Preparation and application of cellulose-based hydrogels derived from bamboo

Xiaobing Cao[1,6*], Fei Li[2], Yanjun Li[1,3], Siyu Chen[1*], Xin Li[4*], Yi Lu[5*]

[1] School of Art and Design, Zhejiang Agriculture and Forestry University, Hangzhou, China

[2] School of Science and Technology, Huzhou College, Huzhou, China

[3] School of Materials Engineering, Nanjing Forestry University, Nanjing, China

[4] Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

[5] Institute of Biotechnology, RWTH Aachen University, Aachen, Germany

[6] Department of Chemical and Biological Engineering, University of British Columbia, Vancouver BC, Canada

*** Correspondence:** y.lu@biotec.rwth-aachen.de (Yi Lu)

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Abstract

Hydrogels have outstanding research and application prospects in various fields. Among them, the design and preparation of cellulose-based functional hydrogels derived from bamboo have attracted increasing research interest. Cellulose-based hydrogels not only have the skeleton function of hydrogels, but also retain excellent specificity, smart structural design, precise molecular recognition ability, and superior biocompatibility. Cellulose-based hydrogels show important application prospects in various fields such as environmental protection, biomedicine, energy, food packaging, and plant agriculture. Recently, researchers have extracted cellulose from bamboo and generated a variety of cellulose-based functional hydrogels with excellent properties by various cross-linking methods. In addition, a variety of multifunctional hybrid cellulose-based hydrogels have been constructed by introducing functional components or combining them with other functional materials, expanding the breadth and depth of their applications. Herein, we elaborate advances in the field of cellulose-based hydrogels and highlight their applications in various fields. Meanwhile, the existing problems and prospects are summarized. The review provides a reference for further development of cellulose-based hydrogels.

1 Introduction

Bamboo is a kind of biomass material with short growth cycle and excellent performance. Known as the “Kingdom of Bamboo”, China is the world's richest country in bamboo resources [1, 2]. Compared with other wood materials, bamboo has high output and low price. Similar to wood, the chemical compositions of bamboo are cellulose, hemicellulose, and lignin, as well as other ingredients such as sugars, fats, proteins, and inorganic salts [3]. In bamboo, cellulose accounts for 44% of the total bamboo, and lignin accounts for 20%. Additionally, the content of pentosan in bamboo is close to that of broadleaf wood and other non-wood plant materials. Parenchyma cells even make up 80% of bamboo processing residues produced in China every year, indicating that parenchyma cells are an excellent raw material for the preparation of nanocellulose. Bamboo fibers and parenchyma have a multi-layered structure [4, 5]. Compare with wood, the parenchyma of bamboo has thinner cell walls, larger microfibril angles, lower lignification, and easy peeling of wall layers, which facilitates cell wall dispersion [6-8].

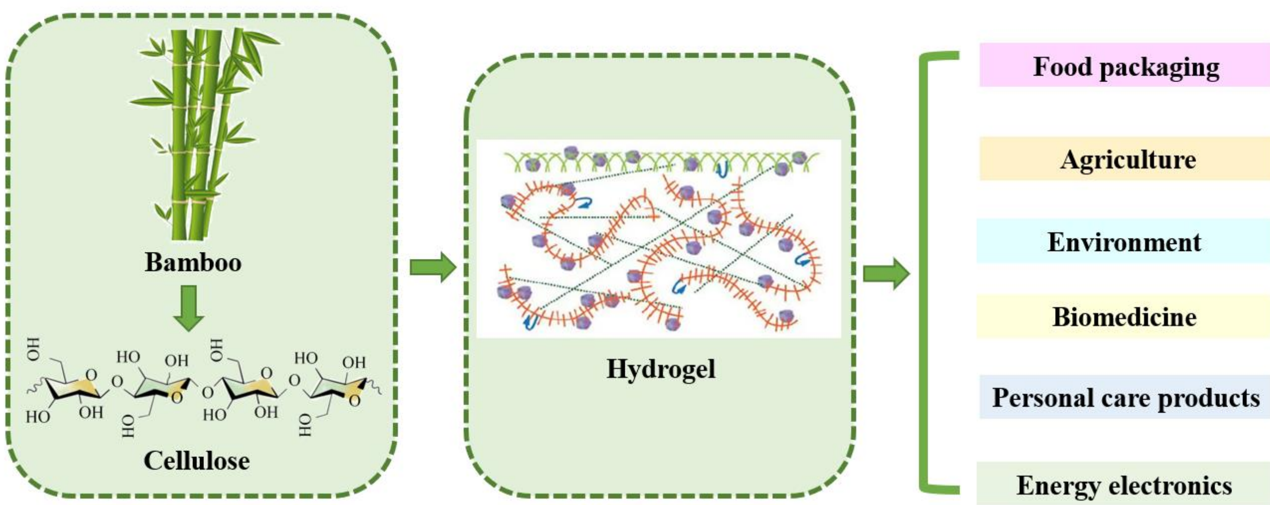

Figure 1. Schematic illustration of the preparation and application of cellulose hydrogels.

