that several publications are in the literature on the proposed topic. For instance, almost 3000 number publications have appeared in the Scopus database under the keywords "nanocellulose + self-healing" and "nanocellulose + shape-memory behaviour" from the past eight years, 2016 to 2024 (April 30). Thus, the exponential trend demonstrates that the ever-growing research interest and efforts have been paid to develop smart nanocellulose-based materials [151]. Moreover, 3D printing of nanocellulose materials is an emerging and growing technology. It has been successfully used to solve problems of issues such as synthetic plastic consumption in 3D printing. The ability to change their shape, property or structure under a stimulant environment is a driving force for their potential roles in many challenging applications. Especially with the boom of self-healing materials, green, flexible, smart and wearable electronics, the miniaturization, shape-morphing characteristics, biocompatibility and functional integration of materials are the primary evaluation criteria [388]. Nanocellulose, particularly CNF and CNC, is increasingly used to hopefully realize the "green" and eco-friendly concept for various emerging applications such as smart detection devices, precision medicine, information security functional sensors, and biomedical highlights, which is imperative for affecting people's daily lives [389]

Although this review has shown that this field is a relatively new but promising avenue and has great application prospects in the fields of building materials, soft robotics, and e-electronic applications. However, there are many challenges and limitations which hinder the further development of biomimetic nanocellulose-based materials. Moreover, moving forward these serious challenges and necessary tasks are inescapable, this requires dedicated efforts to unlock smart functionalities for opening a new smart world.

6.2.1 Commercialization

Reduced manufacturing costs, while ensuring a high performance can lead towards a commercialization process. Even though efficient scalability and yield are considered critical aspects for nanocellulose materials in their commercial applications. It has been commonly observed that variations in different properties due to batch-to-batch synthesis are the main issue while devising CNF-based hybrid materials. Moreover, CNF-based materials are highly sensitive to temperature, moisture, pH, and surface modifications or oxidation treatments which triggers their degradation over time. Further, their limited compatibility in terms of interfacial bonding, good aggregation and dispersion

Table 5

Smart features of sustainable CNF materials for groundbreaking applications.

Nanocellulose-based hybrid materials	Synthesis technique	Self-healing/shape-memory behaviour	Applications	Ref.
Methacrylate chitosan, spherical nanocellulose, and β-glucan nanocellulose	DLP	The proposed multifunctional composite hydrogels displayed superior shape-memory characteristics under moisture stimulus and self-healing characteristics.	Sensors and moist electric generator applications	[375]
CNF methacrylate	DIW	The CNF methacrylate-based hydrogel reswells in water and expands in all directions to restore its original dimension after being air-dried.	Tissue engineering	[376]
PCL/PHB/CNFs/Fe_3O_4	FDM	The developed composite PHB/PCL (80:20) composites with 0.5 wt% CNFs and 10 wt% Fe_3O_4 displayed excellent mechanical and magneto-responsive shape-memory properties.	Smart actuators	[377]
PEGDMA/CNF/chitosan	SLA	Results showed that as a result of high temperature deswelling occurred, resulting in a decrease in the volume, which showed the remarkable shape-memory property under the heat stimulus.	Tissue engineering	[378]
PNIPAM/CNC/CNF	DIW	The proposed methodology is highly effective for synthetically creating structures that can bend or twist upon hydration.	Wound healing applications	[379]
PCL/PBAT/CNFs	FDM	The intelligent bionic gripper with thermo-responsiveness behaviour exhibited excellent shape-memory and fast response times.	Bionic soft gripper	[380]
CNF phenyl propylene ketone ethers/CNT	Self-assembly method	The developed CNFPPK/CNT composite exhibited rapid and dynamic humidity response abilities while preserving excellent electrical stability for demonstrating as a smart switch.	Smart Switches	[381]
CNF/PDMS-PU composite	Condensation polymerization	The PDMS-PU containing disulfide bonds with CNF content of 1 % demonstrated a remarkable healing efficiency of 95.58 %.	Biomedical and, packaging.	[382]
CNFs/PLA and nanoparticles of lanthanide aluminate (NLA)	-	The developed photochromic self-healable hydrogels under UV lightening became greenish printed on an off-white sheet.	Anti-counterfeiting	[383]
All-cellulose aerogel CMFs/CNFs/regenerated cellulose RC all-cellulose aerogel (ACA)	Freeze dying process	The ACA demonstrate excellent shape-memory properties under water stimulus such as highly instantaneous fold-expansion behaviours and reversible compression-resilience for multifunctional scaffold material.	EMI shielding, and pressure sensing applications,	[384]
Microcrystalline CNF-rGO-(COOH)	Filtration method	The 0.5 wt% GO nanocomposites showed excellent water-induced shape-memory performance such as the maximal shape recovery ratio reached almost 100% after immersion for 25 s.	Biomedical applications.	[385]
TOCNF	Spray drying	The crosslinked microsponges displayed a high drug loading efficiency, as well as excellent pH- responses in terms of swelling and drug release behaviour.	Controlled drug delivery.	[386]
Epoxy nanocomposite with iron oxide decorated CNF	Solvent-assisted mixing technique	The drug-loaded nanocomposite demonstrated a pH-responsive release profile in a medium of pH 7.4. and antimicrobial activities.	Controlled delivery system	[387]

