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Progress on chemical modification of cellulose in "green" solvents

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Cellulose is an excellent candidate for the fabrication of sustainable materials owing to its good availability, renewability, biodegradability and biocompatibility. Chemical modification is an appealing way to broaden the utilization of cellulose. However, the poor solubility of cellulose in water and common organic solvents restricts chemical modification of cellulose to heterogeneous conditions or in a few limited specific systems. In recent years, advances have been made in more efficient and greener solvents for cellulose. Some of them have greatly changed the chemical modification of cellulose, and their influence on the future cellulose industry is anticipated. In this review, novel "green" solvents for cellulose dissolution, including ionic liquids (ILs), deep eutectic solvents (DESs), aqueous alkali/urea solutions and aqueous quaternary onium hydroxides (QOHs) are introduced. Recent advancements in chemical modification of cellulose in these solvents, especially those made in the past five years, are highlighted and discussed.

1. Introduction
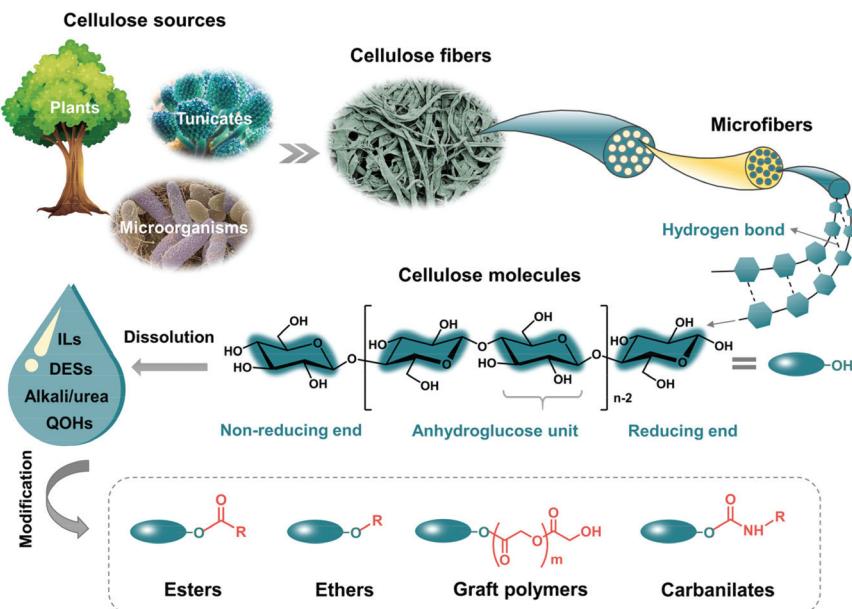
Cellulose, as the most abundant biobased polymer, is widely distributed in diverse natural sources including plants, tunicates and microorganisms.[1–3] Structurally, cellulose is a regular and linear polymer consisting of D-glucose subunits linked by β-1,4-glycosidic bonds with strong inter- and intramolecular hydrogen bonds (Scheme 1).[4,5] Each cellulose chain has a reducing end behaving as an aldehyde form and a non-reducing end equipped with secondary hydroxyl groups.[6] With a number of advantages like renewability, biodegradability, biocompatibility, non-toxicity, low cost, thermal and chemical stability,[7,8] cellulose is considered an ideal feedstock for the production of materials, chemicals and biofuels.[9] Unfortunately, owing to its extensive hydrogen bonding and high crystalline, cellulose can hardly be dissolved in common organic solvents and water. Furthermore, cellulose exhibits a melting point that is higher than its degradation temperature.[10] Both characteristics seriously hamper the utility and processing of cellulose.

Chemical modification is one way to improve the solubility and processability of cellulose.[8] It provides a means of conferring new properties on cellulose without destroying its many intrinsic properties.[11] Industrially, the synthesis of cellulose derivatives [*e.g.*, cellulose acetate (CA), carboxymethyl cellulose (CMC), methyl cellulose (MC), nitrocellulose] still employs a heterogeneous reaction approach.[12,13] The heterogeneous route involves a direct modification of cellulose under poor

solvent media with insolubilization or incomplete solubilization of cellulose. The reaction process is often limited to the surface of cellulose and is hard to control, which is associated with unwanted side reactions, degradation of cellulose, a limited degree of substitution (DS) and large amounts of waste.[14] On the contrary, the homogeneous approach contributes to achieving better controllable reactions with a high conversion rate.[8] Cellulose molecules in homogeneous media are assumed to have full and equal accessibility of all hydroxyl groups for chemical reagents. However, efficient dissolution of cellulose is a prerequisite for homogeneous reactions. Hence, the development of cellulose solvents is an urgent need as well as a long-term goal in the cellulose research area.

In this regard, many attempts have been carried out to search for suitable solvent systems for cellulose dissolution and modification. Traditional solvents for cellulose dissolution involve several types of derivatizing solvents (*e.g.*, CS_2/NaOH) and non-derivatizing solvents [*e.g.*, N-methylmorpholine-N-oxide (NMMO), N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), tetrabutylammonium fluoride trihydrate/DMSO (TBAF/DMSO)]. However, these solvents are accompanied by significant drawbacks involving a cumbersome operation process, high energy consumption, environmental issues and inefficient recyclability.[15,16] Sustainable development has promoted research into more efficient and greener substitutes for cellulose dissolution.[17] In recent years, novel non-derivatizing solvent systems for cellulose dissolution have been developed, and they can be subdivided into two categories: non-aqueous solvents [*i.e.*, ionic liquids (ILs), deep eutectic solvents (DESs)] and aqueous solvents [*i.e.*, alkali/urea, quaternary onium hydroxides (QOHs)]. These solvents can serve as desired media

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Scheme 1 Structures of cellulose and cellulose derivatives synthesized in green solvents.

for cellulose derivatization, and provide a versatile platform to fabricate functional cellulose materials. Here, the main objective of this review is to focus on recent advancements in these novel green solvents for chemical modification of cellulose. Comments on the ongoing research and perspectives on future directions of cellulose modification in green solvents will also be given.

2.   A brief overview of green solvents for cellulose dissolution

Cellulose contains abundant hydroxyl groups which are easy to form extensive inter- and intramolecular hydrogen bonding. The hydrogen bonded supramolecular structure of cellulose makes it difficult to dissolve in either aqueous solutions or conventional organic solvents. To address this issue, numerous solvent systems for cellulose classified as derivatizing and non-derivatizing solvents have been developed. The dissolution process of derivatizing solvents involves the formation of derivatized cellulose intermediates and subsequent dissolution.[18] A typical example of derivatizing solvents is the CS_2/NaOH system which has been used on an industrial scale to produce viscose fibers. However, the viscose process is accompanied by a massive discharge of hazardous by-products (e.g., CS_2, H_2S, heavy metals).[19] Non-derivatizing solvents, such as NMMO, are available for direct dissolution of cellulose without any derivatization. Generally, non-derivatizing solvents are more eco-friendly than derivatizing ones, because less by-products of chemical reaction are involved.[20] Other solvents combining organic solvents with salts, like DMAc/LiCl, TBAF/DMSO, are well developed but have environmental concerns such as high toxicity and volatility.[10]

Solvents are critical in the cellulose industry. As discussed above, some conventional solvents of cellulose bear several health and environmental risks. Therefore, continuing academic efforts have been made aiming to replace them with greener solvents. According to the principle of green chemistry, a green solvent should be of low waste production, less hazardous chemical syntheses, high safety, and small environmental impact. The sustainability of a solvent should also be related to recyclability, availability, stability, flammability, efficiency, and cost. Based on these considerations, we mainly introduce four types of "green" non-derivatizing solvents for cellulose in this minireview, and subdivide them into two categories, namely, non-aqueous solvents (i.e., ILs, DESs) and aqueous solvents (i.e., alkali/urea, QOHs).

