



Multifunctional nanocellulose/metal and metal oxide nanoparticle hybrid nanomaterials

Ahmed A. Oun, Shiv Shankar & Jong-Whan Rhim

To cite this article: Ahmed A. Oun, Shiv Shankar & Jong-Whan Rhim (2019): Multifunctional nanocellulose/metal and metal oxide nanoparticle hybrid nanomaterials, Critical Reviews in Food Science and Nutrition, DOI: [10.1080/10408398.2018.1536966](https://doi.org/10.1080/10408398.2018.1536966)

To link to this article: <https://doi.org/10.1080/10408398.2018.1536966>



Published online: 27 May 2019.



Submit your article to this journal [↗](#)



Article views: 107



View Crossmark data [↗](#)

REVIEW



Multifunctional nanocellulose/metal and metal oxide nanoparticle hybrid nanomaterials

Ahmed A. Oun^a, Shiv Shankar^b, and Jong-Whan Rhim^b

^aFood Engineering and Packaging Department, Food Technology Research Institute, Agricultural Research Center, Giza, Egypt; ^bCenter for Humanities and Sciences, BioNanocomposite Research Center, Department of Food and Nutrition, Kyung Hee University, Seoul, Republic of Korea

ABSTRACT

Nanocellulose materials are derived from cellulose, the most abundant biopolymer on the earth. Nanocellulose have been extensively used in the field of food packaging materials, wastewater treatment, drug delivery, tissue engineering, hydrogels, aerogels, sensors, pharmaceuticals, and electronic sectors due to their unique chemical structure and excellent mechanical properties. On the other hand, metal and metal oxide nanoparticles (NP) such as Ag NP, ZnO NP, CuO NP, and Fe₃O₄ NP have a variety of functional properties such as UV-barrier, antimicrobial, and magnetic properties. Recently, nanocelluloses materials have been used as a green template for producing metal or metal oxide nanoparticles. As a result, multifunctional nanocellulose/metal or metal oxide hybrid nanomaterials with high antibacterial properties, ultraviolet barrier properties, and mechanical properties were prepared. This review emphasized recent information on the synthesis, properties, and potential applications of multifunctional nanocellulose-based hybrid nanomaterials with metal or metal oxides such as Ag NP, ZnO NP, CuO NP, and Fe₃O₄ NP. The nanocellulose-based hybrid nanomaterials have huge potential applications in the area of food packaging, biopharmaceuticals, biomedical, and cosmetics.

KEYWORDS

Nanocellulose; nanometals; metal oxides; multifunctional; hybrid nanomaterials; active packaging

Introduction

Due to the rapid growth of nanotechnology in recent years, nanomaterials including clays, metals, metal oxides nanoparticles and nanocellulose have received considerable interest and attention in a variety of applications, such as food packaging, pharmaceuticals and cosmetics (Ingle, Duran, and Rai 2014). In this regard, cellulose-based nanomaterials or nanocellulose have attracted considerable attention as one of the most well-known renewable, environmentally friendly, and biocompatible materials. Cellulose is the most abundant and sustainable natural polymer on the planet, with an annual output of one trillion tonnes (Liu, Dong, and Sui 2016). Cellulose nanofibers are isolated from various lignocellulosic sources such as wood, flax, hemp, sisal, cotton, ramie, and jute (Nascimento et al. 2015), forest residues (Mariana, Vilaplana, and Ek 2016), agricultural wastes (Oun and Rhim, 2016a, 2016b; Zhang et al. 2016), fruits wastes (Hiasa et al. 2014), marine biomass (Bettaieb et al. 2015), and bacterial cellulose (Reiniati, Hrymak, and Margaritis 2016). The nanocellulose materials have several attractive characteristics such as biodegradability, sustainability, excellent mechanical properties (Young's modulus of 100–140 GPa and tensile strength of 1.7 GPa), large aspect ratio (around 70), high surface area (ca. 150 m²/g), low density, low environmental impact and low cost as well as tailorable surface properties

(Pickering, Efendy, and Le 2016). The unique physical and mechanical properties of nanocellulose materials have increased the applicability as reinforcing nanofiller in the food packaging films to improve their mechanical (Khan et al. 2014; Abdul Khalil et al. 2016), water vapor and gas barrier properties (Ferrer, Pal, and Hubbe 2017). They are also used in a various fields including CO₂ capture (Gebald et al. 2011), paper and nanofiber filters industry (Boufi et al. 2016), cosmetics (Ul-Islam et al. 2014), enzyme immobilization (Mahmoud et al. 2009), sensors technology (Ummartyotin and Manuspiya 2015), DNA biosensors (Liu et al. 2011), automotive (Ashori 2008), and electronic device (Kim et al. 2015).