with other hybrid materials are some of the main bottlenecks which limit their commercialization. Thus, today's commendable efforts with highly innovative strategies are required to overcome these challenges to achieve CNF-based sustainable and smart devices.

6.2.2 Mechanical strength

Inferior mechanical properties with low electrical conductivity, and limited self-healing capability, are some of the confronting challenges for nanocellulose materials [390]. Improvement of mechanical properties of nanocelluloses is critical for their structural integrity and practical applications. Therefore, a complete understanding of processing techniques including solvent evaporation, printing techniques, or freeze-drying is a key that can remarkably enhance nanocellulose material alignment, dispersion, and interfacial bonding. This certainly can be a foremost research direction regarding the mechanical strength of nanocellulose. Moreover, for CNF, TEMPO-oxidized and various surface modifications, and several optimized mechanical processes such as ultrasonication and grinding will control the interfacial adhesion and dispersion while preserving the highest structural integrity of nanocellulose materials. The role of crosslinking or gelation techniques is critical for improving the stability of the nanocellulose-based hydrogel matrix. These techniques control chemical stability and provide sufficient mechanical strength [391].

6.2.3 Biocompatibility and toxicity

Nanocellulose, derived from naturally available materials, is considered highly biocompatible and biodegradable. However, in literature, CNC and CNF are generally used as hybrid materials, which can lower their biocompatibility and raise concerns about toxicity. The non-biodegradable materials typically used in hybrid nanocellulose materials can be toxic, posing environmental hazards that hinder their promising applications such as biosensors. Therefore, preference should be given to other biomaterials such as PLA and PCL for developing nanocellulose hybrid materials [392,393]. Moreover, surface modifications of nanocellulose, such as functionalization or coatings, can jeopardize biocompatibility and cause adverse effects for their applications in biomedical fields.

6.2.4 Controlled programming

Controlled programming for SMPs remains one of the biggest challenges. Achieving more precise shape programming with tunable responses to potential stimuli presents new opportunities for highly responsive and functional structures, offering enormous potential for pioneering applications. Additionally, simpler cold programming, without the need for heating and cooling steps, reduces energy and time consumption [394]. However, issues such as springback due to entropic elasticity still occur during unloading. SMPs usually exhibit low mechanical properties, shape recovery stress, prolonged recovery time, poor stiffness due to low rubbery moduli, and limited responsivity due to inferior thermal conductivity [395]. Furthermore, challenges such as longevity, durability, and maintaining multifunctionalities over time are still considered major drawbacks [396].