2.1.   Non-aqueous non-derivatizing solvents for cellulose

2.1.1.   Ionic liquids. ILs are generally defined as organic molten salts with melting points below 100 °C.[21] They are typically composed of a relatively large organic cation (e.g., imidazolium, pyridinium, morpholinium, ammonium, phosphonium and surperbase) paired with a smaller inorganic anion (e.g., Cl^-, Br^-, and I^-) or organic anion (hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$ and carboxylate $[RCOO]^-$).[22–25] ILs exhibit many attractive properties, including negligible vapor pressure, good thermal and chemical stability, non-flammability, high ionic conductivity, structure tunability and notable recyclability.[26] The physicochemical properties of ILs can be altered by adjusting the structures and arrangements of cations and anions.[27] The first report on cellulose solubilization in imidazolium-based ILs containing 1-butyl-3-methylimidazolium cations ($[BMIM]^+$) paired with a range of small or large anions was published by Rogers et al.[28] This research significantly simulated the development of ILs in cell-

ulose dissolution.[29] So far, a number of ILs based on imidazolium, quaternary onium, pyridinium and superbase have been developed.[30–32] Generally, the dissolving capacity of ILs with distinct cations follows the order of imidazolium-based ILs > pyridinium-based ILs > ammonium-based ILs.[33] ILs consisting of Cl^-, $[OAc]^-$, $[HCOO]^-$ or $[(EtO)_2PO_2]^-$ anions are more effective solvents for cellulose dissolution than those containing non-coordinating anions such as $[PF_6]^-$ or $[BF_4]^-$.

Recently, a combination of two single ILs is revealed to show improved dissolution capacity for cellulose. A mixture of [EMIM][Cl] and [EMIM][OAc] with 30 : 70 mol/mol was exploited to display comparable solubility (40 g per 100 g of solvent) to individual ILs such as [EMIM][Cl], [EMIM][OAc], and [BMIM][Cl].[34] Moreover, research has shown that adding certain highly dipolar aprotic co-solvents (e.g., DMSO, DMF, and DMAc) into ILs can lower the viscosity of the solvent system and promote cellulose dissolution.[35–41] It can be anticipated that ILs co-solvent will become an important direction in the future. Although a large number of articles and reviews have been published, most of them are devoted to the dissolution of cellulose, the attention in cellulose modification is still scarce. In addition, some critical issues associated with the industrialization of ILs in cellulose processing and modification, including the sensitivity to water, the feasibility to recycle, and the high viscosity, still need to be addressed.

2.1.2. Deep eutectic solvents. DESs are currently emerging as a new class of promising solvents. Different from ILs that are a combination of cations and anions, DESs are generally liquid eutectic mixtures composed of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) with desired molar ratios.[42–44] Although being different substances, DESs and ILs have many similar characteristics, including good solvent capacity, low vapor pressure, nonflammability, compositional tunability, and good chemical and thermal stability.[45–47] Unlike ILs, DESs can be easily prepared from non-toxic and biodegradable components at a low cost.[44] Owing to these remarkable advantages, DESs have attracted considerable interest in lignocellulose fractionation,[48] dissolution[49] and modification.[50] The most popular solvents among all DESs involve mixtures of choline chloride (ChCl) as a hydrogen bond acceptor with a safe and inexpensive hydrogen bond donor (e.g., urea, oxalic acid, glycerol).[49] It has been found that ChCl/resorcinol can dissolve up to 6.10% cellulose at 90 °C with the assistance of ultrasonic irradiation (20 Hz).[51] Last year, Yan et al. designed a new DES consisting of choline and L-lysine hydrochloride.[52] Natural cellulose (DP > 3000) from wheat straw can be well dissolved in the DES at 90 °C to form a uniform and stable solution with a solubility of ~5%.[52] The solubility of microcrystalline cellulose (MCC) in the solvent system can also reach ~8%. Kuroda et al. discovered in 2021, that zwitterion-based DESs containing 5 wt% sucrose can dissolve 15 wt% cellulose at 120 °C.[53] These findings have boosted the enthusiasm of researchers to design more DESs for high dissolution of cellulose. However, the solubility of cellulose in the reported DESs is far from that in ILs.

2.2. Aqueous non-derivatizing solvents for cellulose

2.2.1. Aqueous alkali/urea systems. The alkali/urea systems, as typical aqueous non-derivatizing solvents for cellulose, have received considerable attention due to their simplicity, low cost, low toxicity, environmental friendliness, and easy recovery.[54] The solvent systems are composed of alkaline metal hydroxides and urea-based components. Zhang et al. designed and prepared a variety of aqueous solutions, including 7 wt% NaOH/12 wt% urea,[55] 4.6 wt% LiOH/15 wt% urea,[56] and 9.5 wt% NaOH/4.5 wt% thiourea.[57] Such solutions can dissolve cellulose within several minutes after a low temperature treatment procedure. Interestingly, the dissolution only occurs at low temperatures, which is particularly different from other solvent systems. The mechanism of cellulose dissolution by cooling is related to the formation of a cellulose-solvent inclusion complex driven by fast dynamic self-assembly between cellulose macromolecules and solvent components.[58] The inclusion complex is relatively stable at low temperatures, contributing to forming a transparent cellulose aqueous solution.[59] However, the dissolving capacity of high molecular weight cellulose in these solvent systems raises great concern. According to the report by Cai et al.,[60] up to cellulose with a weight-average molecular weight of below 4.12×10^5 can be soluble in the alkali/urea systems, which should be able to satisfy most applications.

