



## 3D printing using plant-derived cellulose and its derivatives: A review

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### ABSTRACT

Three-dimensional (3D) printing is classified as a revolutionary, disruptive manufacturing technology. Cellulose (the most abundant natural polymer) and its many derivatives have been widely studied for many applications. The combination of 3D printing with cellulose-based feedstocks is therefore of critical interest. This review highlights many studies on 3D printing applications of plant-derived cellulose and its derivatives. Potential materials include cellulose ethers/esters, microcrystalline cellulose, nanocellulosic materials, and other products. It focuses on their roles and functions in 3D printing processes and the performance of the resultant printed objects. The outlook for future work is also provided, to underscore critical issues and opportunities.

### 1. Introduction

Three-dimensional (3D) printing (also referred to as additive manufacturing) is driving major innovations in a broad range of areas, including energy, biotechnology, medical devices, and many more (Fu, Yao, Dai, & Hu, 2017; Gunasekera et al., 2016; Jungst, Smolan, Schacht, Scheibel, & Groll, 2016; Murphy & Atala, 2014). The first 3D printing process was patented in 1986 by Charles W. Hull, under the name “stereolithography” (Hull, 1986). With 3D printing, objects can be digitally designed and precisely produced in a layer-by-layer fashion without the need for moulds, dies, or lithographic masks (Melocchi et al., 2016; Truby & Lewis, 2016). It offers a high degree of automation and reproducibility, and allows the direct fabrication of structures that can only be produced with difficulty using classical subtractive manufacturing techniques (Henke & Treml, 2013; Jungst, et al., 2016). 3D printing is becoming increasingly popular due to its potential for providing prototypes, customer-specific designs, high structural complexity, and rapid on-demand fabrication of small production volumes at a low-cost (Guvendiren, Molde, Soares, & Kohn, 2016). Therefore, it is regarded as the next revolution in manufacturing (Berman, 2012; Håkansson et al., 2016).

3D printing techniques are generally grouped into four categories: (1) extrusion-based methods such as fused deposition modeling (FDM) and direct ink writing (DIW), (2) particle fusion-based methods such as selective laser sintering (SLS), (3) Stereolithography (SLA), and (4)

inkjet printing (Ambrosi & Pumera, 2016; Gross, Erkal, Lockwood, Chen, & Spence, 2014; Guvendiren et al., 2016). Descriptions of these techniques can be found in previous reviews (Ambrosi & Pumera, 2016; Guvendiren et al., 2016; Jungst et al., 2016; Truby & Lewis, 2016). Although it is possible to print the same material using different 3D technologies, “ink formulations”, i.e., compositions of the printable material, vary significantly (Guvendiren et al., 2016). In general, printable 3D inks must show a well-controlled viscoelastic response, to counteract low resistance to extrusion through the nozzles. They must also form stable networks that can resist compressive stresses from capillary forces, and must have limited shrinkage during drying, to avoid object deformation and/or crack formation (Shao, Chaussy, Grosseau, & Beneventi, 2015; Smay, Gratson, Shepherd, Cesarano, & Lewis, 2002). The most common commercial 3D printing “inks” are based on metals, thermoplastics, and ceramics (Curodeau, Sachs, & Caldarise, 2000; Gross et al., 2014; Gunasekera et al., 2016; Murr et al., 2012; Wang & Liu, 2014).

Bio-based materials are receiving increased attention due to interests in a “bio-based society” (Håkansson et al., 2016), and environmental issues associated with the use of fossil-based resources (Xu, Wang, Sandler, Willför, & Xu, 2018). For this reason, there are great incentives for the use of cellulosic materials in 3D printing. As the principal component of plants, cellulose is a sustainable and almost inexhaustible polymeric raw material, with the potential to meet the increasing demand for environmentally friendly products (Klemm,

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**Table 1**  
Summary of various products using cellulosic paper as a platform.

Type of product	Function	Advantages	Disadvantages	References
Sensors and microfluidic paper-based analytical devices ( $\mu$ -PAD)	Substrate/scaffold; channel provider	Low-cost, hierarchical network, high porosity, large surface area, and nanofiber-based bundling flexibility and disposability	Weak wet strength	(Cha et al., 2012; Dungchai, Chaillapakul, & Henry, 2011; Gu & Huang, 2013; Han et al., 2012; Nie et al., 2010; Zhu et al., 2014)
Paper-based electronics (supercapacitors, field effect transistors, Lithium ion batteries, etc.)	Substrate; electrolyte reservoir; channel/pathway provider; dielectric layer; separator membrane	Widespread availability, low cost, flexibility, high-surface-area, porous structure and good electrolyte absorption properties	Low conductivity, durability and lifetime	(Fortunato et al., 2008; Gui et al., 2013; Hu, Wu, La Mantia, Yang, & Cui, 2010; Martins et al., 2008; Razaq et al., 2012; Weng et al., 2011)
Organic solar cells	Substrate; light management layer	Low cost, ultrathin and ultra-lightweight features	Surface roughness and poor wettability	(Barr et al., 2011; Fang et al., 2014; Wang, Chen, Xiao, Qi, & Gong, 2010)
Titanium carbide nanoparticles	Substrate; carbon precursor	Hierarchical structure and low cost	/	(Shin et al., 2004)
Surface enhanced Raman spectroscopy (SERS) substrates	Substrate	Low-cost, high porosity and disposability	/	(Yu & White, 2010)

Heublein, Fink, & Bohn, 2005; Roy, Semsarilar, Guthrie, & Perrier, 2009). Cellulose consists of repeating  $\beta$ -D-glucopyranose units that are covalently linked through acetal functions between the C1 carbon atom and the equatorial –OH group of C4 ( $\beta$ -1,4-glycosidic bonds) (Gunasekera et al., 2016; Klemm et al., 2005). Cellulose has many derivatives including cellulose ethers/esters, micro/nano-sized cellulose products, etc. A number of cellulose derivatives, such as cellulose ethers/esters and microcrystalline cellulose (MCC) have been important commercial products for many years (Elanthikkal, Gopalakrishnapanicker, Varghese, & Guthrie, 2010; Klemm et al., 2005; Siro & Plackett, 2010). Cellulose-based paper has of course been used in printing for centuries. With the emergence of 3D printing technology, cellulose and its derivatives also become promising “inks” for 3D printing (Gunasekera et al., 2016), offering an attractive pathway for fabricating sustainable structures (Siqueira et al., 2017). So far, several significant review articles related to this research area were published (Chinga-Carrasco, 2018; Guvendiren et al., 2016; Sultan, Siqueira, Zimmermann, & Mathew, 2017; Xu et al., 2018). Chinga-Carrasco (2018) summarized the recent progress of nanocellulose-based 3D-printed biomedical devices. Xu et al. (2018) reviewed the state-of-the-art research work on applications of wood-derived biopolymers, which focuses on pharmaceutical products and biomedical devices. It is still desirable to provide a broad review on the applications of cellulose and its derivatives in 3D printing. The scope of this review is to summarize the work done so far on the use of cellulose and its derivatives in 3D printing techniques. First, we introduce the studies of cellulose in 3D printing as the substrates and building blocks, followed with the recent progress in applications of cellulose derivatives, including cellulose ethers/esters, MCC and nanocelluloses in 3D printing. Finally, we share our perspective on future work in this area. This review will attract the attention of researchers from both cellulosic materials and 3D printing areas, and will facilitate the development of new ideas in this hot area.

## 2. Use of cellulose in 3D printing

### 2.1. Cellulose papers as substrates

Cellulose fibers have the advantages of widespread availability, low cost, and high flexibility (Gui et al., 2013; Razaq, Nyholm, Sjodin, Stromme, & Mihranyan, 2012). They are held together by mechanical interlocking, electrostatic interactions, van der Waals forces, and hydrogen bonds, resulting in paper: essentially a fiber network that is a light, green, adaptable, and economical substrate (Cha, Wang, He, & Ni, 2012; Zhu et al., 2014, 2016). Paper not only acts as a substrate with natural hierarchical network and porous structure, but cellulose fibers also have abundant functional groups (particularly –OH groups) on their surface that can strongly bind other materials (Gu & Huang, 2013; Gui et al., 2013; Shin, Li, Wang, Coleman, & Exarhos, 2004; Weng et al., 2011). For instance, graphene nanosheets (GNS) can be bound to the hydroxyl groups on cellulose fibers to form a conductive interwoven network that combines the macroporous texture and high strength of cellulose paper with the electrical conductivity and electroactivity of GNS (Weng et al., 2011).

These paper-based devices can be used for flexible, biodegradable and foldable applications such as biosensors, energy-storage devices, electronic devices, and intelligent packaging (Han, Kim, Li, & Meyyappan, 2012; Mahadeva, Walus, & Stoeber, 2015; Wang et al., 2009; Zhu et al., 2016). For instance, paper substrates have high porosity and large specific surface area. This increases the opportunity for sensor materials to capture analyte molecules, thereby enhancing chemical detection. Moreover, due to its hydrophilic nature, the cellulose swelling behavior in aqueous environments also leads to high sensitivity, since good analyte entrapments can be obtained as paper substrates swell up, increasing the local concentration of analyte molecules (Gu & Huang, 2013). Cellulosic paper-based glucose test strips were developed using 2,4,6-tribromo-3-hydroxy benzoic acid (TBHBA) as the

chromogen agent. Since cellulose paper is a good carrier substrate for the chromogen agents and other chemicals, quantitative analysis can be done by colorimetry based on the color intensity of the developed compounds (Cha et al., 2012). An overview of products using cellulose paper as substrates is listed in Table 1.

In particular, microfluidic paper-based analytical devices ( $\mu$ -PADs) can be used to quantify the concentrations of various analytes in aqueous solutions (Wang et al., 2013), and so can be ideal platforms, especially for point-of-care (POC) diagnosis (Wang, Deng, Shen, Yan, & Yu, 2016). However,  $\mu$ -PADs are usually fabricated using printing techniques like wax-printing (Costa et al., 2014; Li & Liu, 2014). In fact, 3D printing technique shows advantages in fabricating sophisticated three-dimensional structures. He, Gao, Wu, Nie, and Fu (2016) used a desktop 3D printer to manufacture novel  $\mu$ -PADs, driven by the capillary force of cellulose powder since it can transport liquid with capillary effect, similar to fluid transport in paper. A programmable capillary flow speed within the cellulose powder can be achieved due to the ease of printing microchannels with different depths. The flow speed is linear with the channel depth.