Various approached have been used for the preparation of hydrogels from cellulose, indicating the huge application value of bamboo in the production of cellulose-based hydrogels because of the large content of cellulose in bamboo. Cellulose-based hydrogels can be prepared by physical cross-linking of natural cellulose molecules or by chemical/physical cross-linking of cellulose derivatives with single or multiple process steps [9]. The single-step process typically includes polymerization techniques and parallel cross-linking of multiple monomers. The multiple steps include the synthesis of reactive groups of individual polymer molecules. Hydrogels can be designed and synthesized by scale control of a variety of hydrogel properties such as structures, crosslink density, biodegradability, mechanical strength, chemical response, and hydrogel hydrology to stimuli [10, 11]. In recent years, biomass resources have become impressive materials for hydrogel manufacturing due to their outstanding biodegradability and biocompatibility [12]. For example, cotton staple pulp has been used as a hydrogel material to form cellulose-based hydrogels through a single cross-linking agent [13, 14]. Zhao et al. [15, 16] prepared chitosan-based hydrogels by using chitosan extracted from chitin and dextran and applied hydrogels in drug delivery. Zhang et al. [17] produced hydrogels through a molding and acidification process, and utilized generated hydrogels for self-healing applications as well as a sealant and gastric mucosa repair .

Due to the biodegradability, biocompatibility, nontoxicity, and functionality of cellulose, its derivatives have prompted scientists to explore their numerous applications [2, 18-21]. The low cost, light weight, and biodegradability of cellulose based hydrogel lead its application in food packaging. Due to the hydrophilic property of hydrogels, cellulose hydrogels hold great promise for plant agriculture application [22]. Cellulose-based hydrogels are also considered as useful biocompatible materials in medical devices [23] (**Figure 1**).

In this review, the basic compositions of bamboo are firstly introduced. The extraction methods of cellulose or nanocellulose from bamboo and the strategies of preparing hydrogels with extracted cellulose are elaborated. Besides, the applications of cellulose-based hydrogels in various fields, including food packaging, plant agriculture, environment, biomedicine, personal care products, and energy electronics are discussed. Finally, the future outlook of hydrogels in usage scenario, preparation technology is presented.

2 Extraction of cellulose and nanocellulose from bamboo

Bamboo, an abundant lignocellulosic material with high cellulose content, also has strong potential to act as a biomass source for the production of cellulose nanofibrils (CNFs). Cellulose or nanocellulose extracted from bamboo has the characteristics of small environmental load, low weight, high adaptability, and relatively high strength [8]. Chang et al. reported that a combined procedure of hot compressed water (HCW) pretreatment and disk milling could efficiently isolate CNFs from bamboo fibers [24]. CNF was confirmed to reinforced polyurethane composites and exhibited enhanced tensile performances. For the extraction methods of cellulose and nanocellulose from bamboo, there are many literatures has been reported. In recent years, the development of extraction methods of cellulose and nanocellulose have been summarized in **Table 1**.

2.1 Extraction method of bamboo cellulose

The bleach treatment-alkali treatment method is currently a relatively common method for extracting pure cellulose from moso bamboo [25-29]. The method, consisting of bleaching treatment step and alkali treatment step, was employed to remove lignin and hemicellulose from moso bamboo materials respectively and therefore obtain cellulose with high purity. During process of cellulose extraction, bleach with strong oxidizing property was utilized to remove lignin from moso bamboo materials. Afterwards, a large amount of hemicellulose remains in the plant materials, and further removal of hemicellulose is required. Subsequently, under certain temperature conditions, lignin removed moso bamboo was immersed in alkali solution to dissolute and degrade remaining hemicellulose. The bleaching oxidants in this method are mainly sodium chlorite, sodium hypochlorite or chlorine, and the alkali reagents are mainly strong alkali reagents such as lithium hydroxide, sodium hydroxide and potassium hydroxide, etc. Chen et al. [30] treated the moso bamboo with acidic sodium chlorite solution under the pH of 4.0-5.0. The above operation was repeated six times to remove the lignin from the samples. The samples were then stirred for 2.0 h at 90 ℃ with different concentrations of potassium hydroxide solution to remove hemicellulose, and finally chemically purified cellulose with high cellulose purity was obtained. This method can effectively remove the lignin and hemicellulose from moso bamboo materials. During extraction process, the aggregation state and the physicochemical properties of cellulose were not affected significantly. As a result, the prepared purified cellulose can be widely used in nanocellulose materials production [31]. Additionally, Yang et al. [32] explored the potential application of green solvent ionic liquids (ILs) [Amim]Cl pretreatment on the extraction of cellulose from bamboo (**Figure 2)**. As a result, increased accessibility of cellulose and partially fracture side-chains of hemicelluloses of [Amim]Cl were confirmed. And the slight degradation of lignin and hemicelluloses fractions were observed during [Amim]Cl treatment.