2.2.2. Quaternary onium hydroxides. Another promising solvent class of aqueous non-derivatizing solvents is aqueous QOHs. Such solvents include quaternary ammonium hydroxides [QAHs, e.g., tetraalkylammonium hydroxide (TAAH),[10] tetrabutylammonium hydroxide (TBAH),[61] tetraethylammonium hydroxide (TEAH),[62] tetramethylammonium hydroxide (TMAH),[63] benzyltrimethylammonium hydroxide (BTMAH)[64]] and quaternary phosphonium hydroxides [QPHs, e.g., tetraalkyphosphonium hydroxide (TAPH),[65] tetrabutylphosphonium hydroxide (TBPH)[66]]. Compared to aqueous alkali/urea solutions, QOHs can be used to dissolve cellulose at a higher concentration under mild conditions. In 2019, an aqueous solution of TBPH (50 wt%) was found to dissolve 20 wt% cellulose in minutes at room temperature.[66] An aqueous TBAH solution with a concentration of ca. 50–60 wt% was available to dissolve cellulose with a maximum solubility of ~25 wt% at 40 °C.[67] Temperature also plays a vital role in adjusting the solubility of cellulose. A remarkably improved dissolution of MCC in 40 wt% TBAH aqueous solution can be achieved by lowering the temperature to 16 °C, demonstrating a more efficient and economical solvent with a lower concentration.[68] Besides, incorporating co-solvents (e.g., urea, thiourea, N-methylurea, crown ether, NaOH) with QOHs is an alternative approach to promote cellulose solubilization,[61] reduce the consumption of QOHs,[10] and improve solvent stability.[63]

2.3. Comment and comparison of the green solvents

ILs, DESs, alkali/urea, and QOHs represent the most prevalent solvents for cellulose dissolution, processing, and modifi-

cation in the past decade. Compared with conventional solvents, they all present some characteristics of green chemistry, like low vapor pressure, nonflammability, and good stability. Among them, the alkali/urea systems are prominent in terms of availability, cost, and hazard potential. Before this system comes onto the market, there are many problems that need to be resolved. The relatively low solubility of high molecular weight raw materials remains a challenge. Other challenges come from the difficulty of industrialization with low temperature treatment, high energy consumption, and special instruments. From a scientific point of view, the influence of hydrogen bond network on the dissolution and reaction behavior of cellulose in alkali/urea is not clear. QOHs present a more powerful aqueous solvent of cellulose. Concerns about QOHs may come from the required high concentration, which not only leads to increased cost, but also impacts the chemical reactions in them. For example, the effect of salts is significant in many reactions. Compared with other green solvents, ILs are much more studied as reaction media for cellulose modification due to their good stability and dissolving capability. ILs are the ones most possibly being utilized in the controlled synthesis of cellulose derivatives with precisely determined structures. For future practical applications, the cost and viscosity of ILs need to be greatly reduced. DESs have shown exciting potential. The advantage of DESs majorly comes from their low cost and ease of synthesis. However, studies on the dissolution and modification of cellulose in DESs are very rare. Much more academic effort should be put into DESs in the future.

3. Chemical modification of cellulose in green solvents

According to its molecular structure, cellulose comprises of repetitive anhydroglucose units (AGU) which are covalently linked through acetal functions between the OH group of C4 and C1 carbon atoms.[69] Each glucose repeating unit of the cellulose chain has three hydroxyl groups, namely, a primary hydroxyl group at C6 position, and secondary hydroxyl groups at C2 and C3 positions. These hydroxyl groups along macromolecule chains are readily available for chemical modification *via* reacting with functional groups, thus contributing to a variety of cellulose derivatives. Furthermore, the reactivity of the three hydroxyl groups in AGU is diverse, which is affected by inherent reactive ability, reaction media, steric effects of reagents, and steric effects of the supramolecular structure of cellulose.[11] To date, numerous cellulose derivatives (*e.g.*, esters, ethers, carbamates, carbonates) have been synthesized in the aforementioned solvent systems *via* esterification, acylation, grafting, etherification, and carbalination.
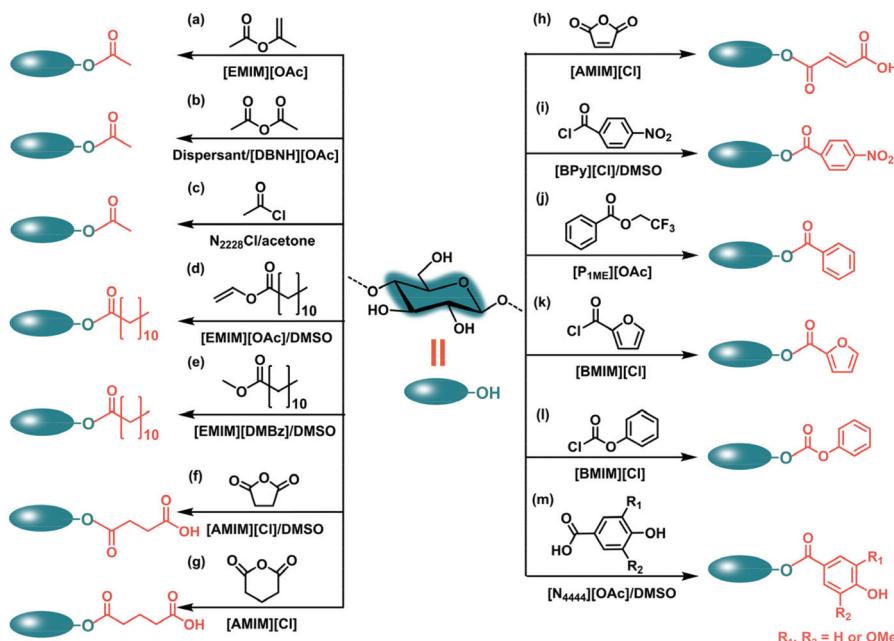
3.1. Chemical modification of cellulose in ionic liquids

3.1.1. Esterification and acylation. Among the most widespread cellulose derivatives, esterified cellulose has attracted the most attention. Generally, conversion of cellulose can be achieved by two main routes, namely, esterification of cellulose with free acids, and acylation of cellulose with acyl chlorides or acid anhydrides, in the presence or absence of catalysts. Several types of cellulose esters, such as aliphatic esters and aromatic esters, have previously been synthesized in IL media.[70]

Cellulose acetate (CA), a frequently studied aliphatic cellulose ester, can be synthesized by acetylation of cellulose with reagents such as acetyl chloride (AcCl), acetic anhydride (Ac$_2$O), isopropenyl acetate (IpeAc), vinyl acetate (VinAc) in the absence or presence of a catalyst. In this regard, the reaction can be performed in various ILs including 1-allyl-3-methyl-imidazolium chloride ([AMIM][Cl]),[71,72] 1-*N*-butyl-3-methyl-imidazolium chloride ([BMIM][Cl]),[73,74] 1-*N*-ethyl-3-methyl-imidazolium chloride ([EMIM][Cl]),[73] 1-ethyl-3-methyl-imidazolium acetate ([EMIM][OAc]),[75,76] triethyloctylammonium chloride (N$_{2228}$Cl),[77] 1,5-diazabicyclo[4.3.0]non-5-ene acetate [DBNH][OAc][78,79] and 1,8-diazabicyclo[5.4.0]undec-7-ene acetate [DBUH][OAc].[80] Such solvents exhibit good cellulose solubilization behavior and some of them even can act as organocatalysts. As an example, Kakuchi *et al.* took advantage of the dual function of [EMIM][OAc], namely, dissolving capacity and organocatalytic property, for the facile acetylation of cellulose (Scheme 2a).[75] The reaction with IpeAc in the IL media can proceed smoothly and rapidly to obtain highly substituted cellulose triacetate (DS = 2.96). Kakko *et al.* demonstrated a superbase-derived IL (*i.e.*, [DBNH][OAc]) for rapid and efficient acetylation of cellulose with Ac$_2$O, IpeAc, VinAc. They carried out the reactions under mild conditions (60–70 °C, 1 h) without the assistance of catalysts.[78] It was found that acetylation with IpeAc produced CA with a DS as high as 2.97, whereas the use of vinylic reagents resulted in CA products with a maximum DS of 1.58.