It was demonstrated that 3D printing could be used to fabricate radio-frequency (RF) passive components on a cellulose paper (Mariotti, Alimenti, Roselli, & Tentzeris, 2017). The results indicated that the maximum inductance and capacitance per unit area of the as-prepared RF devices were 1.4 nH/mm<sup>2</sup> and 6.5 pF/mm<sup>2</sup>, respectively, which is one order of magnitude higher compared with other similar technologies on less lossy flexible substrates. Furthermore, a 3D printed RF mixer on paper substrate was demonstrated and its conversion loss was below 10 dB.

3D printing technology is also an effective means to create variable tactile patterns such as braille on cellulose papers. Jo, Kim, Lee, Lee, and Moon (2014) used conventional A4 paper with a basis weight of 80 g/m<sup>2</sup> as the build platform for 3D printing of braille. Fig. 1 illustrates the 3D printing system and a printed tactile braille pattern. In contrast to punched patterns, the printed dots maintained their original shape after the tribology test. This good wear resistance can be attributed to the excellent interfacial adhesion strength of the printed pattern onto the cellulose paper. The interfacial adhesion strength was enhanced after thermal reflow treatment that was performed within 1 min at 160 °C on a hot plate in air, allowing melted polylactic acid (PLA) filament to diffuse into the cellulose network. Therefore, 3D printed tactile braille patterns provide several advantages (aside from printing conventional printing braille characters) that might be useful in helping the visually-impaired to enhance their sense of touch or to practice tactile recognition.

## 2.2. Solubilised cellulose as building blocks

Cellulose and its derivatives are suitable materials for 3D printing.

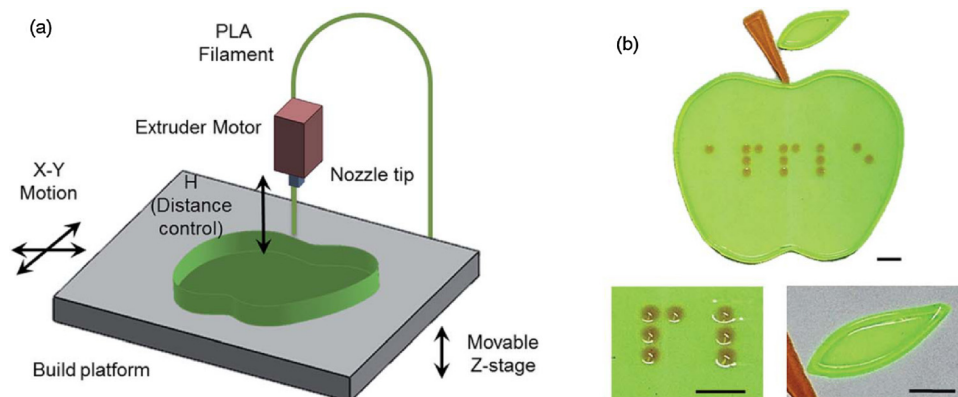


Fig. 1. (a) A schematic diagram of the 3D printing system. (b) A graphic type of tactile braille pattern: a 3D printed image of an apple. Scale bars of 5 mm. Reproduced from Ref. (Jo et al., 2014) with permission from The Royal Society of Chemistry, Copyright© 2014.

For this purpose, identification/development of good solvents for cellulose is critical to its utilization since cellulose cannot be melt-processed. However, cellulose is insoluble in water and in common organic solvents due to the preferential formation of intra- and intermolecular hydrogen bonds (Lindman, Karlström, & Stigsson, 2010; Olsson & Westman, 2013; Sen, Martin, & Argyropoulos, 2013; Swatloski, Spear, Holbrey, & Rogers, 2002). To date, only a few solvent systems have been found to be capable of dissolving cellulose. In general, cellulose solvents can be classified as derivatizing and non-derivatizing solvents (Medronho & Lindman, 2014; Sen et al., 2013). With derivatizing solvents, functionalization reactions, such as xanthation, esterification and etherification occur on the cellulose hydroxyl groups. These can disrupt the intra- and intermolecular hydrogen bonds between cellulose molecules, resulting in cellulose dissolution. Non-derivatizing solvents such as ionic liquids can dissolve cellulose via physical intermolecular interactions, without prior derivatization (Sen et al., 2013), which makes them preferred in many cases (Swatloski et al., 2002). However, most of them have limitations, and some of the most common direct cellulose solvent systems are listed in Table 2, together with their advantages and disadvantages.

As shown in Table 2, existing aqueous and non-aqueous cellulose solvents suffer either from high toxicity or from insufficient solvation power (Olsson & Westman, 2013; Pinkert, Marsh, Pang, & Staiger, 2009). These existing cellulose dissolution methods generally require relatively harsh conditions (high temperatures and pressures) and the use of expensive and uncommon solvents which may also be environmentally harmful (Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010; Pinkert et al., 2009). Besides, due to the process and/or cost problems, most of these are not easily scaled up except for the N-methylmorpholine-*N*-oxide (NMMO) monohydrate process (Olsson & Westman, 2013). The NMMO process has been successful on the industrial scale, leading to a new class of man-made cellulosic fibers with the generic name Lyocell®, even if the recovery of the NMMO solvent is complicated, energy demanding, and costly (Luo & Zhang, 2013; Medronho & Lindman, 2015). The success at the industrial scale gives NMMO a big advantage over other cellulose solvents when considering dissolved cellulose for 3D printing. Li, Zhu, and Yang (2018) adopted NMMO to solubilize dissolving pulp and subsequently produced complex structures with ordered, interconnected pores through 3D printing of the dissolved cellulose. The 3D-printed cellulose products show good Young's compressive modulus (12.9 MPa) and tensile modulus (160.6 MPa). The success in 3D printing of NMMO-dissolved cellulose shows the potential of utilizing 3D-printed cellulose for various industrial applications, especially those that would need complicated 3D structures.

Ionic liquids (ILs) are another promising class of cellulose solvents. These are a group of salts that exist as liquids below 100 °C (Mäki-Arvela et al., 2010; Pinkert et al., 2009). They are chemically and

**Table 2**  
Selected non-derivatizing solvents of cellulose.

Solvent Type	Solvents	Advantages	Disadvantages	References
Aqueous solvents	Aqueous alkali containing solvents (e.g. 10% NaOH, NaOH/urea systems)	No degradation of cellulose	High processing cost; recovery issue; and low maximum concentration	(Budtova & Navard, 2016; Isogai & Atalla, 1998; Sathitsuksanoh, George, & Zhang, 2013; Zhang, Ruan, & Gao, 2002)
Non-aqueous solvents	Aqueous inorganic complexes (e.g., Cuam, Cuen)	Good solution properties	Harsh conditions; strongly colored; and toxicity	(Hattori, Koga, Shimaya, & Saito, 1998; Kamida, Okajima, Matsui, & Kowasaka, 1984)
	Molten salt hydrates (e.g., LiClO <sub>4</sub> ·3H <sub>2</sub> O, LiSCN·2H <sub>2</sub> O)	Effective for cellulose with high degree of polymerization	Thermal instability; and high cost	(Fischer, Leipner, Thümmel, Brendler, & Peters, 2003; Leipner, Fischer, Brendler, & Voigt, 2000)
	N-methylmorpholine-N-oxide (NMMO)	Capable of dissolving high concentrations of cellulose directly; and high recycle ratios	Instability of NMMO; and cellulose degradation	(Hauru et al., 2012; Liebert, 2010; Olsson & Westman, 2013; Rosenau et al., 2002)
	Ionic liquids (ILs)	High maximum concentration; ILs themselves are chemical and thermal stable and non-flammable	High cost, high viscosity, sensitivity to moisture content and cellulose degradation	(Medronho & Lindman, 2015; Pinkert et al., 2009; Swatloski et al., 2002; Wu et al., 2004; Zhang, Du, Qian, & Chen, 2010)
	Dipolar aprotic solvents/LiCl (e.g., N, N-dimethylacetamide (DMAc)/LiCl)	No degradation of cellulose; and good cellulose solution stability.	High cost; harsh conditions (activation, water content)	(Dupont, 2003; Henniges, Kostic, Borgards, Rosenau, & Porthaast, 2011; Nayak, Chen, & Kim, 2008)
	Dimethyl sulfoxide (DMSO) containing solvents (e.g., DMSO/tetrabutylammonium fluoride (TBAF))	Capable of dissolving cellulose with a DP of up to 1200	Harsh conditions (water content in the system plays a crucial role)	(Heinze & Köhler, 2010)

thermally stable, and display immeasurably low vapor pressure, and are thus less hazardous (Hauru, Hummel, King, Kilpeläinen, & Sixta, 2012; Turner, Spear, Holbrey, & Rogers, 2004). Cellulose can be easily dissolved in ILs, and then be regenerated through a coagulation process in a non-solvent system such as water, which extends the potential applications of cellulose. Cellulose solutions in ILs may have high viscosities (Zhong, Wang, Huang, Jia, & Wei, 2013). This is a drawback for some applications, but may be an advantage of a 3D printing ink. Markstedt, Sundberg, and Gatenholm (2014) examined the feasibility of using extruded 3D printing technology to print 3D structures of cellulose dissolved in an IL (1-ethyl-3-methylimidazolium acetate, EmimAc), followed by water coagulation. At high molecular weight and concentration, the cellulose solutions exhibited shear thinning behavior. The viscosity significantly decreased under high shear rates during printing. The viscosity then quickly increased once the solution was printed and the high shear had stopped, which is desirable for a dimensionally stable product. The results showed that a solution of 4% dissolving pulp worked best for printing, since it had a viscosity high enough to keep its shape after dispensing, while the pressure needed for dispensing was low enough to be produced by a syringe pump. Regenerated cellulose gels were obtained after the removal of IL through a coagulation process using water as a nonsolvent. The printed structures consisted of amorphous cellulose gels with an interconnected porous structure, as depicted in Fig. 2. This novel method allows the production of spatially tailored gel structures made from cellulose, with many potential industrial applications.

### 3. Use of cellulose ethers/esters in 3D printing

Cellulose ethers and esters, which are the most important cellulose derivatives (Fox, Li, Xu, & Edgar, 2011), have been commercial products for many years (Klemm et al., 2005). These are used in many products such as thickeners, binders, emulsifiers, coatings and membranes (Chang & Zhang, 2011; Clasen & Kulicke, 2001; Edgar et al., 2001). Common industrial water-soluble cellulose ethers include carboxymethyl cellulose (CMC), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and hydroxypropyl methylcellulose (HPMC) (Clasen & Kulicke, 2001). Esterification of cellulose affords the possibility of processing cellulose into various forms including solutions, fibers and three dimensional objects (Edgar et al., 2001). The common cellulose esters include cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), nitrocellulose, etc.