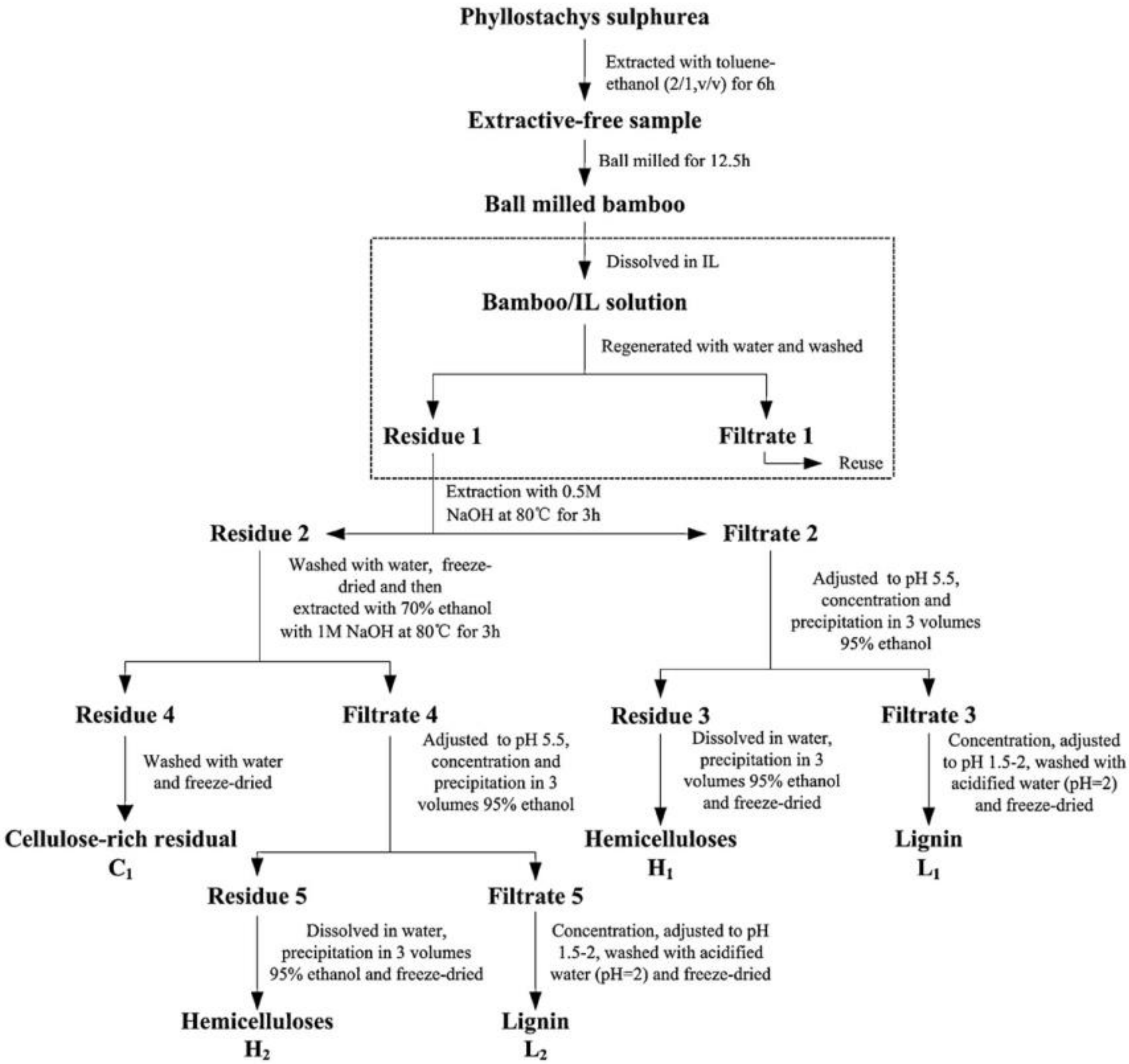

Figure 2. The process of extracting cellulose, hemicellulose and lignin from bamboo with the assistance of ILs. Reprinted from Ref. [32] with permission from ELSEVIER.

2.2 Extraction method of bamboo nanocellulose

Nanocellulose is a kind of natural, non-polluting, bio-tolerable and environmentally friendly material. It possesses special nano-size structure, excellent mechanical properties, biodegradable properties, and no rejection to biological organisms. Utilization nanocellulose derived from bamboo is also an alternative to improve the values of bamboo residues and advance nanocellulose hydrogel development

[33-36]. To extract nanocellulose from bamboo, various process has been applied. For example, Liu et al. [37] delignified moso bamboo and prepared nanocellulose by using a deep eutectic solvent (DES), which consisted of choline chloride (ChCl) and lactic acid (LC). With this method, the produced nanocellulose films show a high tensile strength within the range between 163 and 213 MPa. Recently, combination of microwave liquefaction with co-solvent dissolving system with dimethyl sulfoxide (DMSO) and tetrabutylammobium acetate (TBAA) has been developed to prepare nanocellulose from bamboo residues [38]. As a result, produced nanocellulose films exhibited good tensile strength (15 ~ 25 MPa) and displayed homogeneous network structure. For the application, nanocellulose is mainly used in polymer matrix composites and plasticizer of cellulose materials such as transparent nanocellulose films.