Besides individual IL systems, researchers also applied binary mixtures of ILs and co-solvents as acylation media. The co-solvents typically include DMSO, DMF, DMAc, acetonitrile (ACN) and acetone, which are supposed to promote the acetylation process. A gram-scale production of polysaccharide (*i.e.*, cellulose, xylan, dextrin, pillulan) acetates was achieved in [EMIM][OAc] combined with a co-solvent of DMSO.[76] The co-solvent acted as an efficient accelerator for the organocatalytic ability of the IL, is mainly due to nucleophilic assistance by IL anions of alcoholic species.[81] Synthesis of CA in binary solvents of [DBNH][OAc] and dispersants (*i.e.*, DMSO, DBN, ACN and acetone) was studied by Jogunola *et al.*, as shown in Scheme 2b.[79] In the presence of ACN, the DS of CA reached 2.68 within 0.5 h using 5 equiv./AGU at 80 °C. However, if no co-solvent was added, similar conditions only resulted in a DS of 0.9 after 3.0 h. Hanabusa *et al.* prepared nine protic ILs composed of amidine and acetic acid for cellulose dissolution, and validated that [DBUH][OAc] exhibited the best catalytic performance for the acetylation of cellulose.[80] The addition of DMSO led to the DS of CA increasing from 2.61 to 2.87. An ammonium-based IL (N$_{2228}$Cl) in combination with acetone was employed for homogeneous acetylation (Scheme 2c). The synthesized CA showed a maximum DS value of 2.79.[77]

Scheme 2 Esterification and acylation of cellulose in ILs.

By adjusting the types of reactants, cellulose esters with diverse aliphatic groups can be obtained. Among them, vinyl esters are frequently used as acylating agents for the synthesis of aliphatic cellulose esters. As an example, vinyl ester-based modification of cellulose was carried out in [EMIM][OAc] without external catalysts.[82] Accordingly, aliphatic groups with chain lengths of C8 to C16 were introduced to the cellulose backbone. Vinyl laurate modified cellulose with a DS of 2.4 was obtained at 80 °C for 4 h with a molar ratio of 3 equiv./ AGU. Interestingly, Milotskyi et al. adopted a rapid reactive extrusion method for cellulose acylation with vinyl laurate in [EMIM][OAc]/DMSO medium (Scheme 2d).[83] The DS values of vinyl laurate synthesized at 120 °C for 10 min varied from 2.65 to 2.73. Yuan et al. performed homogeneous acylation of α-cellulose with vinyl esters in a mixture of [EMIM][OAc] and γ-valerolactone (GVL).[84] After operating at 80 °C for 4 h, cellulose laurate, cellulose pivalate and cellulose chloroacetate were synthesized with DS of 3.0, 3.0 and 1.43, respectively.

Researchers still use relatively inactive but easily available alkyl esters instead of vinyl esters to produce esterified cellulose. However, reaction with alkyl esters leads to cellulose esters with lower DS values. Wang et al. designed a binary IL mixture containing a hydrophilic [BMIM][Cl] and a hydrophobic [BMIM][BF$_4$] as a reaction medium for the acylation of cellulose.[85] As reported, cellulose was acylated with methyl esters (methyl laurate, methyl palmate and methyl stearate) in the presence of a catalyst of lipase. Long-chain cellulose easters were formed and the DS values were in the range of 0.213–1.452. Acylation with methyl laurate was also attempted in another IL of 1-ethyl-3-methylimidazoium 2,4-dimethoxy-benzoate ([EMIM][DMBz]). With the assistance of DMSO as a co-solvent, the reaction occurred without any external

catalysts to acquire cellulose laurate with a DS of 0.52 (Scheme 2e).[86]

Aliphatic cellulose esters bearing a pendant carboxylic acid group could be synthesized through ring-opening esterification of cyclic anhydrides [e.g., succinic anhydride (SA), maleic anhydride (MA) and glutaric anhydride (GA)] with cellulose in ILs. In this regard, [AMIM][Cl] and [BMIM][Cl] are widely employed as the reaction media. Succinylated banana cellulose with a maximum DS of 0.37 was produced by modification with SA in AMIMCl/DMSO mixtures (Scheme 2f).[87] Sun's group has made many attempts to modify cellulose with cyclic anhydrides as reagents.[88–90] They proceeded with a succinyla-tion reaction in a binary solvent of [BMIM][Cl]/DMSO using another catalyst, N-bromosuccinimide (NBS).[88] Succinylated cellulose with DS values of between 0.24 and 2.31 can be attained. In the following study, three main components (cell-ulose, hemicellulose and lignin) were isolated from extractive-free bagasse and were homogeneously esterified with GA in [AMIM][Cl] (Scheme 2g).[89] The group extended the reaction of the three main components to homogeneous maleylation (Scheme 2h).[90] The maleylated cellulose showed a percentage of substitution of 13.5%.
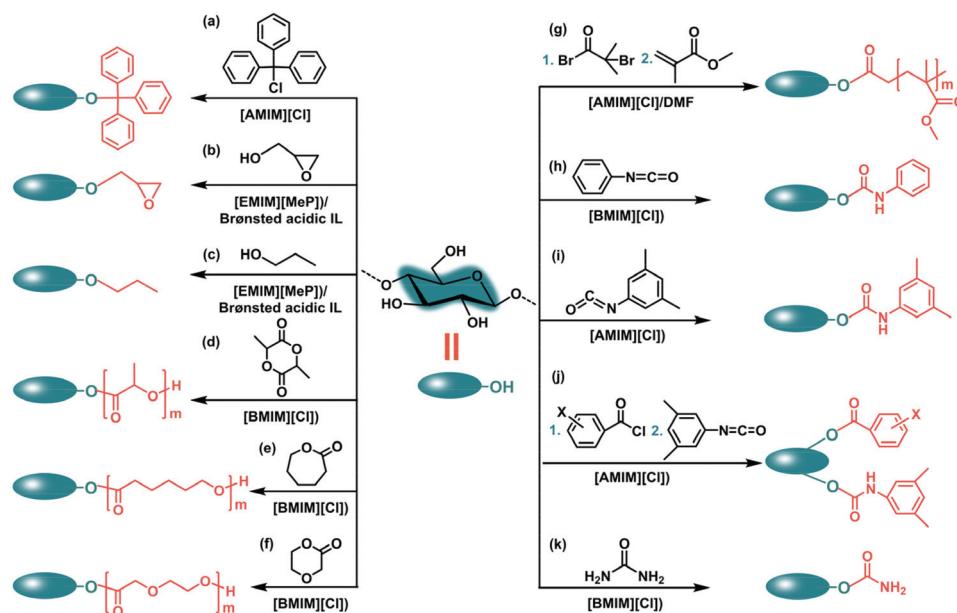
In the case of cellulose aromatic esters, benzoyl chlorides bearing diverse p-substituted groups are widely applied for the benzoylation of cellulose. El Hamdaoui et al. described an efficient strategy with low reagent consumption and a short reaction time for the acylation of cellulose.[91] Accordingly, the reaction with p-nitrobenzoyl chloride was carried out in a binary mixture of 1-butylpyridinium chloride ([BPy][Cl]) and DMSO (Scheme 2i). With processing at 80 °C for 1.30 h, cell-ulose p-nitrobenzoate with DS values of 0.12–1.5 was obtained. Similarly, kraft cellulose p-iodobenzoate with DS values of