Cellulose ethers are abundant, low cost, green materials with outstanding properties including good solubility, high chemical stability, and physiological safety (Clasen & Kulicke, 2001; Drofenik et al., 2003; Jeong, Böckenfeld, Balducci, Winter, & Passerini, 2012; Klemm et al., 2005). Studies claim cellulose ethers also have good biodegradability. For example, Wach, Mitomo, Yoshii, and Kume (2001) reported that CMC hydrogels could be degraded within a couple of days in the presence of cellulase. By varying the alkyl, hydroxyalkyl, or carboxyalkyl groups, it is possible to produce cellulose ethers with very different properties including water retention capacity, surface activity, film formation and pseudoplasticity, which afford them many applications in food products, pharmaceuticals, cosmetic products, and other commercial products (Clasen & Kulicke, 2001; Roy et al., 2009). Table 3 lists some common cellulose ethers with specific applications. Thanks to their multiple functions, cellulose ethers are also widely used in 3D printing, performing different roles.

#### 3.1. Cellulose ethers as viscosity modifiers

Inks properties are of critical importance in 3D printing (Fu et al., 2017; Jungst et al., 2016). In particular, 3D printing inks require a well-controlled viscoelastic response (high viscosity and shear-thinning behavior) (Fu et al., 2017). The shear thinning properties of polymer

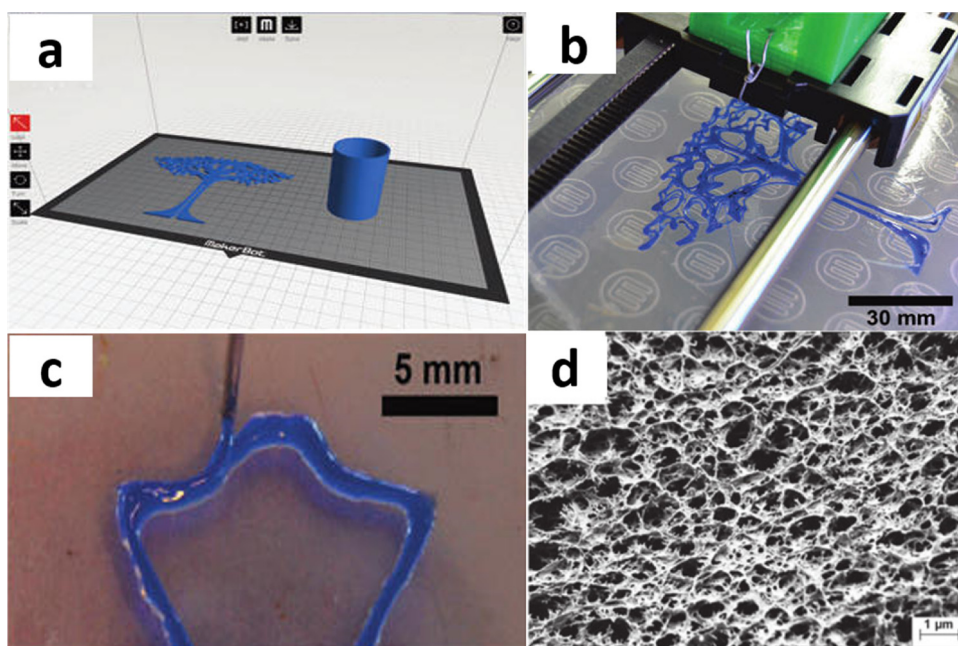


Fig. 2. (a) 3D printing controlled by MakerWare software utilizing stereolithography file format files. (b) 3D printing of an EmimAc solution of 4% (w/w) dissolving pulp on an agar plate to obtain instant coagulation. (c) A close-up presenting the viscous liquid being dispensed layer by layer. (d) SEM image of printed cellulose structure after regeneration and freeze-drying (Scale bar of 1  $\mu\text{m}$ ). Reproduced from Ref. (Markstedt et al., 2014) with permission from Mary Ann Liebert, Inc., Copyright© 2014.

solutions are often used to achieve this result (Fu et al., 2017; Jungst et al., 2016). Cellulose ethers have been used as the viscosity modifiers in a wide range of industrial products for many years (Kelessidis, Poulakakis, & Chatzistamou, 2011; Paiva, Silva, Labrincha, & Ferreira, 2006; Zhang, 2001). The vicinal cellulose chains can form hydrogen bonds between each other, restricting the water motion and further increasing the viscosity (Izaguirre, Lanas, & Álvarez, 2010; Saric-Coric, Khayat, & Tagnit-Hamou, 2003). However, when an external force is added, the mixing energy will break the hydrogen bonds between cellulose chains, and subsequently the chains will be aligned in the direction of flow, leading to the decreased viscosity through shear-thinning or pseudoplastic behavior (Saric-Coric et al., 2003). The rheological properties of cellulose ether solutions therefore provide the desired low viscosity at high shear rates, while providing high viscosity as the high shear rates are stopped (Fu et al., 2017). The thixotropic property of cellulose ethers makes them reasonable 3D printing inks.

Cellulose ethers such as EC, HPC and CMC are often used as viscosity modifiers in 3D printing inks (Brindha, Privita Edwina, Rajesh, & Rani, 2016; Sun et al., 2013), increasing the ink viscosity and slowing the flocculation kinetics, facilitating the fabrication of unsupported spanning structures (Smay et al., 2002). Mixtures of different kinds of cellulose ethers can be used to further adjust the ink viscosity. For instance, in the fabrication of 3D interdigitated microbattery

architectures, Sun et al. (2013) used an aqueous solution containing HPC and HEC to adjust the viscosity of the inks.

### 3.2. Cellulose ethers as binders

In 3D printing, the sliced two-dimensional (2D) profile of a computer model is printed and combined with the prior layer using a suitable binder (Vaezi & Chua, 2011). The choice of binder is crucial to 3D printed products to provide products with good mechanical properties (Avery et al., 2014; Inzana et al., 2014). Binder properties and saturation level can also affect the surface quality of the 3D printing process (Vaezi & Chua, 2011).

HEC was used as a binder in 3D printing of powdered glass frit. The resultant products showed enough structural stability (Avery et al., 2014). The same group also found that different cellulose-based binders led to different product porosities. Specifically, CMC sodium salt (CMC-Na) created a glass foam, while HEC had little influence on the product porosity (Klein et al., 2015). Tanwilaisiri, Zhang, Xu, Harrison, and Fyson (2016) fabricated an electrochemical supercapacitor using a 3D printing technique in which CMC was used as a binder for the carbon electrode material. MC was also tested as a binder when using wooden chips in 3D printing. However, results were not satisfactory, since the products showed poor mechanical strength (Henke & Tremel, 2013).

**Table 3**  
Common cellulose ethers, with applications.

Cellulose ether	Roles in product	Applications	References
Methyl cellulose (MC)	Water absorbent; tablet disintegrant; binder; extrusion aid; stabilizer; strengthener; viscosity modifier; emulsifier	Tablet; battery; edible barrier; etc.	(Buqa, Holzapfel, Krumeich, Veit, & Novák, 2006; Debeaufort, Quezada-Gallo, & Voilley, 1998; Kamel, Ali, Jahangir, Shah, & El-Gendy, 2008)
Ethyl cellulose (EC)	Matrix; binder; thickener; film former; coating (as a protective layer);	Solar cell; tablet; cosmetic; etc.	(Ahn et al., 2010; Marczak et al., 2011; Reki & Jambhekar, 1995)
Hydroxyethyl cellulose (HEC)	Tablet disintegrant; film former; viscosity modifier; stabilizer; suspending agent; and sizing aid	Tablet; solar cell; sensor; etc.	(Albareda-Sirvent, Merkoçi, & Alegret, 2000; Kamel et al., 2008; Zardetto et al., 2013)
Hydroxypropyl cellulose (HPC)	Viscosity modifier; binder; coating; film matrix; stabilizer	Sensor; ophthalmic inserts; tablet; etc.	(Abdel-Halim & Al-Deyab, 2011; James et al., 2014; Kamel et al., 2008; Nguyen & Latkany, 2011)
Hydroxypropyl methyl cellulose (HPMC)	Water binder; viscosity modifier; tablet disintegrant; film former; and sizing aid	Edible film; drug; emulsion; etc.	(Hagenmaier & Shaw, 1990; Sievens-Figueroa et al., 2012)
Carboxymethyl cellulose (CMC)	Stabilizer; emulsifier; tablet disintegrant; viscosity modifier, suspending aid; binder; film former; water absorbent; sizing aid; and metal ion adsorbent	Barrier substance; detergent; mining; paper; textile; oil drilling; food; pharmaceutical; etc.	(Heinze & Koschella, 2005; Sannino et al., 2004; Yuwen et al., 2014)

### 3.3. Cellulose ethers as excipients

3D printing has been shown to be effective for developing drug delivery systems, through which complex, structured and tailored drug delivery regimes can be realized (Goole & Amighi, 2016; Sastry, Nyshadham, & Fix, 2000; Wu et al., 1996; Yu et al., 2009). Previous research showed that 3D-printed tablets exhibited longer drug release time than the directly compressed tablets, due to their smoother surfaces and tighter structures (Zhang, Feng, Patil, Tiwari, & Repka, 2017). Programming the drug release time is of significance in oral delivery, and can be realised through a system composed of a drug-containing core and a functional polymeric barrier (Maroni et al., 2016).

The release-retardation effect of materials in hydrophilic matrix is mainly derived from two aspects: one is to change the penetration characteristics of the matrix tablets, and the other is to reinforce the intensity of the gel barrier through different kinds of interactions (Yu et al., 2007). Hydrophilic cellulose ethers are widely used as excipients in the pharmaceutical industry due to their versatility in achieving controlled, swelling-driven release of a drug upon contact with water or physiological fluids (Dürig & Fassih, 2002; Sannino, Demitri, & Madaghiele, 2009).