6.3 Outlook

Addressing the above-multifaceted challenges will provide advance research for sustainable smart materials. Thus, theoretical guidance for follow-up research summarizes that in the future more work needs to be done to develop creative solutions for processing, characterization, synthesis, and multifunctional performance. Overcoming these challenges will unlock the full potential of the materials, forms, and scale features that can significantly advance the performance of soft devices. The following areas should be explored for further development in the shape-memory behaviour and self-healing performance:

6.3.1 Sustainability

Sustainability involves considering the availability of sources of raw materials and the use of applicable process technologies to encourage a transition to sustainable material systems [397]. Currently, tedious manufacturing techniques and large consumption of organic solvents are the main constraints in its larger application prospect damaging its sustainability aspects. Thus, by adopting more sustainable alternatives including both biomaterials and implementing more environmentally friendly synthesis techniques such as 3D printing for realizing more practical applications in line with multidisciplinary and multifunctionality green technology goals. Future goals should be to reduce reliance on finite resources, reduce environmental impact, and work towards a more sustainable future that will benefit us all. In this regard, more initiatives need to be set up for developing more sustainable resource-based soft devices. There is no doubt that nanocelluloses have excellent biocompatibility, but we are yet very far from their recyclability as flexible sensors when they reach their end life or point there they can be repaired their electronic waste must be reduced [398].

6.3.2 Improving stability

Several nanocellulose-based hybrid materials have been developed for cutting-edge manufacturing technique to support their crosslinking. However, there are still much to be done in order to meet and compete the performance of other biomaterials (1) the natural hydrophilicity of nanocellulose material particularly for CNCs hindering the strongly mutual dispersion of cellulose crystals into the polymeric lipophilic chains, thus lowering cellulose loadings and efficacy, (2) there are limited studies on nanocellulose for structural colour-based devices, (3) aggregation of CNCs that prevent solubility in different solvents, difficulties in processing, aligning, resulting in poor fiber/matrix interface and heterogeneous dispersion and poor viscoelastic properties of these gels and films, as reported by Masese et al. [399], (4) The high production cost of nanocellulose due to immature processes, high energy consumption, and low yield are main bottlenecks in the commercialization of nanocellulose-based devices (5) During the service life of nanocellulose devices, substrates will be subjected/exposed to operating stress due to different environmental factors including heat, moisture, sunlight, and mechanical load. Thus, the

reliability of such devices is of particular concern [7], and shape morphing behaviour and their programming for archiving complex motions, are not up to the mark in comparison to that of elastomeric materials.

6.3.3 Interfacial properties

Despite the exponential growth of research publications in the past decade, nanocellulose research still is missing a measuring tool that can effectively characterize its smart features with good accuracy and reliability. Advanced characterization techniques will offer an in-depth understanding of the interfacial interactions. Thus, control the design with improved compatibility. Additionally, interface engineering for all nanocellulose materials also plays a crucial part in their structural and functional performance. To meet the pressing demand for more sustainable nanocelluloses in exciting applications such as smart displays they are confronting challenges that need to be addressed urgently by improving poor interfacial adherence, low processing temperature, high moisture absorption, and poor mechanical properties [400].

6.3.4 Manufacturing routes

Unleashed the true potential of manufacturing processes, 3D printing seems to be deemed as a promising synthesis route for demonstrating complex structures with notable shape-memory function and self-healing capabilities. Substantial efforts are needed to explain the sophisticated machine learning algorithms for easy interpretations to unlock unexplored potentials for both higher performance and adaptability of shape-memory materials. Naturally available nanocellulose is derived from plant cell walls and is now used as promising nanofillers for many natural and synthetic polymers [401]. In this regard, sustainable and nano-AM is considered as impulsive force behind modern science and technology working under the guidelines set by SDGs. This unique combination of nanocellulose with AM permits advanced high-performance green and tailored materials for innovative applications, particularly for e-electronics. Moving forward, researchers have now achieved the dynamic characteristics of nano cellulosic materials [402]. The nanocellulose structure changes its shape or function when it comes into contact with external stimuli such as humidity, temperature, light, pH, and magnetic and electric fields for their promising use in many cutting-edge fields [403].