0.18–2.05 was attained by the reaction with *p*-iodobenzoyl chloride in [BMIM][Cl].[92] Homogeneous cellulose acylation with 2,2,2-trifluoroethyl benzoates proceeded in *N*-methyl-*N*-(2-methoxyethyl) pyrrolidinium acetate ([P$_{1ME}$][OAc]), affording corresponding cellulose benzoates with full substitution (DS = 3) (Scheme 2j).[93] In the same medium, cellulose benzoates with DS values of 2.38 and 2.67 were produced by reactions with 4-[(4-hydroxyphenyl)diazenyl]benzoate or 4-[(4-methoxyphenyl)diazenyl]benzoate. Highly selective benzoylation of cellulose at the 6-position was conducted in [AMIM][Cl].[94] The DS values of cellulose 6-benzoates ranged from 1.04 to 1.29. The unreacted hydroxyl groups at 2- and 3-positions of the cellulose monoesters could be further reacted with 3,5-dimethylphenyl isocyanate. Buchanan *et al.* prepared cellulose benzoate propionates through the phased addition of Pr$_2$O and Bz$_2$O to cellulose in an IL of tributylmethylammonium dimethyl phosphate (TBMADMP).[95] The benzoate was selectively located at the C2 and C3 positions. Moreover, Heinze's group reported that in the presence of pyridine, fully substituted cellulose furoate and cellulose phenyl carbonate were accessible using [BMIM][Cl] as a reaction medium (Scheme 2k and l).[96,97] Recently, Niu *et al.* selected three phenolic acids (*p*-hydroxybenzoic acid, vanillic acid, and syringic acid) to modify cellulose fibers. The homogeneous esterification was performed in a mixture of a recyclable IL (tetrabutylammonium acetate ([N$_{4444}$][OAc]) and DMSO (Scheme 2m).[98] The esterified cellulose-generated films displayed good hydrophobicity and barrier properties, although the DS of cellulose derivative was less than 0.25.

3.1.2. Etherification. Cellulose ethers are typically synthesized by reacting cellulose with electrophiles such as epoxides or alkyl halides.[99] Many efforts have been devoted to the synthesis of cellulose ethers [*e.g.*, CMC, carboxyethyl cellulose (CEC), carboxypropyl cellulose (CPC), hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC)] in ILs. Homogeneous hydroxyalkylation of cellulose with epoxides (ethylene oxide and propylene oxide) was conducted in ILs in the absence of inorganic bases.[100] In this case, water-soluble hydroxyalkyl cellulose with a molar degree of substitution (MS) up to 2.79 was acquired. It was revealed that the catalytic effect of acetate ion led to a favorable conversion of cellulose in [EMIM][OAc], while no derivatization of cellulose occurred in other ILs such as [BMIM][Cl]. Lv *et al.* carried out tritylation of cellulose with triphenylmethyl chloride in [AMIM][Cl] applying pyridine or 1-butylimidazole (BIM) as a base (Scheme 3a).[101] Using pyridine as a base, the reaction exhibited a heterogeneous–homogeneous–heterogeneous process with regioselective substitution at the C6 position. The DS of trityl cellulose (TC) reached ∼1. As a comparison with BIM as a base, the entire reaction was performed under homogenous conditions. The DS of TC was as low as ∼0.22, and the trityl groups of TC were located at the C6 and C2 positions. Binary IL mixtures consisting of 1-ethyl-3-methylimidazolium methylphosphonate ([EMIM][MeP]) and Brønsted acidic IL were demonstrated to be both solvents and catalysts for the etherification of cellulose with glycidol (Scheme 3b).[102] By varying the reaction time and the structural compositions of acidic ILs, the epoxidized cellulose derivatives with DS values of 0.1–2.2 were obtained. Cellulose dissolved in the same binary IL mixtures was allowed to react with propanol, attaining propoxy cellulose with a maximum DS of 2.5 (Scheme 3c).[103]

3.1.3. Grafting. Grafting polymerization, a commonly used approach for cellulose modification, is to covalently bond grafted polymer side chains to the cellulose backbone to form a copolymer with branched structures. Such an approach endows the native cellulose with new properties (*e.g.*, hydro-
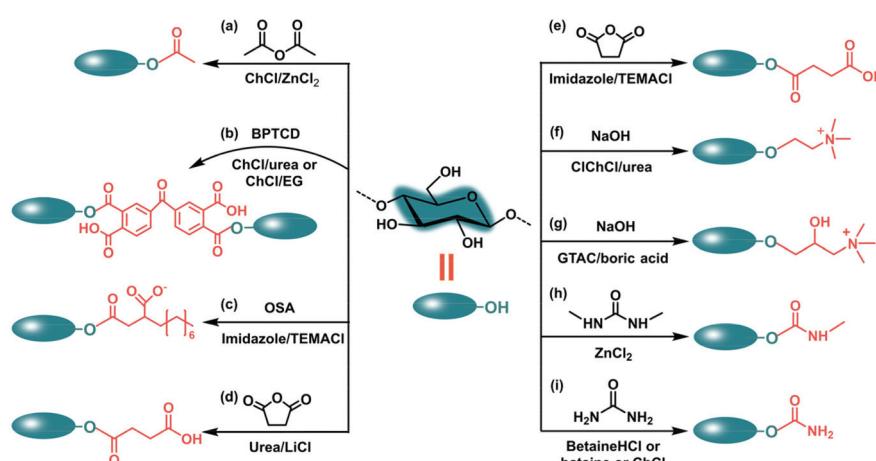

Scheme 3 Etherification, grafting and carbanilation of cellulose in ILs.