The hydration and swelling of a cellulose ether on the surface of tablets takes place in contact with aqueous liquids, resulting in chain entanglements and physical hydrogel formation. Subsequently, the drug dissolves in water and diffuses out through the polymer network when the swelling of cellulose ether proceeds from the swollen surface to the center of the tablet (Sannino et al., 2009; Siepmann & Peppas, 2001). Depending on the structure of the particular cellulose ether used, chain dissolution may take place along with swelling due to the physical nature of the hydrogel network. Therefore, drug release results from the complex combination of swelling, diffusion, and erosion mechanisms (Sannino et al., 2009). Cellulose ethers, such as HPMC, HPC, EC and HEC are commonly used for erodible delivery systems (Gazzaniga, Palugan, Foppoli, & Sangalli, 2008; Maroni et al., 2016).

HPMC is regarded as one of the most significant hydrophilic carriers for controlled drug delivery systems, owing to its high swellability, that mostly determines the release kinetics of an incorporated drug (Khaled, Burley, Alexander, Yang, & Roberts, 2015; Khaled, Burley, Alexander, Yang, & Roberts, 2015; Siepmann & Peppas, 2001). In particular, the drug release from HPMC matrices can be described by two mechanisms: drug diffusion through the swelling hydrogel layer, and drug release with matrix erosion of the swollen layer (Reynolds, Gehrke, Hussain, & Shenouda, 1998).

As reported by Wang et al. (2006) HPMC mixed with Kollidon SR (a mixture of 80% polyvinyl acetate (PVAc), 19% poly(vinylpyrrolidone) K30 (PVP K30), and trace amounts of sodium lauryl sulfate and silica as stabilizers) served as drug carriers in the fabrication of near zero-order release dosage forms by 3D printing. They found that HPMC formed diffusional pathways for drug release, making it the key release-regulating material. In another study, HPMC was used as the excipient for 3D printed guaifenesin tablets. The concentration of HPMC was found to affect the drug release rate of the resultant tablets, due to the variation in hydrophilicity the final products. The results showed that the drug release from the tablets containing 14 wt% HPMC was similar to the control (Khaled, Burley, Alexander, & Roberts, 2014). In fact, several studies showed that the overall release rate increased with increasing HPMC fraction in the polymer blend, due to improved wettability, water uptake, and swelling of the matrix with increased HPMC content (Khaled et al., 2015b; Wang et al., 2006).

Boetker et al. (2016) also incorporated HPMC into their 3D printed drug-release products, in which HPMC facilitated the formation of a porous network in the printed structures. The drug-release results showed that both initial rate and the overall total release of nitrofurantoin (the model drug) for the samples containing 40% HPMC were higher than those of the samples containing 20% HPMC.

HPC was adopted by Melocchi et al. (2015) as a swellable/erodible

polymer to manufacture capsular devices for oral pulsatile release, which proved the feasibility of 3D printing in this area. Pulsatile release is defined as the rapid release of a certain amount of drug molecules within a short time-period immediately after a predetermined off-release period. The release test exhibited a lag phase before rapid and quantitative liberation of the drug. HPC was also reported to be used with other polymers to fabricate personalised tablets through 3D printing. The resultant products showed slower drug release performance than those non-printed counterparts (Pietrzak, Isreb, & Alhnan, 2015).

EC was studied by Yu et al. (2007; 2009) as a release-retardant material in the 3D printing of hydrophilic HPMC matrix tablets. Due to its insolubility in water, EC could retard water penetration into the tablets. Moreover, EC could also improve the strength of HPMC gel, owing to its strong adhesive interactions with HPMC (Yu et al., 2007). It was also pointed out that the effect of EC on drug release from a hydrophilic matrix made by 3D printing might be greater than those made by conventional pressing. This can be explained by the adhesive interactions between EC and the matrix (i.e. HPMC), since strong adhesive interactions would reinforce the strength of HPMC gel in the dissolution media, slowing the drug release. As a consequence, the release-retarding performance of EC in a hydrophilic matrix can be generally ascribed to two reasons: (1) changing the penetration characteristics of the matrix tablets and (2) enhancing the intensity of the gel barrier through different types of interactions (Yu et al., 2009). Kempin et al. (2017) reported that less than 5% of quinine release in 100 days was found for the drug loaded implants made of EC through 3D printing, which confirms the good release retarding performance of EC.

### 3.4. Cellulose ethers as plasticizers

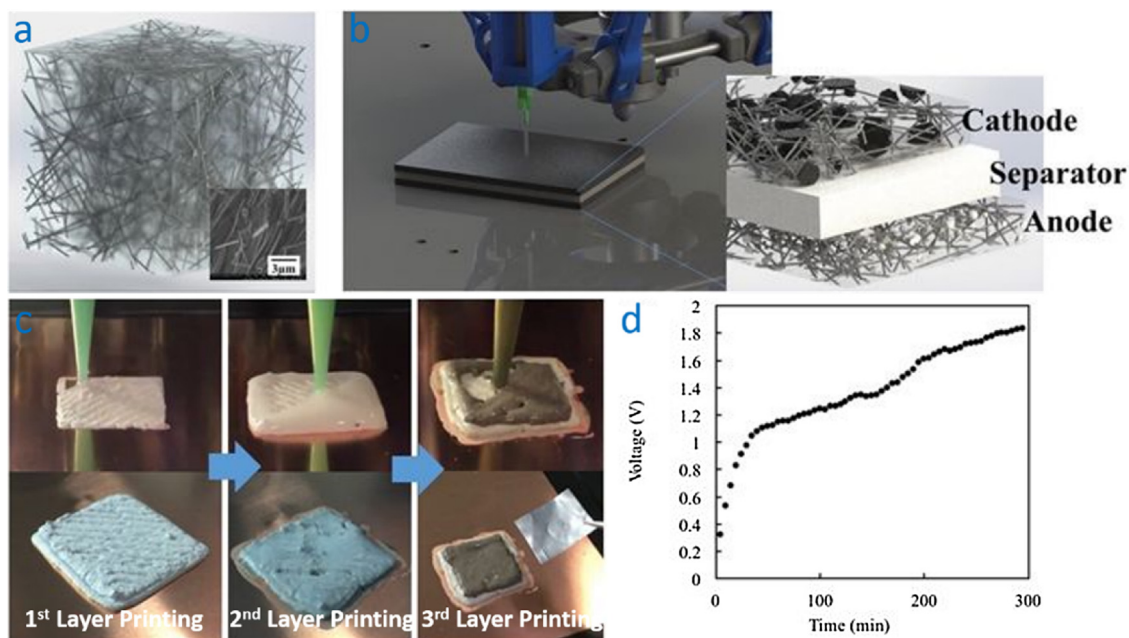
Plasticizers help to maintain an ink viscosity appropriate for processing the material at a desired, lower temperature; reducing the risk of thermal degradation of the polymer (Khaled et al., 2015b; Serra, Planell, & Navarro, 2013; Serra, Ortiz-Hernandez, Engel, Planell, & Navarro, 2014). Thakkar et al. (2017) used MC as a plasticizer to adhere the binder (bentonite clay) and adsorbent particles (aminosilica) for the preparation of aminosilica-based CO<sub>2</sub> adsorbents by 3D printing.

### 3.5. Cellulose ethers as matrixes

CMC is a widely used matrix material due to its viscosity thickening capability and thixotropic rheology. Park, Kim, and Kim (2017) prepared a silver nanowire (AgNW) based 3D conductor using the CMC matrix (Fig. 3a–c). A list of samples with their compositions and resistivity is given in Table 4. The voltage profile of the 3D-printed battery during charging is shown in Fig. 3d. The voltage increased to around 1.2 V after 85 min and reached 1.8 V after 275 min.

### 3.6. Cellulose esters as matrixes

Although cellulose esters have been commercially available for a long time and found various applications in different industries, only a few studies have been done in their applications for 3D printing. Pattinson and Hart (2017) dissolved cellulose acetate (CA) in acetone and then 3D printed the viscous, yet flowable solution. The schematic of the 3D printing process is shown in Fig. 4a. The results show that a concentration of 25–35 wt% was appropriate for 3D printing since it reached compromise between flowability and shape retention. The resultant 3D-printed CA products had a Young's modulus and strength of 2.2 GPa and 45.0 MPa, respectively (Fig. 4b). No anisotropy is observed within the statistical spread. As shown in Fig. 4c and d, miniature eyeglass frames and a small rose were printed.



**Fig. 3.** (a) Computer aided design (CAD) model of AgNW/CMC 3D conductor (the inset presents the SEM image of the as-prepared conductor). (b) CAD representation of 3-layered 3D printed battery. (c) Pictures of 3D printing process of the 3D-printed battery. (d) The charging profile of the as-prepared battery. Adapted with the permission from Ref. (Park et al., 2017), Copyright© 2017.

**Table 4**

The composition and resistivity of the AgNW/CMC composites (Park et al., 2017).

Samples	CMC (vol. %)	AgNW (vol. %)	Solid Content (wt. %)	Resistivity ( $\Omega$ cm)
1	99.7	0.3	25	$3.74 \times 10^7$
2	99.3	0.7	25	$2.57 \times 10^7$
3	98.9	1.1	25	$1.25 \times 10^3$
4	98.5	1.5	25	$5.92 \times 10^1$
5	98.1	1.9	25	$8.38 \times 10^{-3}$

#### 4. Use of microcrystalline cellulose (MCC) in 3D printing

Microcrystalline cellulose (MCC), another cellulose derivative which has been commercially important for many years, is usually prepared via the hydrolysis of cellulose fibers using mineral acids at relatively low concentration (Elanthikkal et al., 2010). It is a white crystalline powder with length dimension of greater than  $1 \mu\text{m}$  (Haafiz, Eichhorn, Hassan, & Jawaid, 2013; Siro & Plackett, 2010). MCC is insoluble in common solvents, and forms colloidal suspensions in water (Araki, Wada, Kuga, & Okano, 1998). It is extensively used as an emulsifier, an excipient for pharmaceutical products, a water retention aid, a rheology modifier, a compression binder, and a reinforcing agent, among other end-uses (Elanthikkal et al., 2010; Thoorens, Krier, Leclercq, Carlin, & Evrard, 2014). MCC has been used in 3D printing to serve different purposes, as follows.