Nanocellulose has been used not only to improve the mechanical properties of polymer films (Maia et al. 2017) but also to develop functional nanocelluloses via mixing nanocelluloses with various antibacterial agents (Heng Zhang et al. 2017) and metal/metal oxide NP such as Ag NP, ZnO NP, CuO NP, and Fe₃O₄ NP (Hannon et al. 2015; Maleki and Kamalzare, 2014; Zarei, Niad, and Raanaei 2018). Large hydroxyl groups on the nanocellulose surface can be easily functionalized through surface modification. The surface modification of cellulose increased application fields through the introduction of functional groups with antibacterial and antioxidative action (Noguchi, Homma, and Matsubara 2017; Zhang et al. 2017). Functional

nanocelluloses with antibacterial, antioxidant and UV barrier properties are generally obtained by two approaches. The first method is to modify the surface of the nanocellulose through cationization or oxidation of the hydroxyl group of the nanocellulose (Saini et al. 2016; Zhang et al. 2017). The second approach is to form a hybrid with metal NP such as Ag NP, ZnO NP, CuO NP, and Fe₃O₄ NP using a nanocellulose material as a template to impart functional properties (Kaushik and Moores 2016; Shankar, Oun, and Rhim 2018). Here, the abundant hydroxyl groups on the surface of the nanocellulose itself act as a template and a capping agent for the synthesis of hybrid nanocellulose/metal or metal oxide NP (Azizi et al. 2013a; Xiong et al. 2013). The hybrid nanocellulose/metal or metal oxide NP compounds showed high antibacterial activity, excellent catalytic performance and electrical conductivity (Khandanlou et al. 2016; Khalil, Hassan, and Ward 2017), and they have been used to increase the mechanical properties, UV-barrier, thermal stability, and antimicrobial activity of biopolymer films (Fortunati et al. 2013; Xu et al. 2013), and also to prepare functional hydrogel and aerogel (Dong et al. 2013), and absorbent pads (Fernández, Picouet, and Lloret 2010).

Over the past several years, several book chapters, review articles, and research papers have been published and focused on the application of nanocellulose as a reinforcing agent in a variety of areas (Pickering, Efendy, and Le 2016; Azeredo, Rosa, and Mattoso 2017; Jawaid, Boufi, and Abdu 2017). The use of nanocellulosic materials for metal NP support and their application in catalytic reactions has also been reported (Kaushik and Moores 2016). Nonetheless, only a few articles on multi-functional hybrid nanocellulose/metal or metal oxide NP nanocomposite films have been published (Pinto et al. 2012). This paper reviewed on the synthesis and characterization of multifunctional nanohybrids of nanocelluloses and metal or metal oxide nanoparticles, and their potential applications in the field of packaging.

Nanocellulose

Generally, two types of nanocelluloses, cellulose nanofiber (CNF) and cellulose nanocrystal (CNC), can be obtained according to the isolation method. The main characteristic properties of CNF and CNC are shown in Table 1. CNF is usually obtained by disrupting cellulosic fibers along an axis using mechanical means such as ultrahigh friction grinding, high-pressure homogenization, wet grinding, cryogenic cooling and ultrasonic treatment (Abdul Khalil et al. 2014; Li et al. 2014; Adel et al. 2016). Mechanical methods are commonly performed together with various chemical pretreatments such as TEMPO-oxidation (Sun et al. 2015), carboxymethylation (Siró et al. 2011), enzymatic hydrolysis Szabo and Csiszar (2017), and phosphorylation (Noguchi, Homma, and Matsubara 2017). TEMPO-oxidation is the most commonly used chemical pretreatment method for the isolation of CNF. The CNF produced nanofibrils composed of long fibrous webs of lengths exceeding 1000 nm and generally includes amorphous cellulose with high aspect ratio

Table 1. Characteristic properties of cellulose nanocrystal (CNC) and cellulose nanofiber (CNF).