phobility, sensitivity, antibacterial ability) without destroying its intrinsic characteristics.[104] Generally, cellulose graft copolymers can be prepared by ring opening polymerization (ROP), atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization. ILs are favorable solvents for cellulose and grafting reagents. So far, grafting cellulose copolymers with diverse side chains [e.g., poly(lactide) (PLA),[105–107] poly(caprolactone) (PCL),[105,108–110] poly(dioxanone) (PDO),[111] polyacrylic acid (PAA),[112] poly(N-isopropylacrylamide) (PNIPAM),[113,114] poly (methyl methacrylate) (PMMA),[115,116] poly(N,N-diethyl-acrylamide) (PDEAAm),[114] poly(N,N-dimethylamino-2-ethyl methacrylate (PDMAEMA)[117]] have been synthesized by using ILs or binary ILs/co-solvent systems as reaction media. Our group applied ROP strategy to design and synthesize a series of amphiphilic cellulose graft copolymers with PLA, PCL and PDO chains (Scheme 3d–f).[105] The reactions were carried out in an IL-BMIMCl medium. The obtained copolymers were capable of self-assembling into core–shell structured micelles and then used as carriers for hydrophobic drugs to be applied in drug delivery and cell imaging fields.[107,109,118] Recently, Liu et al. synthesized cationic amphiphilic cellulose copolymers via ROP in [BMIM][Cl]. The DS of the resultant products was up to 1.79, indicating a high ROP grafting efficiency.[111] Zhang et al. synthesized well-designed cellulose-graft-PMMA copolymers through activators regenerated by electron transfer ATRP method (Scheme 3g).[119] In this regard, 2-bromoisobutyryl groups were first introduced to the cellulose backbone by using AMIMCl/DMF as a solvent. The resultant macroinitiators were used for the copolymerization of MMA to obtain the final copolymer products. Compared with linear PMMA films, the copolymers exhibited similar transparency and greatly improved tensile toughness. Hufendiek et al. produced cellulose macro-chain RAFT agents (cellulose-CTA) in BMIMCl media. PDEAAm and PNIPAM could be subsequently grafted on these cellulose-CTAs, resulting in temperature-responsive cellulose graft copolymers.[114] However, there are limited reports on the RAFT polymerization of cellulose in ILs.

3.1.4. Carbanilation. In general, the carbanilation of cellulose can be carried out in ILs using isocyanate as a reagent. Heinze's group provided an example of carbanilation of cellulose with three different degrees of polymerization (DP) in [BMIM][Cl]. The reaction was conducted with phenyl isocyanate in the absence of catalysts.[73] Fully substituted cellulose carbanilates were produced using 10 equiv./AGU at 80 °C for 4 h. The group changed the subject of carbanilation to bacterial cellulose (BC) that is greatly different from plant cellulose (Scheme 3h).[120] The DS values of BC carbanilates were in the range of 0.29–3.0, depending on the reaction time and molar ratio. Reaction between cellulose and 3,5-dimethylphenyl isocyanate in [AMIM][Cl] resulted in the synthesis of cellulose-tris(3,5-dimethylphenylcarbamate) (CDMPC), as shown in Scheme 3i.[121] The prepared CDMPC were further applied to prepare a chiral stationary phase for the chiral separation of seven pesticides.[121] Recently, a series of regioselectively substituted cellulose hybrid esters, cellulose 6-benzoate-2,3-phenylcarbamates, were synthesized in [AMIM][Cl] by a facile two-step method (Scheme 3j). The preparation was not required for a protection-deprotection process.[94] The results showed that highly chiral recognized cellulose derivatives with electron-donating substituents (e.g., 4-tert-butyl) on the benzene ring can be comparable to commercial Chiralcel OD column.[94] Cellulose carbamate is a bio-based and environmentally friendly material and is considered an interesting alternative to petroleum-based polymers.[122] Zhang et al. modified cellulose through in situ reactive extrusion with urea in the presence of [BMIM][Cl] and attained cellulose carbamate with a DS of 0.24 (Scheme 3k).[123]

3.2. Chemical modification of cellulose in deep eutectic solvents

3.2.1. Esterification and acylation. Abbott et al. employed ChCl based DES (i.e., ChCl/ZnCl$_2$) as both solvent and catalyst to carry out O-acetylation reactions on monosaccharides and cellulose (Scheme 4a). The DES system allowed access to acetylated cellulose with DS values ranging from 0.15–0.47.[124] Park

Scheme 4 Chemical modification of cellulose in DESs.

et al. prepared novel antibacterial cotton by treating cotton fabrics with a photoactive antibacterial compound 3,3′4,4′-benzophenone tetracarboxylic dianhydride (BPTCD) in a combined process of shaking immersion in a dyeing machine and pad-dry-cure (Scheme 4b).[125] In this case, ChCl/urea and ChCl/ethylene glycol (ChCl/EG) were developed as environmentally-acceptable and economically-feasible treatment media. The treated cotton fabrics exhibited excellent antibacterial activity before and after UV irradiation. Besides ChCl-based DESs, a recent DES system comprising imidazole and triethylmethylammonium chloride (TEMACl) has been proven as a simple and fast reaction medium for the modification of cellulose nanofibers (CNFs) films and all-cellulose composite (ACC) films with octylsuccinic anhydride (OSA) (Scheme 4c).[126] The reaction was performed under relatively mild conditions (80 °C, 1 h). The OSA modified CNF films exhibited better mechanical properties and increased hydrophobicity compared to the original CNF film.

Moreover, DESs have also been applied as green pre-treatment routes combining with mechanical disintegration to produce derivatized nanocellulose. Anionic CNFs with diameters of 2–7 nm were produced through ring-opening esterification of succinic anhydride (SA) with hydroxyl groups of wood cellulose following mechanical treatment (Scheme 4d).[127] The reaction was conducted in a non-degrading and non-dissolving urea/LiCl DES medium at 70–110 °C for 2–24 h, resulting in anionic cellulose with carboxyl content ranging from 0.34 to 0.95 mmol g^{-1}. Another DES system consisting of imidazole and TEMACl was reported as a pre-treatment media in the anionic functionalization of groundwood pulp (GWP) with SA (Scheme 4e).[128] The modified GWP treated at 70 °C for 2 h gave a carboxyl content as high as 3.34 mmol g^{-1}, and formed highly anionic charged wood nanofibers. Such nanosized fibers could form self-standing films with good mechanical properties. More recently, Liu *et al.* applied a series of ChCl/carboxylic acid based DESs as both pretreatment media and reagents to produce esterified CNFs from the raw material of hardwood bleach kraft pulp.[22] The presence of DES was conductive to the esterification and effective swelling of cellulose, thereby giving CNFs after mechanical treatment. The esterified CNFs showed high yields of 72%–88% and still maintained the cellulose I crystal structure.