Table 1. Methods for extracting cellulose and nano cellulose

Extracted materials	Extraction method	Evaluation of method	Reference
Cellulose	Cross Bevan method	Serious environmental pollution	[39]
	Nitric acid ethanol hair	Low product extraction rate	[30, 40, 41]
	Alkali bleaching process	Good effect	[25-28, 42, 43] [32]
Nanocellulose	Acid hydrolysis	Main preparation methods	[44-46]
	Physical mechanical method	Environmentally friendly	[47-50]
	Enzymolysis	Mild process conditions	[51]
	Solvent method	Limited	[52, 53] [37]

3 Preparation of hydrogels with cellulose

The attractive properties of cellulose and its derivatives, such as biodegradability, biocompatibility, non-toxicity, usability, and functionality, have led worldwide scientists and researchers to develop cellulose-based hydrogels that can be used in a variety of applications [9, 54-59].

Cellulose based hydrogels are generally prepared by physical crosslinking, chemical crosslinking, and polymerization technology. Physical crosslinking method could be employed to improve hydrogels structures and mainly includes freeze-thawing technology [60-62], photoinitiator technology [63-65], and radiation induced technology [66-68]. Zhang et al. introduced the latest progress of polysaccharide based frozen gel, which is a new physical hydrogel prepared by freeze-thaw technology under mild conditions, without organic solvents and toxic cross-linking agents [60]. Chemical crosslinking method is utilized to form the bonds between the polymer and crosslinking agents. In chemical crosslinking method, many crosslinking agents such as citric acid (CA) [69-71], epichlorohydrin (ECH) [72, 73], and glutaraldehyde [74-76] were used. Tan et al. used glutaraldehyde (GA) as crosslinking agent to synthesize hydrogels through crosslinking reaction [76]. The results showed that the hydrogel and its physical mixture had no cytotoxicity to human corneal epithelial cells at low concentration. Additionally, polymerization technique is also used for crosslinking in the preparation of hydrogel. Polymerization could be classified into three approaches, which are bulk polymerization, solution copolymerization, and polymerization by irradiation [77, 78]. Chu et al. reduced the overall hydrogel crosslinking density by consuming the crosslinker concentration between the dithiol crosslinker and the free mercaptan on the cell surface [77]. Copolymerization can also be used for cell encapsulation and tissue repair applications [79].

4 Applications of hydrogels

Nowadays, cellulose-based hydrogels have wide applications in food packaging, plant agriculture, environment, biomedicine, personal care products, and energy electronics due to their hydrophilicity, biodegradability, biocompatibility, nontoxicity, and remarkable solvent uptake (**Figure 3**).

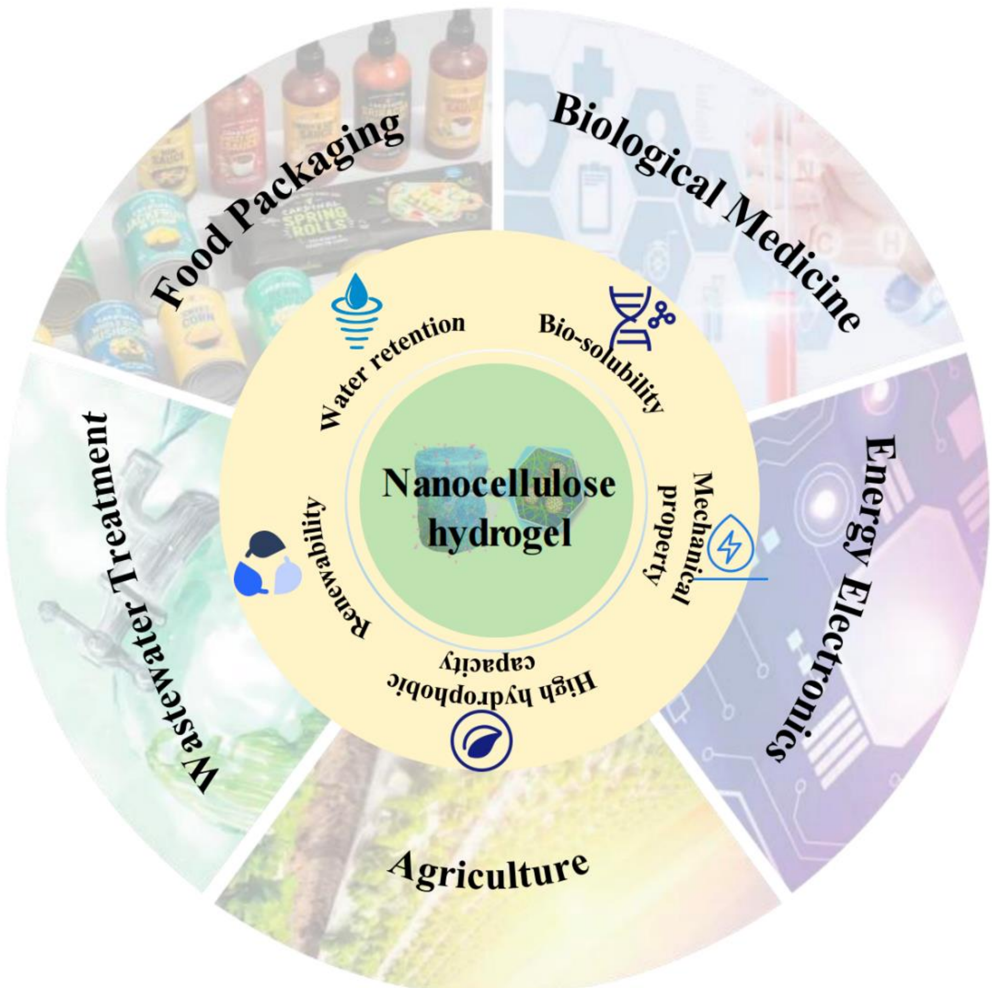

Figure 3. Characteristics and applications of nanocellulose-based hydrogels.