6.3.5 High-performance SMP

Shape-memory nanocelluloses have the potential to be deployed in human body for long-term monitoring and sensing [404]. The tunned microstructure as well as multi-level deformation and multimode response performance under numerous stimuli can be truly realized by incorporating different functional additives and adjusting the crosslinking level crystal structure. This offers SMP materials to achieve material/structure/function integration with self-deforming, self-healing, self-sensing, and self-learning functions. Thus, futurist intelligent SMP will eventually become the cornerstone of modern scientific research, which will support more revolutionising innovation and convenience for modern people's lives. This will promote the future intelligent society of SMP materials for paving the way for product innovation in flexible electronics, strain sensors, biomedical engineering, energy storage, and other emerging applications [405]. It is crucial to maintain SMEs while preserving the highest mechanical properties [406]. This will ensure the structural integrity of under possible actuation performance. Adding reinforcements (particles, nanofibers) into the SMP termed SMP composites can be an interesting approach to improve their structural and functional performance [407]. So far only the shape transformation and structural colour variations have been observed to visualize the potential stimuli for SMP between the initial and temporary shapes. Therefore, advancing towards both actuation methods and multi-segment SMPs with numerous temporary shapes must be addressed urgently to ensure interest in this exciting and fast-moving field [408]. Commercialization of SMPs relies on the low costly and facile manufacturing routes for SMPs. To date, only laboratory-scale synthesis routes are found to be used for SMP. Moreover, an efficient mimicking of the smart morphing function of SMP will prompt researchers to produce smart and artificial intelligent actuators under specific external stimuli [409].

6.3.6 Intrinsic self-healing property

As burgeoning technology self-healed polymer continues to expand and deepen its performance and application prospects. Overall, the self-healing and shape-memory performance of sustainable materials such as CNFs in its early-stage research but continuously evolving progressively for a stable domain due to their compatibility and potential in designing and developing a resilient structure for innovative applications with preserving smart features. Moreover, to truly realize the self-healing mechanism from sustainable materials, both self-healing ability and higher mechanical properties must maintained [410]. Thus, mechanically robust nanocellulose material with self-healing performance will boost this flourishing field.

The healing mechanism is difficult to achieve for smart devices during their service life as it often requires an outside heat source to initiate or speed up the healing process. Currently, combining both shape-memory and self-healing behaviour with preserving the highest excellent mechanical properties and good electrical conductivity seems far away. In particular, the complete integration of self-healed polymers with embedded electronic applications for ensuring comfort, reliability, and cyclic stability is still far from maturity. This considered as main obstacle in the self-healable flexible electronics field where long-term physiological signals are monitored through direct contact with human skin or tissues [411].

However, the improved mechanical performance of nanocellulose material weakens self-healing ability and delays their healing time. In further advances, multiple dynamic cross-linking into a double network can be introduced to further enhance self-healing ability preserving the highest mechanical properties ideal for the flexible electronics field [412]. Additionally, other novel features such as anti-drying, anti-freezing, self-adhesive, conductivity and anti-swelling must be considered with self-healing features for opening huge

opportunities and impressive innovations for practical flexible electronics applications [413].