##### 4.1. MCC as an excipient

Currently, MCC is perhaps the most common direct compression excipient (de la Luz Reus Medina & Kumar, 2006; Kumar, de la Luz Reus-Medina, & Yang, 2002; Reus-Medina, Lanz, Kumar, & Leuenberger, 2004). As an excipient, the functionalities of MCC depend on the concentration at which it is used. MCC can act as an anti-adherent (5–20%), a disintegrant (5–15%) and a diluent (20–90%) (Jivraj, Martini, & Thomson, 2000). Katstra et al. (2000) used a pharmaceutical grade MCC to fabricate oral dosage forms through 3D printing. Active

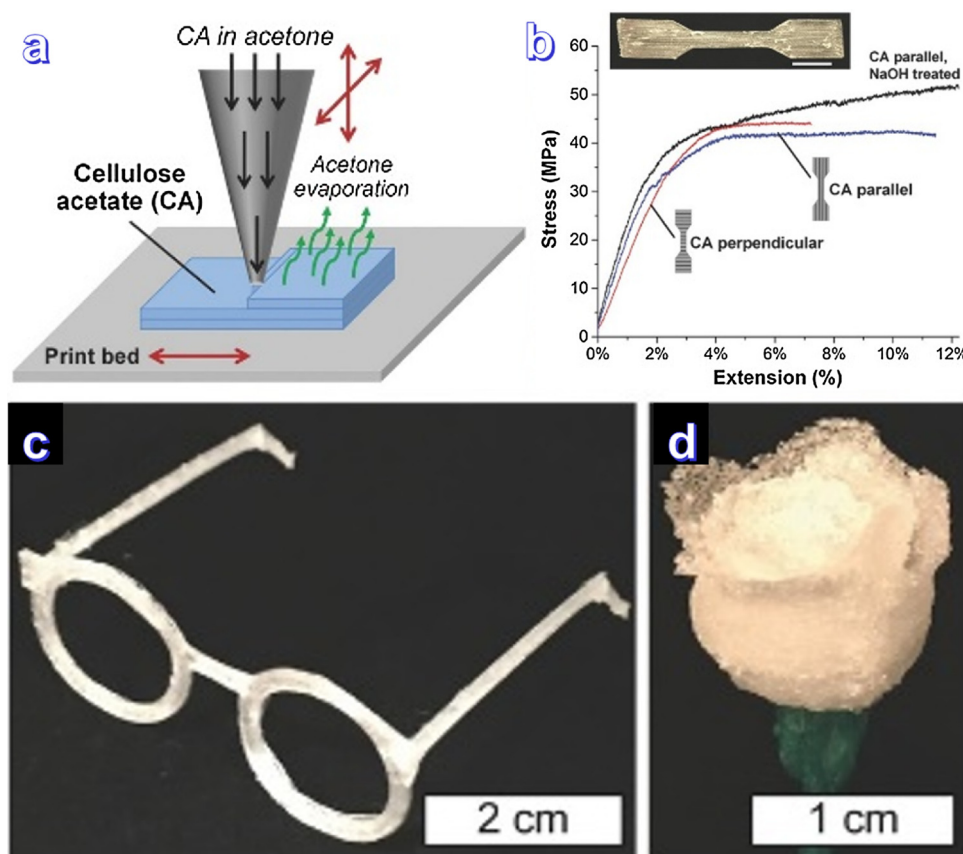
delivery studies with fluorescein indicated that 3D printing is capable of accurately constructing dosage forms with active content as low as  $10^{-12}$  moles per tablet. Hardness and friability testing showed that samples fabricated via 3D printing are comparable to other standard pharmaceutical products (Katstra et al., 2000). MCC was also used for the bulk of tablets in another study, in which four types of complex oral drug delivery devices have been fabricated using 3D printing (Rowe et al., 2000). Disintegrants help tablets to break up on exposure to water, and lead to the rapid release of active ingredients. Khaled et al. (2014) used MCC as a disintegrant for an immediate release layer of 3D printed tablets, which provided an initial burst release of < 20% in 30 min.

##### 4.2. MCC as a reinforcing aid

MCC can reinforce the mechanical strength of other materials even at low dosage. This can be attributed to stress transfer from the matrix to the MCC, preventing the formation of stress concentrations (Ashori & Nourbakhsh, 2010; Wu, Henriksson, Liu, & Berglund, 2007). MCC has a high Young's modulus of  $25 \pm 4$  GPa (Eichhorn & Young, 2001). In comparison to other materials such as glass fibers, silica, or carbon black, the benefits of MCC include sustainability, biodegradability, low-cost, reduced weight, and less abrasion of equipment (Ashori & Nourbakhsh, 2010). MCC was used to reinforce polylactic acid (PLA)-based 3D printing bio-composites, in which the MCC was surface-modified using a titanate coupling agent (Lica 38) to improve its compatibility with the PLA matrix (Murphy & Collins, 2016). The addition of MCC increased the crystallinity and storage modulus of the resultant bio-composites, with the most significant increase associated at 3 wt% MCC.

##### 4.3. MCC as a matrix

MCC can also be used as the matrix for materials preparation through 3D printing, after dissolution in an appropriate solvent. Gunasekera et al. (2016) reported the 3D ink-jet printing of MCC, in which the MCC was dissolved in a co-solvent system consisting of ionic liquids (1-Ethyl-3-methylimidazolium acetate ( $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ ) and 1-



**Fig. 4.** (a) Schematic of cellulose acetate (CA) 3D printing process. (b) Tensile stress–strain curves of dogbone samples noted. (c) 3D printed miniature eyeglass frames. (d) 3D printed rose. Reproduced from Ref. (Pattinson & Hart, 2017) with permission from John Wiley and Sons, Copyright© 2017.

butyl-3-methylimidazolium acetate ( $[C_4C_1Im][OAc]$ ) and organic solvents (1-butanol and dimethyl sulfoxide (DMSO)). DMSO was used to decrease the viscosity of the MCC solution while maintaining the cellulose solubility, since the viscosities of the ionic liquid and MCC solutions were out of the printing range. The printed cellulose samples were then regenerated using deionised water. Viscosity is a key factor affecting the 3D printing process and a lot of work can be done to explore appropriate solvents for MCC. For example, NMMO is a good cellulose solvent.

## 5. Use of nanocelluloses in 3D printing

Nanocelluloses including cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) can also be made from cellulose through physical, chemical, or enzymatic approaches, or combinations thereof (Klemm et al., 2011). CNF (sometimes called as nanofibrillated cellulose (NFC)) and the related microfibrillated cellulose (MFC) are flexible materials, with length dimension greater than  $1\ \mu\text{m}$  and widths in the nanometer range. CNC, also known as nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW), is composed of rigid rod-like particles with length in the range of 100–200 nm (Liu, Geng, Chen, & Wang, 2017), and a diameter of 3–10 nm (Cao, Ding, Yu, & Al-Deyab, 2012; Leung et al., 2011). Nanocelluloses are emerging natural and sustainable nanomaterials with fascinating properties, such as high strength, high surface area and tuneable surface chemistry (De France, Hoare, & Cranston, 2017; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Nanocelluloses can potentially be applied in a wide variety of applications including biomedical products, the energy industry, the construction industry, and many more (De France et al., 2017; Hettrich, Pinnow, Volkert, Passauer, & Fischer, 2014). Recent advances have enabled 3D printing of biocompatible materials, cells and supporting

components into complex 3D functional living tissues, which affords the potential application of 3D printing in tissue engineering and regenerative medicine (Markstedt et al., 2015; Murphy & Atala, 2014; Souness, Zamboni, Walker, & Collins, 2018). However, more work is needed for developing bioinks that will be compatible and printable (Murphy et al., 2018). Nanocelluloses are suitable as a substrate for printing functionality and also as a component in bioinks for 3D printing (Rees et al., 2015). In particular, nanocelluloses have been proved to be non-cytotoxic against a series of cell lines (Alexandrescu, Syverud, Gatti, & Chinga-Carrasco, 2013; Lopes, Sanchez-Martinez, Strømme, & Ferraz, 2017; Rees et al., 2015). Consequently, 3D printing of nanocelluloses offers an attractive way to fabricate sustainable structures with a broad range of properties.

### 5.1. Cellulose nanofibrils (CNF) for 3D printing

CNF, which is manufactured by disintegration of native cellulose fibers through several pathways as already discussed (Fujisawa, Ikeuchi, Takeuchi, Saito, & Isogai, 2012; Hamed et al., 2014; Walther, Timonen, Diez, Laukkanen, & Ikkala, 2011), may become a major part of the coming green materials revolution (Svagan, Samir, & Berglund, 2008; Torres-Rendon et al., 2015). CNF can be made into one, two, and three-dimensional nanostructures (Tang, Butchosa, & Zhou, 2015; Zhu et al., 2016), and is also considered to be a highly attractive biodegradable reinforcing ingredient in composite materials (Dai et al., 2017; Fujisawa et al., 2012; Svagan et al., 2008). CNF readily forms a hydrogel due to the existence of abundant hydroxyl groups, as well as flexibility and propensity for fibril entanglement (De France et al., 2017; Ruiz-Palomero, Soriano, & Valcárcel, 2017). In particular, the high zero shear viscosity and strong shear thinning make CNF hydrogels ink appropriate for 3D printing (Håkansson et al., 2016).



Rees et al. (2015) compared two kinds of CNF for use as bioinks, in which one CNF was prepared with TEMPO mediated oxidation (denoted as TEMPO CNF), while the other was manufactured through a combination of carboxymethylation and periodate oxidation (denoted as C-Periodate CNF). C-Periodate CNF with shorter nanofibrils has lower viscosity than TEMPO CNF, and also showed a more pronounced shear thinning behavior. C-Periodate CNF formed a solid structure with defined tracks ( $12 \times 12$  tracks), while the TEMPO CNF structure tended to collapse, probably due to the low consistency (0.95%) of the dispersion. However, increasing the concentration of CNF might also result in printing problems due to undesirable changes in rheological properties (Malda et al., 2013). In future work, a co-solvent might be used to address this issue.

Lille, Nurmela, Nordlund, Metsä-Kortelainen, and Sozer (2018) studied the printability of CNF-based material, in terms of the ease and uniformity of extrusion, as well as the high printing resolution and stability of the printed pattern. They found that when pastes contained high CNF concentration ( $> 0.8\%$ ), the clogging problem would appear, which might be caused by some larger fiber particles remaining in the CNF after fibrillation, or the shear-induced flocculation of the material when forced through the small tip of the syringe. Interestingly, the paste consisting of 0.8% CNF and 50% semi-skimmed milk powder (SSMP) resulted in excellent shape retention of the printed samples (Lille et al., 2018).