4.1 Hydrogels in food packaging

In recent years, efforts have been made to explore alternatives to replace petroleum-based packaging materials to solve ecological problems such as energy crisis and global warming. Cellulosic paper has received widespread attention of researchers because of its low cost, light weight and biodegradability. Dai et al. [80] used 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofiber

(TOCN)/cationic guar gum (CGG) hydrogel film to modify traditional cellulose paper and produce food packaging materials with good mechanical properties, barrier properties and oil resistance (**Figure 4**). The results showed that compared with the unmodified paper, the tensile strength and elongation at break of the hydrogel film-modified paper increased by 13.4% and 27.1%. And the water vapor transmission rate and the oil absorption rate decreased by 17.5% and 73.5%. In addition, after a period of time storage, the peroxide value of mooncake bags made from hydrogel film modified paper was still within the maximum value (0.25 g/100 g) specified by GB 7099-2015, which proved that the hydrogel film modified paper has good resistance to acid decay and provided new possibilities for the development of novel food packaging materials. The development of an intelligent food packaging material that integrates packaging, detection and recording functions is of great interest. And the intelligent food packaging material can be used to monitor the freshness, maturity and spoilage of food, mainly by reacting with microbial growth or a gas produced during food spoilage. CO_2 is a common by-product of food spoilage process, and monitoring CO_2 content in food is one of the common methods to measure freshness [81]. The freshness of fruits, which reflected by CO_2 content, can be detected by the produced weakly acidic carbonic acid in the reaction of CO_2 with water in the hydrogels.