3.2.2. Etherification. Although DESs show promising properties as reaction media, some DESs have been proven to lack stability under specific conditions. Thus, DESs can directly participate in cellulose modification, especially etherification of cellulose. For example, an eutectic mixture of ChCl derivative and urea was developed for the cationization of cellulose (Scheme 4f).[129] The DES serves both as a solvent and a reagent which can react with all the available hydroxyl groups on cellulose to obtain cationic cellulose derivatives with significantly improved hydrophilicity. Another example of cationic cellulose derivatives applied to biobased flocculants was synthesized by utilizing a mixture of glycidyl trimethyl ammonium chloride (GTAC) and boric acid to modify cellulose (Scheme 4g).[130] In this case, cationization of cellulose can be achieved without
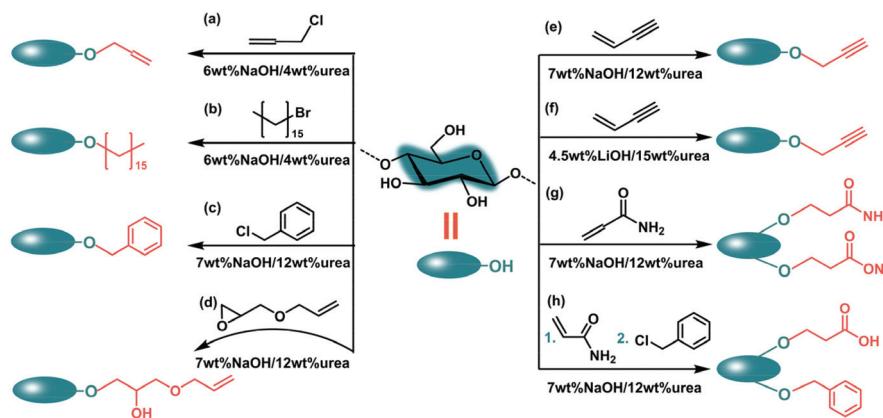
any additional solvents or costly solubilization methods. Following that, an alternative green solvent based on chlorocholine chloride (ClChCl)/urea DES was investigated for the cationic functionalization of cellulose monoliths.[131] The resulting materials were applied as adsorbents for the removal of acid red 70 dye from water. In addition, a reactive sulfamic acid/urea DES both as a reaction medium and a reagent for the sulfation of cellulose was reported by Sirviö *et al.*[132] The charge density of the sulfonated samples reached the range of 1.40–3.00 mmol g^{-1}. The sulfonated cellulose with sulfate groups of 2.40 mmol g^{-1} could easily form transparent gel-like CNFs after only passing once through the microfluidizer.

3.2.3. Carbanilation. Urea and many of its derivatives are promising chemicals for chemical modification of cellulose.[133] Thus, carbamate conversion can be achieved when cellulose is treated with urea-based DESs. Sirviö *et al.*[133] demonstrated a reactive DES consisting of dimethylurea and $ZnCl_2$ to synthesize cellulose methyl carbamate with a DS of 0.17 (Scheme 4h). The carbamation reaction was carried out at 150 °C for 3 h. The product showed good alkaline-solubility in 3% NaOH while the original cellulose fibers were nearly insoluble, even in a 9% NaOH solution. In the following, cellulose carbamate was prepared in three different urea-based DESs systems (*i.e.*, urea/ChCl, urea/betaineHCl and urea/betaine), as shown in Scheme 4i.[134] The reaction proceeded at relatively low temperatures of 95–120 °C without external solvents. The nitrogen content of cellulose carbamate could be easily adjusted by changing cellulose consistency and reaction temperatures.

3.3. Chemical modification of cellulose in aqueous alkali/urea solutions

3.3.1. Etherification. Since etherification of cellulose is usually undertaken in an alkaline environment, the aqueous alkali/urea systems are well suited as homogeneous reaction media for the synthesis of cellulose ethers due to their initial basicity. So far, cellulose ethers such as MC,[135] CMC,[136] HEC,[137] HPC[135] as well as cyanoethyl cellulose (CEC)[138,139] have been prepared in aqueous alkali/urea systems. These cellulose derivatives are basically obtained by reacting cellulose with etherifying agents such as alkyl halides, epoxides, and vinyl compounds.

Zhang and coworkers applied an aqueous 6 wt% NaOH/4 wt% urea solution as a reaction medium for the synthesis of allyl cellulose (AC) (Scheme 5a). A maximum DS of 1.65 was reached using allyl chloride as an etherification agent.[140] In this case, the AC product was a good intermediate to further react with thiol compounds [*n*-dodecyl mercaptan (NDM), 2-aminoethanethiol hydrochloride (AET), cysteine (Cys) and monothioglycerol (MG)] through thiol–ene click reactions. Recently, an amphiphilic cellulose (MCC-C16) was designed to improve the antifouling and separation properties of poly(acrylonitrile-*co*-methyl acrylate) ultrafiltration membrane.[141] The synthesis of MCC-C16 was achieved by the reaction of MCC with 1-bromohexadecane in the above-mentioned aqueous solution (6 wt% NaOH/4 wt% urea), as shown in Scheme 5b.

Scheme 5 Chemical modification of cellulose in aqueous alkali/urea solutions.

An aqueous solution of 7 wt% NaOH/12 wt% urea is a favorable solvent for initiating the etherification reaction of cellulose. Cellulose dissolved in the 7 wt% NaOH/12 wt% urea aqueous solution was allowed to react with benzyl chloride under mild conditions in the absence of any catalysts (Scheme 5c).[142] The DS values of benzyl cellulose ranged from 0.29 to 0.54, depending on the reaction temperature and the molar ratio of benzyl chloride to AGU. However, the high water content of the reaction medium restricts the benzylation of cellulose and makes it difficult to achieve higher DS.[143]
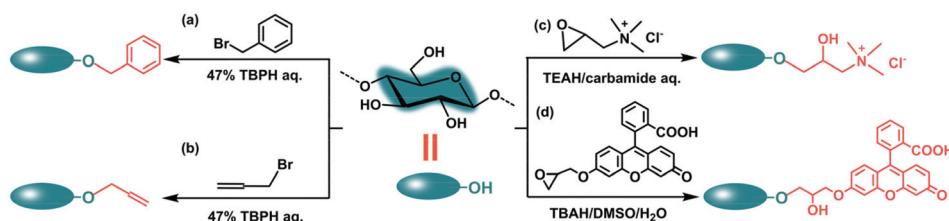
Quaternary ammonium salt-modified cellulose (QMCC) with high positive charges was prepared in an aqueous solution of 7% NaOH/12% urea.[144] The QMCC-added alkaline solid polyelectrolyte membrane showed significantly improved conductivity and tensile strength, and could be applied to flexible Zn–air batteries. Using the same solvent, Qi *et al.* modified cellulose with allyl glycidyl ether (AGE) to obtain 3-allyloxy-2-hydroxypropylcelluloses (AHP-celluloses) with DS ranging from 0.32–0.67 (Scheme 5d).[145] Furthermore, owing to the good dissolving capacity for cellulose and the inherently high content of water, aqueous alkali/urea solutions provide an appropriate aqueous environment for the preparation of cellulose-based hydrogels. These hydrogels can be fabricated by chemical cross-linking of cellulose or cellulose derivatives with the occurrence of cross-linking agents. Liu *et al.* synthesized cellulose hydrogels through chemical cross-linking of cellulose with 1,4-butanediol diglycidyl ether (BDE) in 6 wt% NaOH/4 wt% urea aqueous solution.[146] The synthesis of cellulose ionic hydrogels (CIHs) from cellulose in NaOH/urea aqueous solution was reported by Tong *et al.*[147] The cellulose was etherified with AGE to be endowed with double bonds and then chemically cross-linked by free radical polymerization to fabricate CIHs with high elongation and compressibility.