3D-printed hydrogels have been used extensively in the biomedical research field where an aqueous state is favorable for cell culturing (Håkansson et al., 2016; Malda et al., 2013; Murphy & Atala, 2014). 3D printing can be used to convert CNF hydrogels into 3D structures with controlled architectures. CNF hydrogels have advantages over classical polymer hydrogels, for instance, by providing a stiff microenvironment for the mechanosensation of cells (Torres-Rendon et al., 2016). They are biocompatible and are reported to support/promote the growth of different types of cells in a few cases (Bhattacharya et al., 2012; Lou et al., 2013; Malinen et al., 2014; Torres-Rendon et al., 2016). The most significant and the most challenging difference between injectable hydrogels versus printable hydrogels is the lack of geometrical constraints and the need for rapid gelation to ensure shape fidelity (Jungst et al., 2016). The presence of CNF is believed to improve the shape stability of the printed structures, and enhance mechanical properties together with other functionalities of the textured 3D printed composites, due to its shear-induced alignment (Lille et al., 2018; Shin et al., 2017; Siqueira et al., 2017). From the abovementioned studies CNF-based composite inks might be a good choice for 3D printing.

### 5.1.1. CNF as a building block

It is generally difficult to incorporate sophisticated bottom-up self-assembled hydrogel materials into generative manufacturing methods. However, Torres-Rendon et al. (2015) addressed this issue by the utilization of a reverse templating strategy toward ordered hydrogel scaffolds incorporating nanofibrillar building blocks, which may prove useful for the manufacture of tissue scaffolds. The sacrificial templates

were prepared through 3D printing of methacrylates and acrylamides, with methacrylic anhydride as a labile cross-linker. The void space was filled with CNF hydrogel by centrifugation. A porous hydrogel scaffold can be obtained by dissolving the sacrificial resin template in a sodium hydroxide solution (NaOH, 1 wt%), demonstrating that the macroscopic template structure can be well transferred into the CNF hydrogel. They also found that supercritical drying is not necessary for transferring scaffolds into a new medium, they easily recover their shapes after air drying and re-exposure to water. The excellent shape recovery property can be explained by the stiffness of the nanofibrils and the interfibrillar hydrogen bonds reinforcement resulted from drying, which leads to a buildup of internal stress in the collapse of the macropores that are released with rehydration.

CNF hydrogels were also adopted as sacrificial templates to fabricate freestanding cell constructs by Torres-Rendon et al. (2016), in which they manufactured hollow tubes by 3D printing. CNF was cross-linked either by covalently bound glutaraldehyde or by complexed  $\text{Ca}^{2+}$  ions, allowing the mechanical properties of the hydrogel tubes to be tailored. The ensuing tubes are highly biocompatible, which allows for the growth of mouse fibroblasts into confluent cell layers in their inner lumen. The confluent cell layers can be released from printed CNF scaffold via enzymatic degradation, resulting in macroscale 3D cell constructs.

The development of viscoelastic inks that can readily be extruded and yet form self-supporting features after exiting the nozzle is challenging (Siqueira et al., 2017). As reported by Markstedt et al. (2015), CNF was combined with alginate (SLG 100 with a molecular weight of 150–250 kDa and above 60% of  $\alpha$ -1-guluronic acid) to formulate a bioink for 3D printing of living soft tissue with cells, which takes advantage of outstanding shear thinning properties of CNF and the fast cross-linking ability of alginate. This study provides a promising way to meet the requirements needed for biological, printability, and the bio-fabrication window in 3D printing a scaffold with cells. CNF, as a main component in the bioink, was found to be capable of improving the shape fidelity of the prints. This can be explained by the high viscosity of CNF dispersions. Compared to the prints obtained with pure alginate ink (Fig. 5a1), the counterparts printed with the bioink consisting of a CNF/alginate mixture exhibited a higher printing resolution that gave a grid with visible well-resolved lines. This could be removed by a spatula, since it is gelled by ionic cross-linking of alginate (Fig. 5a3). However, as seen in Fig. 5a2, the printed shape consisting of pure CNF was destroyed by mechanical force, showing that the cross-linking ability of alginate is also important. Shapes resembling cartilage tissues (i.e. an ear and a meniscus) were also successfully printed, as shown in Fig. 5b. These printed products did not collapse or lose their shape during or after printing, due to the high ink viscosity. The human chondrocytes exhibited a cell viability of 73% and 86% after 1 and 7 days of 3D culture, respectively. All of these results lead to the conclusion that CNF-based bioink is suitable for 3D bioprinting with living cells, which demonstrates the potential use in fabricating living tissues and organs.

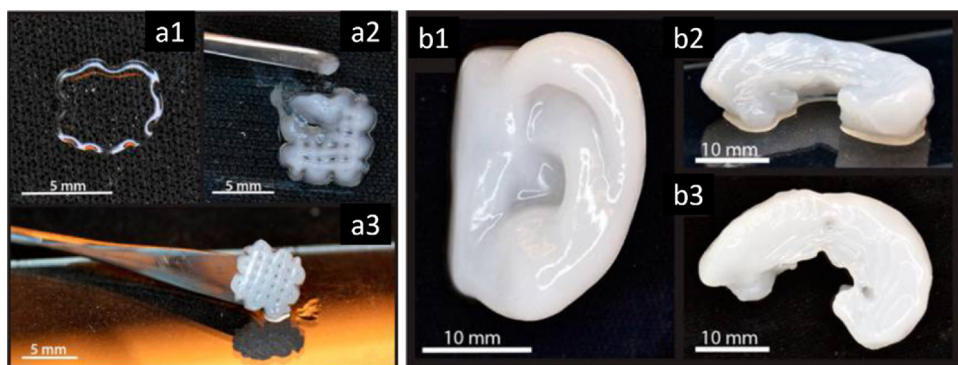


Fig. 5. (a) Small grids printed with different inks (alginate (a1), CNF (a2), CNF/alginate (printed and cross-linked) (a3)). (b) 3D printed shapes resembling cartilage tissues (human ear (b1), side view (b2) and top view (b3) of meniscus sheep meniscus). Adapted with permission from (Markstedt et al., 2015). Copyright (2015) American Chemical Society.

Complex 3D structures, especially structures with high aspect ratio walls or unsupported elements, place extra demands on 3D inks (Smay et al., 2002). Håkansson et al. (2016) utilized a pure CNF hydrogel (2 wt%) possessing shear thinning and high zero shear viscosity. A micro valve (piezoelectric valve) 3D printer was used. They found that the highly charged carboxymethylated CNF held a 3D shape after printing, with dimensions of  $(10 \times 10 \times 10 \text{ mm}^3)$  cubes. The fast relaxation of the hydrogel made it possible to print the top square without support over the 4 mm gap between the corner pillars. The total time was around 5 min for printing one grid cube. The structure was strong enough to support itself. Moreover, a miniature chair with high level of detail was obtained by 3D printing and subsequently freeze-drying. It is noted that freeze-drying is still the most widely used method to dry the hydrogel products to maintain their 3D structure, while its long time and very energy-consuming nature made it difficult to scale-up.

Converting the 3D-printed CNF hydrogel-based products into dry 3D structures is of great importance. As noted above (Håkansson et al., 2016; Torres-Rendon et al., 2015), the shrinkage and collapse of the 3D shapes after air drying is a major challenge with printed CNF hydrogels. Shao et al. (2015) found that with the addition of 50% lignosulfonate (LS) to a CNF hydrogel, the printed cuboids only had a limited deformation after air drying, due to the high viscosity of the suspending medium. In their study, CNF/LS colloidal suspensions were used as the ink for 3D printing of structured electrodes. They tried to increase the solid content of CNF/LS hydrogel blends without deteriorating printability, which can also increase the total carbon content of the products to limit their shrinkage during air drying, and to improve the carbonization yield. The carbonization of the resultant cuboids under the inert gas resulted in highly conductive objects. Air-drying is a preferred way to dry hydrogel-based products. Thus, more work needs to be done to develop advanced technologies for maintaining the structure of prints during air-drying without negative effects on the printability of the inks.

### 5.1.2. CNF as fillers

CNF has been studied as a novel nanofiller to reinforce materials (Benítez, Lossada, Zhu, Rudolph, & Walther, 2016; Fujisawa et al., 2012; Svagan et al., 2008). Sydney Gladman, Matsumoto, Nuzzo, Mahadevan, and Lewis (2016) carried out a biomimetic 3D printing study using wood-derived CNF as a stiff filler. The composite architectures were printed with a hydrogel composite ink containing stiff CNF that had been embedded in a soft acrylamide matrix mimicking the composition of plant cell walls. The CNF underwent shear-induced alignment as the ink flowed through the deposition nozzle during printing, producing printed filaments with anisotropic stiffness, and hence, swelling behaviour in the longitudinal direction (defined by the printing path) (Fig. 6a). CNF alignment was directly observed in the printed samples compared to isotropic cast sheets of the same material (Fig. 6b). Inspired by flower opening/closing, they printed petals in a floral form (Fig. 6c-1). These consisted of a bilayer lattice with a  $90^\circ/0^\circ$  configuration. They observed that the structure closes as it swells.

As a control, they also printed an identical pattern using an ink without CNF, and saw that it remained flat after swelling (Fig. 6c-2). When the petals were printed with the ink filaments oriented at  $-45^\circ/45^\circ$  configuration (Fig. 6c-3) the resulting structure yields a twisted configuration. The chirality of the resulting structures can be attributed to the broken top-bottom symmetry of the bilayer and the differential swelling across the thickness. It is important to note that these constructs contain spanning filaments that are readily fabricated by direct writing of the viscoelastic composite ink. The inter-filament spacing promotes rapid uptake of water through the filament radius ( $\sim 100 \mu\text{m}$ ), leading to shape transformations that occur on the order of minutes (Fig. 6c-1, c-3). This is consistent with diffusion-limited dynamics (Sydney Gladman et al., 2016). The efficacy of this method relies on the ability to deterministically define the elastic and swelling anisotropies by local control of the orientation of CNF within the

hydrogel composite.

Nguyen et al. (2017) investigated the potential of 3D printing human-derived induced pluripotent stem cells (iPSCs) into cartilage mimics using a CNF/alginate (CNF/A) composite bioink, when co-printed with irradiated human chondrocytes. CNF provided structural and mechanical support for forming the physiological mimetic environment. In the case of 3D-printed CNF/A (60/40, dry weight % ratio) constructs, pluripotency was initially maintained, and after five weeks, hyaline-like cartilaginous tissue with collagen type II expression and lacking tumorigenic OCT4 expression was observed. Moreover, a marked increase in cell number within the cartilaginous tissue was detected, indicating the importance of high cell densities in the pursuit of achieving good survival after printing. The conclusion can be drawn that CNF/A bioinks were suitable for bioprinting iPSCs to support cartilage production in co-culture with irradiated chondrocytes.