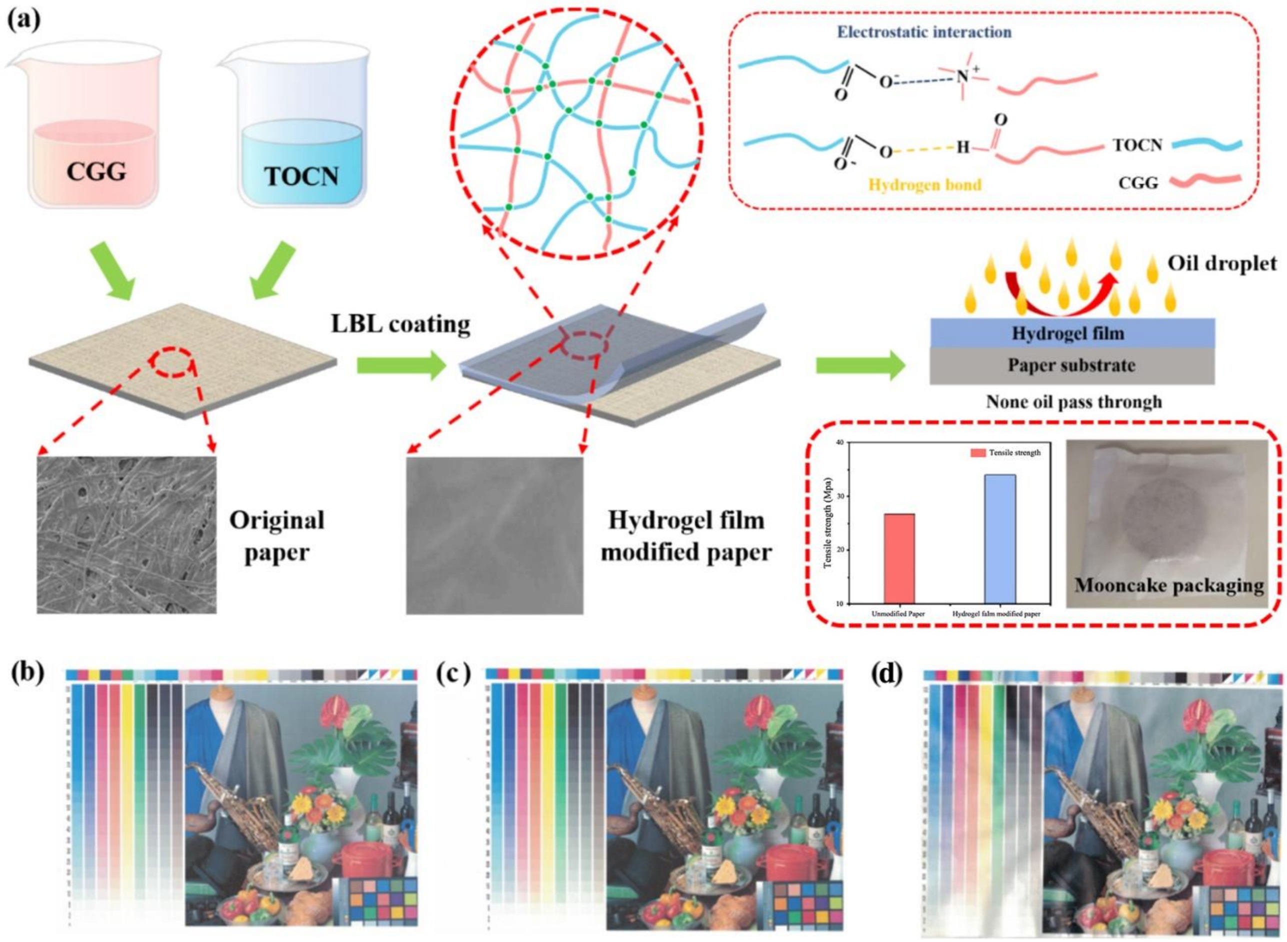

Figure 4. (a) Schematic illustration of the TOCN/CGG self-assembled hydrogel film modified paper for food packaging. Inkjet printing effects on **(b)** ordinary printing paper, **(c)** unmodified paper and **(d)** 4-layer hydrogel film modified paper. Reprinted from Ref. [80] with permission from ELSEVIER.

4.2 Hydrogels in plant agriculture

Hydrogels are receiving great attention in the agriculture since hydrogels are extremely hydrophilic polymers. For instance, Bortolin et al. [82] prepared hydrogels with polyacrylamide (PAAm), methyl cellulose (MC), and calcium montmorillonite (MMt). The produced hydrogels were utilized for the controlled release of fertilizers through sorption and desorption studies of a nitrogenated fertilizer, urea ($CO(NH_2)_2$). As shown in **Figure 5a**, the prepared hydrogels show quite homogeneous foliaceous structures. The pore morphology of hydrogels didn't change significantly with the addition of clay.

However, the pore size increased after the hydrolysis treatment. As results, hydrogels show controlled release of urea in different pHs (4,7, and 9) and the addition of clay mineral improved the controlled release of urea (**Figure 5b**). Ekebafe et al. [83] prepared hydrogels from bamboo-based cellulose and other materials for seed culture applications. The produced hydrogels maintained the soil nutrient balance and improved the water holding capacity of the soil. It was found that this hydrogel resulted in significant increase in plant height, stem thickness, leaf area, biomass accumulation, relative fruit water content, and protein and sugar content.