Benefiting from the basicity of aqueous alkali/urea systems, vinyl compounds are activated in these systems and undergo Michael addition reaction with cellulose under catalyst-free conditions. As a classical example, cyanoethylation of cellulose with acrylonitrile (AN) was accessible in 7 wt% NaOH/12 wt% urea (Scheme 5e)[138] and 4.5 wt% LiOH/15 wt% urea aqueous

solutions (Scheme 5f).[139] In this case, the relative reactivity of hydroxyl groups was in the order of C-6 > C-2 > C-3. Cellulose polyelectrolytes bearing acylamino and carboxyl groups were homogenously synthesized in NaOH/urea aqueous solutions (Scheme 5g). The synthesis process involved two steps, Michael addition reaction with acrylamide followed by saponification of acylamino groups into carboxyl groups.[148] Based on etherification of cellulose with acrylamide and benzyl chloride, an amphiphilic cellulose derivative (BCEC) containing hydrophobic benzyl and hydrophilic carboxyethyl groups was synthesized (Scheme 5h). The reaction was conducted in NaOH/urea aqueous solution without extra catalysts.[149] Considering the pH responsibility and surfactant property of BCEC, microcapsules formed by cross-linking BCEC with polyurea were applied for the encapsulation and controlled release of hydrophobic methyl 1-naphthylacetate (MENA). In addition, methylenebisacrylamide (MBA) was selected as a Michael addition reagent for the cross-linking of cellulose in LiOH/urea aqueous solution. A robust hydrogel was formed and exhibited a superior water uptake capacity.[150]

3.4. Chemical modification of cellulose in quaternary onium hydroxides

3.4.1. Etherification. Similar to aqueous alkali/urea systems, aqueous QOH solutions exhibit strong basicity and are able to provide a suitable environment for homogeneous etherification of cellulose. Abe *et al.* reported a rapid benzylation of cellulose with benzyl bromide in a 47% TBPH aqueous solution (Scheme 6a).[151] Benzyl cellulose with high DS values (>2.5) was synthesized within 10 min at 20–25 °C using 9 equiv. per AGU. This solvent system is more favorable for cellulose benzylation than the aqueous NaOH/urea system because of its lower water content (<50%). The TBPH solution has also been shown to be applicable as a reaction medium for the allylation of cellulose. The reaction with allyl bromide at 25 °C for 10 min resulted in a rapid introduction of allyl into cellulose, yielding an AC product with a DS ~1.9 (Scheme 6b). It was also confirmed that no significant degradation of the cellulose and cross-linking between the allyl sub-

Scheme 6 Chemical modification of cellulose in aqueous QOHs.

stituents could be observed during the allylation process. Sirviö and co-workers developed a series of mixture solvents consisting of TEAH aqueous solution and carbamides (urea, *N*-methylurea, *N*-ethylurea, 1,3-dimethylurea, and imidazolidone) for room-temperature dissolution and etherification of cellulose.[10] The etherification reaction with GTAC was homogeneously performed using a molar ratio of 3 equiv./AGU at room temperature (23 °C) for 24 h (Scheme 6c). The cationic cellulose derivatives produced in all the studied TEAH/carbamide solvents exhibited higher cationic charge densities compared to those obtained in a reference solution of 7 wt% NaOH/12 wt% urea. Cationic wood nanofiber (CWNF) could be fabricated from sawdust by epoxide ring-opening etherification with GTAC in aqueous TEAH/carbamide solutions followed by mechanical disintegration.[152] The films produced from CWNF exhibited superior UV-blocking oxygen barrier and antimicrobial properties. Shi *et al.* adopted a simple and novel strategy to design fluorescent cellulose films in a TBAH/H₂O/DMSO ternary solvent system with a mass ratio of 2 : 3 : 5.[153] In this case, the films were fabricated *via* etherification of cellulose with an expoxypropoxy-contained fluorescein molecule and subsequent cross-linking reaction. The obtained films showed excellent fluorescent property, pH sensitivity and polarized emission behavior after stretching.[153]

4. Conclusions and prospects

Cellulose is the most abundant renewable material with fascinating properties. Homogeneous chemical modification is an efficient technique for converting cellulose into cellulose derivatives with a high degree of uniformity. However, the solubilization of cellulose is a critical step before derivatization. In this review, we have briefly overviewed four types of recent "green" solvents for cellulose dissolution, namely ILs, DESs, aqueous alkali/urea systems and aqueous QOH systems, and summarized recent examples of cellulose modification in these solvents.

Although these solvents have emerged as reaction media for cellulose derivatization, they have their own advantages and disadvantages. Owing to excellent dissolution capacity and structural diversity, ILs fit well with cellulose chemistry. To date, various types of chemical modification of cellulose, such as esterification, etherification, grafting and carbalination, can be performed in ILs. ILs can efficiently dissolve both

cellulose and reactants to provide a homogeneous reaction medium for cellulose functionalization. Several ILs even exhibit catalytic properties during reactions, depending on the structural characteristics of the ILs. Highly substituted cellulose derivatives are readily synthesized in ILs. Unfortunately, most ILs suffer from the drawbacks of high viscosity and high sensitivity to water. Although the incorporation of co-solvents into ILs enables an appropriate decrease in the viscosity, the water content needs to be strictly controlled during the dissolution and modification process. Besides, there are still concerns about the high cost, difficulty in preparation, potential toxicity, and non-degradability of ILs.

DESs are regarded as non- or low toxic, inexpensive and biodegradable alternatives to traditional ILs because they offer the benefits of ILs. However, examples of DESs for efficient dissolution of cellulose are limited, and the solubility of cellulose in the DESs is much lower than that in ILs. Due to the insufficient solubilization of cellulose, current cellulose derivatization using DESs as reaction media is usually performed in heterogeneous conditions.

In the case of aqueous alkali/urea systems, rapid dissolution of cellulose can be achieved, but is limited by precooling requirements and the molecular weight of cellulose. The functionalization of cellulose in alkali/urea aqueous solutions is mainly focused on etherification. Conversion of cellulose to cellulose ethers in aqueous alkali/urea is often plagued by the high water content of the solvents. Moreover, the study of cellulose modification in alkali/urea aqueous solutions is kind of limited to the group of LN Zhang. Input from a broader scientific community is needed.

Compared to aqueous alkali/urea systems, aqueous QOH solutions can rapidly dissolve cellulose at ambient temperatures. Although there are limited studies in the literature on cellulose derivatization in aqueous QOHs, these results will motivate researchers to make more attempts to modify cellulose in these systems.

In response to the 12 principles of green chemistry, important issues such as efficient preparation, toxicity assessment and recovery of cellulose solvents still need to be considered. Most of the green solvents discussed in this minireview are petroleum-based products. Taking the most widespread class of ILs as an example, the synthesis of the imidazolium cations requires a significant number of chemical reaction steps, also involving non-green reactions. Driven by the target of carbon-reduction, bio-derived solvents or solvents from renewable

sources will be an important direction. Given the vast design space of ILs and DESs, many biobased molecules could be considered to make the solvents greener.

Application-oriented research is highly required in the future for the modification of cellulose in green solvents. The market is facing a significant transformation from conventional petroleum resource driven development to a more bioresource driven development. More functional cellulose chemicals and materials will be needed, which will require the cellulose modification industry to be adaptive to much richer products in the future. Future research needs to focus on the green conversion of cellulose into functional cellulose derivatives with higher efficiency, less waste/by-product and high selectivity. In addition, further research on the selection of reaction media, reactants and modification techniques is necessary.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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