Dong et al. (2017) adopted CNF to improve the mechanical performance of polylactic acid (PLA) in 3D printing. They first grafted CNF with L-lactide monomers via ring-opening polymerization, forming PLA-g-CNF. PLA-g-CNF and pristine PLA were blended in chloroform and dried to prepare a master batch that was compounded in a PLA matrix. This mixture was melt extruded into PLA-g-CNFs/PLA composite filaments. The incorporation of PLA-g-CNFs improved the storage modulus of the composite filaments both below and above the glass transition temperature, which could be due to the increased crystallinity of PLA matrix, the tangling effect of CNF network and the uniform dispersion of modified CNF within the PLA matrix.

Markstedt, Escalante, Toriz, and Gatenholm (2017) reported an all-wood-based ink consisting of CNF and xylans for 3D printing, in which cross-linkable tyramine-modified xylans render the prints structure stability while CNF reinforced the cross-linked xylans matrix.

3D printing of polypropylene (PP) is difficult, due to not only the high temperatures required for PP to be printed, but also due to shrinkage and warping during the printing process. Wang, Gardner, and Bousfield (2017) found one path to overcome the shrinkage and warping problem by incorporating CNF into PP, because CNF has a low thermal expansion coefficient of 0.1 ppm/k. The composites were prepared through mixing CNF and PP pellets in a twin-screw co-rotating extruder. Rheological tests showed that the elastic modulus, complex viscosity, viscosity, and transient flow shear stress of PP were all increased with the addition of 10 wt% CNF, while the creep strain of PP was reduced. Flexural strength and modulus of PP were also improved by adding CNF.

### 5.1.3. CNF as a matrix

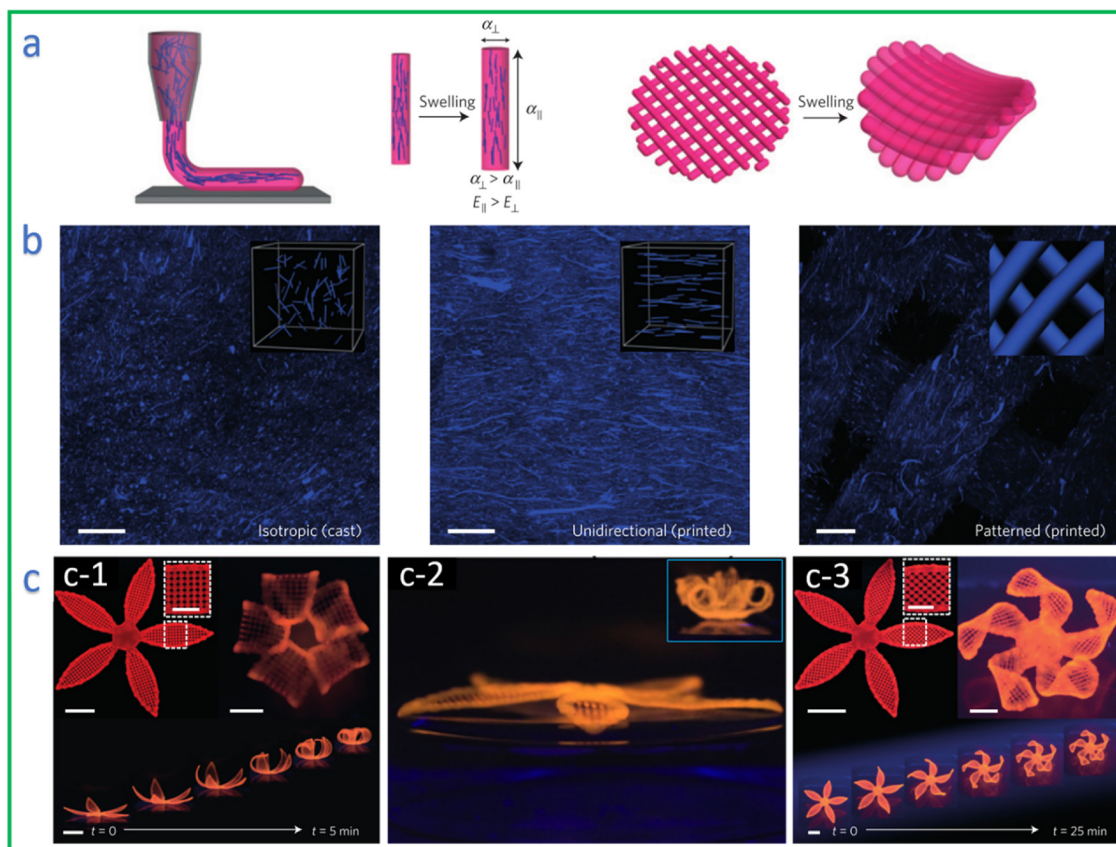
Shin and Hyun (2017) adopted CNF to construct microfluidic devices, using matrix-assisted 3D printing, in which CNF was utilized as a matrix for the microfluidic channels (Fig. 7). This method consists of three steps: (1) printing the channels with a removable ink (i.e. petroleum jelly) inside the CNF hydrogel matrix (Fig. 7b and c); (2) drying the CNF hydrogel matrix with the printed features (Fig. 7d); and (3) removing the ink to create the channels to yield the final transparent, stackable paper-based 3D channel devices (Fig. 7e).

## 5.2. Cellulose nanocrystals (CNC) for 3D printing

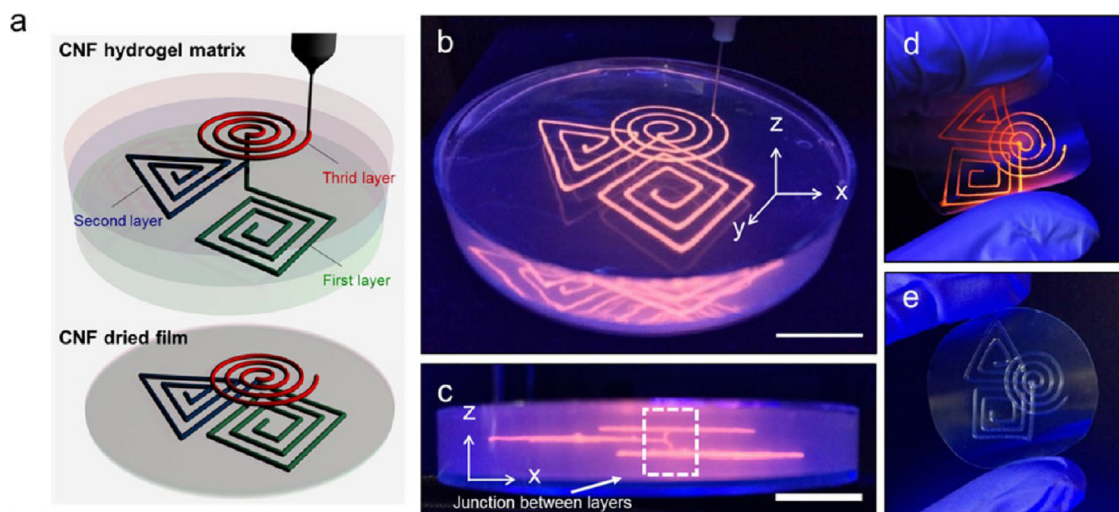
### 5.2.1. CNC as a reinforcing agent

CNC, which has the features of high specific strength and good sustainability, can be used to reinforce a matrix at low loadings, due to its high crystallinity and its ability to channel the mechanical stress from a deformed matrix (Ben Azouz, Ramires, Van den Fonteyne, El Kissi, & Dufresne, 2012; Cha, Wang, Cheng, He, & Jiang, 2014; Feng, Yang, Chmely et al., 2017; Feng, Yang, Rostom et al., 2017; Zhou, Chu, Wu, & Wu, 2011). In particular, a CNC-based ink exhibits shear-thinning behavior at the appropriate CNC loading (over 1 wt% CNC), making it suitable for 3D printing (Siqueira et al., 2017).

CNC can function as a reinforcing agent once the components are



**Fig. 6.** (a) Schematic of the shear-induced alignment of cellulose fibrils during direct ink writing and subsequent effects on anisotropic stiffness  $E$  and swelling strain  $\alpha$ . (b) Direct imaging of cellulose fibrils (stained blue) in isotropic, unidirectional and patterned samples (scale bar, 200  $\mu\text{m}$ ). (c) Complex flower morphologies generated by 3D printing. (c-1) Simple flowers composed of  $90^{\circ}/0^{\circ}$  bilayers oriented with respect to the long axis of each petal, with time-lapse sequences of the flowers during the swelling process (bottom panel) (scale bars, 5 mm, inset = 2.5 mm) (c-2). Control flower architectures composed of hydrogel ink without and with 0.8 wt% (the inset) CNF. Images were taken after 24 h immersion in water. (c-3) Simple flowers composed of  $-45^{\circ}/45^{\circ}$  bilayers oriented with respect to the long axis of each petal, with time-lapse sequences of the flowers during the swelling process (bottom panel) (scale bars, 5 mm, inset = 2.5 mm). Reproduced from Ref. (Sydney Gladman, et al., 2016) with permission from Springer Nature, Copyright© 2016. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 7.** Fabrication of a flexible microfluidic thin film with multilayered channels by matrix-assisted 3D printing in a CNF hydrogel. (a) Series of fabrication processes for three-layered continuous microfluidic channels designed by CAD. (b) The petroleum-jelly-based removable ink was injected in the CNF hydrogel matrix. Ink with fluorescent dye was visualized under UV illumination. (c) The layers were interconnected by continuous injection of the ink. (d) CNF hydrogel matrix was dehydrated and formed a thin compact microfluidic film. (e) Printed ink was liquefied and removed, forming an open-channel 3D microfluidic device (Scale bars are 1 cm in (b) and (c)). Adapted with permission from (Shin & Hyun, 2017), Copyright (2015) American Chemical Society.

compatible. In this sense, surface modification by coating is an easy way to make it compatible with other components in the system. As reported by [Feng, Yang, Chmely \(2017\)](#); [Feng, Yang, Rostom \(2017\)](#), various contents of lignin-coated CNC (L-CNC) were incorporated into methacrylate (MA) resin and their mixture was used to prepare nanocomposites via 3D printing. The results indicated that the mechanical properties of the products increased with the addition of only 0.1% and 0.5% L-CNC after postcure (heat treatment under 120 °C), and the thermal stability was also found to be improved, which can be due to the compatibility and the esterification between L-CNC and MA matrix. They also used L-CNC to reinforce 3D printed acrylonitrile butadiene styrene (ABS) and found that the addition of L-CNC improved the tensile and storage modulus, as well as the thermal stability of the final products ([Feng, Yang, Chmely, 2017](#); [Feng, Yang, Rostom, 2017](#)).