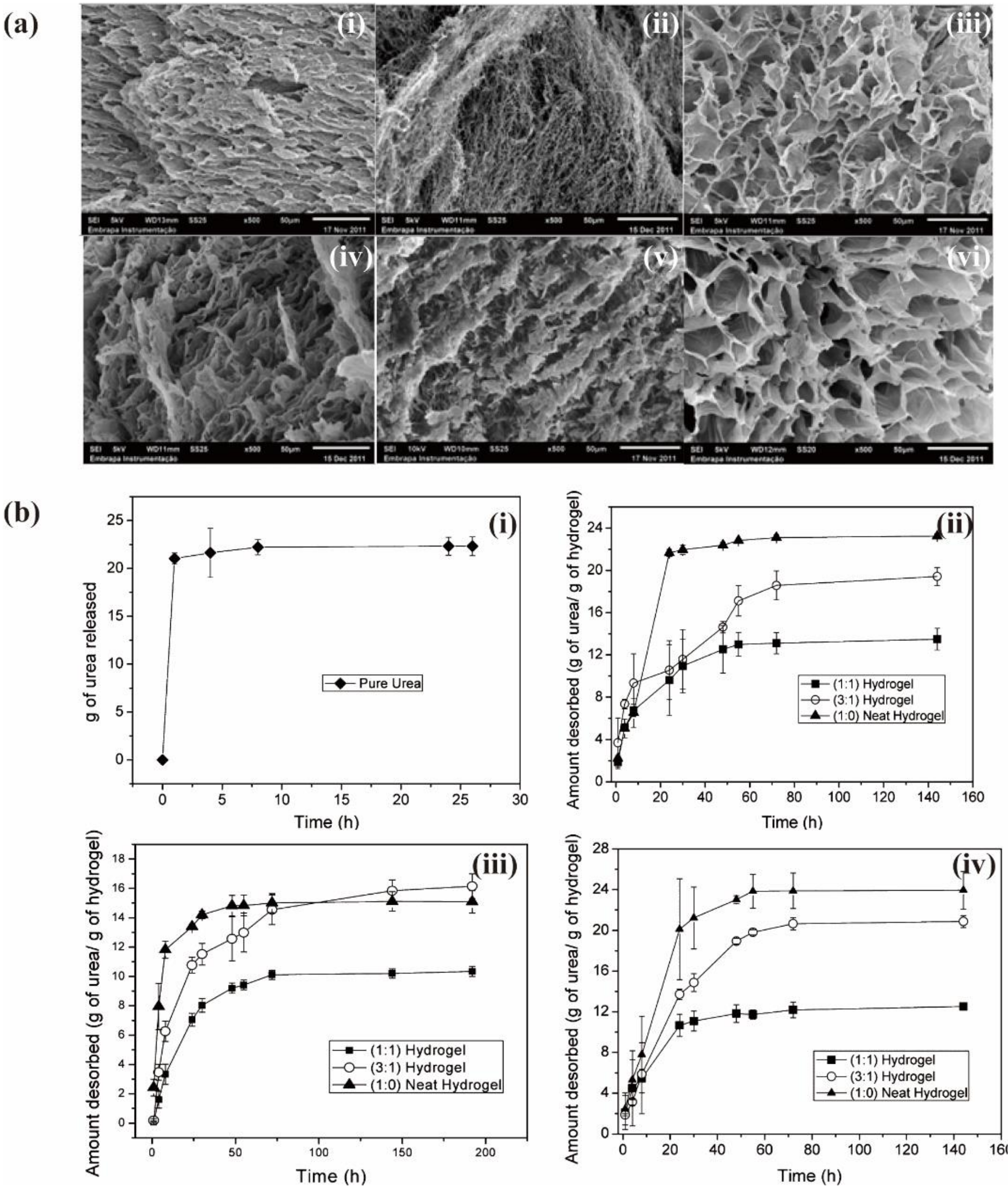

Figure 5. (a) Scanning electron microscopy (SEM) pictures of (i) (1:0) neat hydrogel; (ii) (1:0) hydrolyzed neat hydrogels; (iii) (1:1) hydrogel; (iv) (1:1) hydrolyzed hydrogel; (v) (3:1) hydrogel; (vi) (3:1) hydrolyzed hydrogel. (**b**) Controlled desorption of urea for (i) pure spherical urea, and hydrogels added with different amount of clay mineral at (ii) pH 4.0, (iii) pH 7.0, and (iv) pH 9.0. Reprinted from Ref. [82] with permission from ACS.

4.3 Hydrogels in environment

In wastewater treatment, nanocellulose-based hydrogels are inexpensive, efficient, and recyclable adsorbent materials for adsorption of heavy metal ions, dyes, and oily wastewater, etc. The high porosity and high specific surface area of CNF aerogel make it have excellent adsorption properties, and it has great potential as a high-performance oil absorption material in oil spill treatment. Mohammed et al. [84] made Cap ’n’ collar (CNC)-sodium alginate (ALG) hydrogel from CNC and ALG with good adsorption and recyclability. Compared with pure ALG hydrogel, CNC-ALG hydrogel showed better adsorption of methylene blue (MB) with a maximum adsorption capacity of 256.4 mg/g, and the MB removal rate was still around 97% after five adsorption-desorption cycles. Materials controlled by hydrogel networks significantly reduce the frequency of agricultural irrigation, and film-coated fertilizers can reduce environmental pollution [85, 86]. Hydrogel-coated nitrogen fertilizer formulations based on carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) were developed by M. Liu et al. for controlled and efficient release and to improve the water holding capacity of soils [87]. In a related study, clay and herbicide (ethephon) were wrapped around a carboxymethylcellulose hydrogel, which allowed for slow and controlled release of herbicide [88].

4.4 Hydrogels in biomedicine

In biomedicine, the three-dimensional (3D) network structure of nanocellulose-based hydrogels is similar to that of human tissues. Additionally, nanocellulose-based hydrogels have good mechanical properties, biocompatibility and renderability, which makes them widely used in the fields of drug delivery, tissue engineering, trauma dressing and wearable sensors [89-96]. Liu et al. [97] added aminated silver nanoparticles (Ag-NH_2NPs) and gelatin (G) to TOCNF. When Ag-NH_2NPs were added with the concentration of 0.5 mg/mL, CNF/G/Ag hydrogel showed good mechanical properties, biocompatibility, and wound healing effect. After 14 days of treatment, the wound healing rate and survival rate were nearly 90% and 83.3% respectively. Liu et al. [98] prepared a composite hydrogel by chemical modification of carboxymethyl fibers from bamboo shoot cellulose. Sodium salicylate was used as a model drug to study the adsorption and release behavior of the hydrogels in simulated intestinal (pH 7.4) and gastric juice (pH 1.8) environments. The release rate of the prepared composite hydrogels was higher in simulated intestinal fluid (63.09% after 380 min) than in gastric fluid (22.09% after 400 min). These pH responses of the prepared composite hydrogels, especially as drug carriers, show their potential application of controlled release of drugs in different environmental conditions or human organs. Karla et al. [99] prepared cellulose hydrogel membranes for cell culture scaffolds by using bamboo fibers as raw material. Three types of hydrogel membranes were described and their properties were compared to evaluate the effectiveness of the dissolution methods. The results indicated that the hydrogel membranes prepared with cellulose solution by N-dimethylacetamide (DMAc)/ LiCl method have good cytocompatibility for cell culture scaffolds. Hai et al. [100] developed a ClO^- and SCN^- excited reversible responsive lanthanide luminescent Tb (III)-CMC complex hydrogel for selective detection, protection and storage of fingerprint information. Compared with conventional fluorescent probes, the Tb (III)-CMC complex hydrogel can ensure the confidentiality of fingerprint information.