6.3.7 Precise and uniform actuator preparation

The impressive biocompatibility and versatility of CNF-based hydrogels are promising for crafting intricate designs for cutting-edge fields such as regenerative medicine, targeted drug delivery, smart packaging, tissue engineering, and biosensing [414]. More focused research is needed for advanced processing technologies in the intricate structure designing which will facilitate their integration into electronic skin and wearable devices for a broad spectrum of biomedical applications. Moreover, precise, and uniform soft actuators have captured extensive recognition owing to their unparalleled smart functionalities and interaction/operation with objects in toxic environments correspondingly. From traditional manufacturing techniques, there is a possibility of slight differences in material composition which greatly effects this soft actuation behaviour for performing necessary tasks. This can be tackled by detecting small actuation strain with high degree-of-freedom motion with high miniaturization of soft actuators [415]. This will facilitate their widespread use in smart and sustainable textile actuators. In the near future, the accomplishment of self-healing and shape-memory milestones could pave the way for more sustainable and interesting avenues in the design and fabrication of smart devices.

6.3.8 Nanogenerators

Triboelectric nanogenerators (TENG) are currently an unstoppable global trendand has strong momentum toward self-healing self-energy supplying and bioenergy resources [416]. To this end, further development of sustainable nanocellulose structures with suitable metal can be optimized to obtain the higher electrical properties for TENG attractive in self-powered wireless systems for monitoring various movements in flexible electronic devices [417]. In dynamic cycling, the CNF surface stabilized TENG, and significant improvements in current and voltage were achieved over unfunctionalized nanocellulose film-based nanogenerators [418]. It is expected that these energy solutions with fully powered systems will be integrated with these soft multifunctional sensor systems which allow them to perform for long periods of time [419].

6.3.9 Flexible electronics

Green flexible electronics have demonstrated significant potential for applications in electronic skin and personal healthcare [420]. As such for a more versatile and practical structure, their fundamental design relies on a combination of softness such as flexibility and ductility of smart materials, along with high accuracy for complex parts. They demonstrate shape-morphing functions [421], such as twisting, bending, folding, and rolling with long-term conformal attachment of the sensors on human skins. Thus, the highest level of comfortability must be maintained [422]. Although nanocellulose materials have excellent electrical conductivity but have a large detection limit, sensitivity, and poor stability. These nanocellulose-based flexible devices are typically very thin and are not miniaturized enough. These low characteristics can affect signal processing and easily cause misjudgement while taking the reading from the flexible electronics. Recent scientific advancements have shown that self-healing for nanocellulose-based self-healing flexible sensors under mild conditions (low temperature, short time) can be achieved under the presence of catalysts and repair agents [232]. However, that needs to be addressed urgently as self-healed based flexible bioelectronics will soon be integrated into our daily lives.

It is believed that in the near future, nanocelluloses will appear as potential materials for sustainable solutions in both technological advancements as well social progress. Moreover, if the above challenges are addressed, we can expect many sustainable devices driven by nanocellulose-based green materials, to impact our daily lives. Remarkably, the smart feature of nanocellulose materials will continue to evolve under many aspects such as novel printers, low cost, versatility to different levels of complexity geometry design (auxetic and origami structures), smart materials, micro-scale, simulation and modelling tools [403,423]. Furthermore, cellulose-based porous materials can be recycled. However, recycling through burning and extrusion triggers harmful effects on the foam network structure and thus lowers circulating adsorption capacity and their practical applications [424]. Worldwide substantial efforts from researchers and material scientists for advancements and breakthroughs in smart and sustainable materials characteristics expounded in this review will foster the revolution of the smart and intelligence era. Thus, we conclude that the economical, eco-friendly, and sustainable productions of cellulose nanomaterials remain significant challenges for their effective utilization in practical applications.

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CRediT authorship contribution statement

Muhammad Yasir Khalid: Conceptualization, Methodology, Writing – original draft, Writing – review & editing. **Zia Ullah Arif:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing. **Ans Al Rashid:** Conceptualization, Writing – original draft. **Syed Muhammad Zubair Shah Bukhari:** Writing – review & editing. **Mokarram Hossain:** Supervision, Writing – review & editing. **Muammer Koç:** Conceptualization, Supervision, Writing – original draft.

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