[Wang et al. \(2018\)](#) found that BAPOs (Bis(acyl)phosphane oxides)-attached CNC could convert a conventional mono-functional monomer into a polymeric network without any additional cross-linkers. This was subsequently used in 3D printing to obtain free-standing 3D structured objects. [Palaganas et al. \(2017\)](#) also reported the significant improvement in mechanical properties of 3D printed poly(ethylene glycol) diacrylate (PEGDA) brought by CNC.

For cellulose-based 3D printed materials, efforts to date have focused primarily on hydrogel-based inks with low CNF loading (0.8–2.5 wt%) ([Håkansson et al., 2016](#); [Markstedt et al., 2015](#); [Sydney Gladman et al., 2016](#); [Torres-Rendon et al., 2015](#)), since the inherently entangled state of concentrated CNF suspensions prevents high loadings. However, a high solid content helps to limit the shrinkage of prints in air drying as shown by [Shao et al. \(2015\)](#). By contrast, the use of CNC as a reinforcing agent in inks designed for 3D printing may offer advantages over the semi-crystalline CNF, because higher solid loadings can be achieved at a given viscosity and storage modulus due to the absence of physical entanglements ([Le Goff, Jouanneau, Garnier, & Aubry, 2014](#); [Siqueira et al., 2017](#)). [Siqueira et al. \(2017\)](#) adopted CNC as the ink for the fabrication of textured cellular architectures by 3D printing, in which the concentration of aqueous CNC ink was as high as 20 wt%. They tried inks composed of CNC particles dispersed in either water or a photopolymerizable monomer (2-hydroxyethyl methacrylate, HEMA) solution. The 3D printed structures contain between one and eight layers ([Fig. 8a, b](#)), each of which composed of filamentary features arrayed with a center-to-center spacing varying between 1.0 mm (grids) and 320 μm (blocks). The shear-induced orientation of anisotropic CNC particles in printing was analyzed with optical microscopy in cross-polarized light mode ([Fig. 8c–e](#)). Like the micro-reinforcing effect in plant cell walls, the alignment of CNC in 3D printing process leads to textured composites with improved stiffness in the printing direction, owing to their high aspect ratio and degree of orientation. With the addition of both pristine and methacrylic anhydride-modified CNC to the polymer matrix, the elastic modulus of the composite remarkably increased compared to the neat matrix. Specifically, the elastic modulus increased by 80% when the matrix was reinforced with 20 wt% of modified CNC. A more pronounced reinforcing effect of the CNC was found in a softer matrix. A high dosage of CNC increases the price of final products since CNC itself is expensive, therefore, the mixing of CNC and CNF may provide a promising way to acquire a balance between quality and cost.

### 5.2.2. CNC as building block

Aqueous CNC dispersions were used to replace existing 3D printing thermoplastics, in which pure CNC aerogels with limited structural shrinkage were produced through 3D printing, followed by freeze drying ([Li, Dunn, Zhang, Deng, & Qi, 2017](#)). Specifically, a 20 wt% CNC gel was used to print a wide variety of shapes without supporting materials, including octet cube, pyramid, hexagonally twisting vase, nose model, ear model, and honeycomb. Maintenance of a 3D structure may be due to the high Young's modulus and the strong hydrogen bonding potential of CNC. Moreover, CNC aerogel scaffolds with dual pore

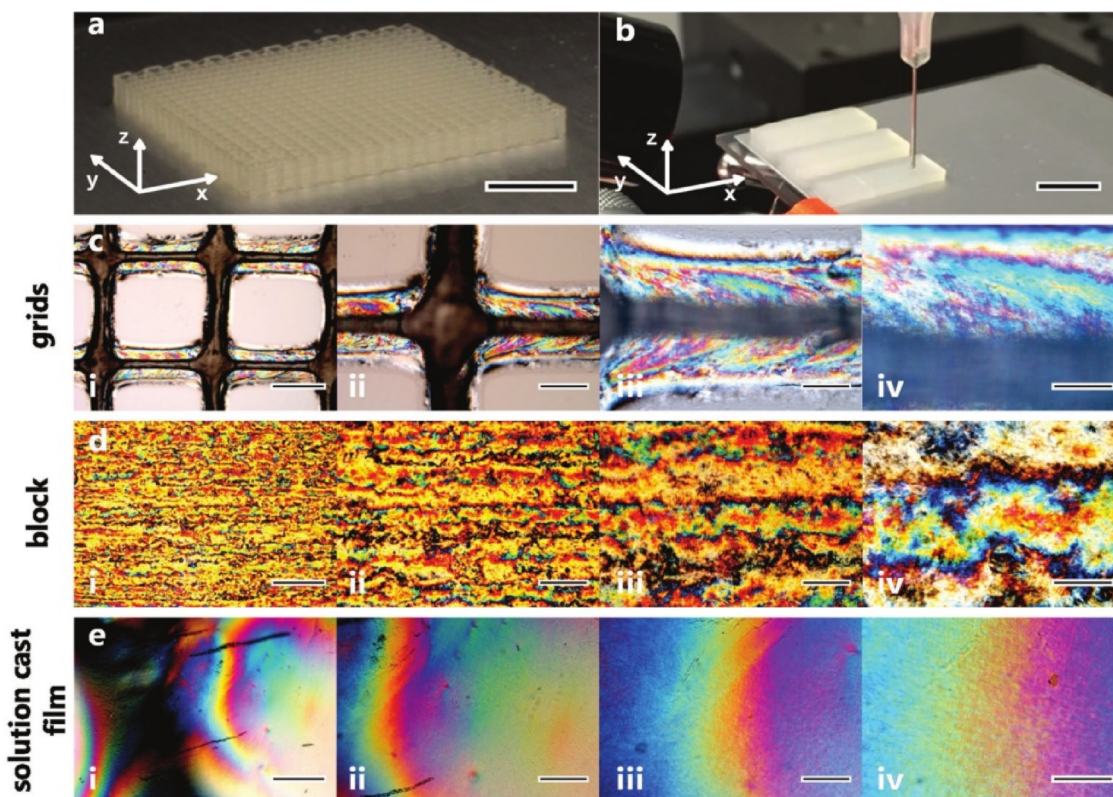
structures (structural and random pores) were successfully obtained in this work, and they have the efficient cell integration capability that is needed in tissue regeneration. A high dosage of CNC was used in this study, which certainly increase the cost of the 3D printed products. Replacing a part of CNC with other materials, such as CNF or guar gum could decrease the cost while maintaining the 3D structure.

## 6. Future and outlook

Sustainable and biodegradable polymeric materials are in high demand by our “green” life pursuit, which highlights the importance of cellulose and its derivatives. 3D printing has huge potential applications, and may provide new opportunities for the use of cellulosic materials. Particularly, 3D printing provides a promising pathway to manufacture cellulose-based functional biomaterials with tailored hierarchical structures and customized functionalities. This topic has attracted a lot of interest from the research community in the last decade, and much work has been done in the application of cellulosic materials in 3D printing.

Interesting topics that should be further investigated include:

- Cellulose solutions in ionic liquids. Such cellulose solutions have the advantage of high viscosity. With proper cross-linking, this material could be used to produce stable, high quality 3D structures.
- Development of cellulose ethers-based hydrogel materials. A large amount of work in cellulose ethers focuses on pharmaceutical applications, whereas nanocelluloses have been widely used for various applications. In fact, other than nanocelluloses, cellulose ethers are promising resources for hydrogel fabrication since most of them are water-soluble and cost-effective. It is expected more interesting results can be obtained when cellulose ether-based hydrogels are used as 3D printing inks.
- Cellulose esters are actually one kind of important cellulosic material. Nevertheless, very few studies have been done in their application for 3D printing. Given the commercial importance and variety of cellulose esters, they may prove to be another suitable material for 3D printing. These include common thermoplastic materials like cellulose triacetate and other commercial cellulose esters. Cellulose monoacetate, a water-soluble type of cellulose acetate ([Malm, Barkey, Salo, & May, 1957](#)), could also make a promising material for 3D printing.
- MCC has high purity and crystallinity, and is less expensive than cellulose nanocrystals (CNC). More attention may be paid to the utilization of MCC in 3D printing. For example, cellulose solvents such as NMMO can be used to dissolve MCC to prepare 3D printing inks. Moreover, MCC can also be used to replace CNC as a reinforcing agent for 3D prints.
- Nanocellulose-based hydrogels are excellent candidates for the fabrication of scaffolds for biomedical applications. However, maintaining the structure during and after 3D printing is a challenge, especially for high-viscosity bio-inks. In this context, cross-linking may be a good way to keep the printed shapes from collapsing. The concept of self-assembly bears significant potential in future research as an in-situ path to cross-linking. Considering that, nanocellulose is an ideal reinforcing agent, and it has already been studied in stereolithographic process ([Kumar, Hofmann, Steinmann, Foster, & Weder, 2012](#)). Therefore, future work can be directed to utilize nanocellulose, even MCC through different 3D printing techniques to meet specific purpose. In water suspension, CNC can form a chiral nematic phase that can be maintained upon drying, so CNC can be used as a template to introduce chirality into other solids, generating new materials for applications including chiral recognition, chiral separation, etc. 3D printing could be an effective technology of manufacturing these chiral materials with other tailored structures.



**Fig. 8.** Photographs of 3D printed (a) grids and (b) blocks composed of parallel lines in eight layers (scale bars: 10 mm). Optical microscopy images in cross-polarized light mode of CNC-based structures 3D printed into (c) grids and (d) top view of block. (e) Films obtained by solution-casting. Scale bars: (i) 500  $\mu\text{m}$ , (ii) 200  $\mu\text{m}$ , (iii) 100  $\mu\text{m}$ , and (iv) 50  $\mu\text{m}$ . Reproduced from Ref. (Siqueira et al., 2017) with permission from John Wiley and Sons, Copyright© 2017.

In light of active research on fabrication and utilization of cellulose-based materials in many other fields, there still requires a great deal of research to unlock the full potential of 3D printing using cellulose-based materials (especially nanocelluloses).

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