4.5 Hydrogels in personal care products

Cellulose-based hydrogels are excellent alternatives for the development of highly absorbent, eco-friendly and compostable materials for personal care products [101]. Barleany et al. [102] produced highly absorbent hydrogels with significant antimicrobial activity that can be applied in baby diapers and sanitary napkins. For hygiene product applications, highly absorbent materials with antimicrobial activity are needed to prevent skin irritation. The hydrogels synthesized by Erizal et al. [103] through radiation copolymerization reaction are fast absorbing and can be used in personal care and hygiene products such as surgical pads, hot and cold therapy packs, medical waste curing, disposable diapers, and sanitary napkins. Shanmugasundaram et al. [104] studied the application of hydrogels made from four different fiber compositions (pure bamboo, cotton, bamboo/cotton (70/30), and bamboo/cotton (50/50)) in infant diapers. The prepared diapers were characterized in terms of absorbency, liquid penetration, acquisition time under load and rewetting of the diapers under load. The performance of bamboo/cotton (70/30) fiber blended diapers was found to be superior to other fiber blends. In addition, many promising applications were explored as a protective barrier for volatile organic compounds into the environment and as an absorbent for waste oil [105]. Liu et al. [106] incorporated linen yarn waste into a highly absorbent hydrogel and produced a sanitary napkin product. As a result, the prepared sanitary napkin product has excellent biodegradability and higher water absorption property than currently marketed sanitary napkin products. Obtaining recyclable disposable diapers, napkins, and other sanitary products is one of the important goals of modern industry. The use of fully biodegradable cellulose-based highly absorbent resins can be a good solution to these problems [107].

4.6 Hydrogels in energy electronics

At energy electronics level, Ge et al. [108] applied polyacrylamide/cellulose nanofibrils /highly soluble salt containing highly hydrated Li^+ ion (PAM/CNF/LiCl) hydrogels as electrolytes in a double layer supercapacitor. The capacitors exhibited good mechanical flexibility, low temperature stability (the hydrogel did not freeze with 50% LiCl concentration at -80 ℃) and cycling stability (96% specific capacitance retention after 10,000 cycles), which helped to compensate for the environmental sensitivity of conventional conductive hydrogels and provided a new idea for the normal operation of devices under extreme cold conditions. Smart wearable devices are a hot research topic due to their potential applications in health monitoring. Self-healing wearable devices can restore their structure and function after damage and enhance their durability, reliability as well as safety [109]. As one kind of typical soft and flexible material, self-healing hydrogels have attracted great interest in the development of self-healing wearable devices for human motion detection due to their good viscoelasticity, electrical conductivity, and biocompatibility [110-112]. Because of the excellent self-adhesive properties, high strain sensitivity, remarkable electrical stability, and rapid self-healing ability of self-healing hydrogels, wearable strain sensors assembled from gels can attach directly to human skin and detect large movements such as joint bending and stretching for various human motions. In addition, gel strain sensors can accurately detect and rapidly identify subtle movements, including pulse and respiration, that help monitor an individual's health in real time during athletic training [113]. This gel with high strain sensitivity is an ideal candidate for assembling scalable and wearable strain sensors in the application of human activity monitoring and personal medical diagnostics.

5 Summary

This article mainly studies the preparation and application of bamboo based cellulose hydrogels. Bamboo based cellulose hydrogels can be used in food packaging, plant agriculture, environment, biomedicine, personal care products, and energy electronics. Compared with other wood, bamboo has many advantages, such as short growth cycle, low cost, and easy access to raw materials, etc. Although cellulose-based composites have obvious advantages over pure cellulose-based composites and wide applications in the field of fillers, reinforcing agents and stabilizers, their applications in biomedical engineering, food packaging, cosmetics still need to be further expanded. Additionally, it is necessary to further investigate the properties of lignin in lignin nanofibers and its mechanism of action with the aim of fully developing the potential value of lignin cellulose materials and applications in various fields. Therefore, the future improvement of the preparation and application of cellulose-based hydrogels can be considered from the following aspects: (1) prepare cellulose-based hydrogels by combining cellulose and its derivatives with excellent properties. it’s needed to optimize the preparation method, reduce the cost, and realize the transition from laboratory to industrialization as soon as possible. (2) introduce more specific functional groups in the surface of cellulose, increase the cross-linking sites on the surface of cellulose and thus improve the adsorption capacity of cellulose-based hydrogels for pollutants. (3) in order to promote the rapid development of bionic electronic devices, develop cellulose-based hydrogel sensors with good stretchability, frost resistance, adhesion, and self-healing properties. (4) develop a smart fluorescent composite hydrogel with tunable luminescence properties and no irritant residue, and use it effectively for sensing detection, information storage and encryption, and water exploration and camouflage. This research can lay a good exploration foundation for the functionalization and high value-added application of bamboo.

Conflict of Interest

The authors declare no conflicts of interest.

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