	CNF	CNC
Shape	Flexible filament	Rod-like
Morphology	Aggregated fibrils	Crystalline
Length	>1 μm	200 nm
Thickness	25 nm	5 nm
Aspect ratio	100	25
Surface area	220 m ² /g	600 m ² /g
Crystallinity index	63	85
Degree of polymerization	230–825	140–200
Surface charge	COOH <50 $\mu\text{mol/g}$	SO ₃ H: 200 $\mu\text{mol/g}$
Accessibility of OH groups	25%	11%
Zeta potential	−10 mV	−31 mV
Degradation temperature	300 °C	220 °C
Elastic modulus	145 GPa	145 GPa

and low crystallinity (Chen, Yu, and Liu 2011). The CNC is the crystalline portion of the CNF which is defined as monocrystalline cellulose region (Azizi, Alloin, and Dufresne 2005). Amorphous region of CNF is removed by hydrolysis using an acid hydrolysis method to produce crystalline CNC (Elazzouzi-hafraoui et al. 2008). Sulfuric acid (H₂SO₄), a most widely used hydrolysis method, produces stable colloidal dispersion by grafting sulfate ester groups on the surface of the nanocellulose, producing CNC with needlelike morphology, a high crystallinity index, a low aspect ratio with 1–100 nm in diameter, and a length of several hundred nanometers (Moon et al. 2011; Xu et al. 2013). The morphology, surface chemistry, dimensions, yield, and crystallinity properties of nanocelluloses are usually dependent on the source of cellulose, isolation method, isolation conditions, and pre/post-treatments (Oun and Rhim 2015a; Oun and Rhim 2016b).

Sources and structure

Cellulose is one the most abundant biological raw materials on Earth. It has been estimated that annually about 10^{10} – 5×10^{10} tons of dry lignocellulosic materials are produced in the world (Zhao, Zhang, and Liu 2012; García et al. 2016). Cellulose is the main component of the plant cell walls in addition to hemicellulose, lignin and relatively small amount of extractives. Cellulose has been used in the polymer industry due to its unique properties such as mechanical strength, biocompatibility, reproducibility, biodegradability, low density, and adjustable surface properties. Approximately 6×10^9 tons of cellulose are used every year in a variety of industries such as paper, fiber, fiber and materials and the chemical industry (Azizi, Alloin, and Dufresne 2005). Timber and timber forestry residues such as wood chips, branches, and pine needles are currently the most important industrial source of cellulose (Akil et al. 2011; Moriana, Vilaplana, and Ek 2016).

However, while timber is considered the most essential source of cellulose fiber, concerns over environmental awareness and deforestation due to increased demand for timber resources have increased interest in the use of non-wood cellulose materials (Li, Mascheroni, and Piergiovanni 2015; Oun and Rhim, 2016b). Non-wood plant fibers are obtained from natural resources such as straw fibers (rice,

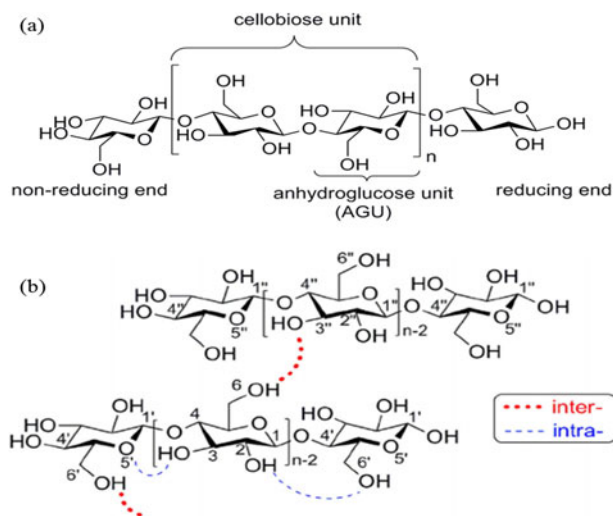


Figure 1. (a) Chemical structure of cellulose and (b) inter- and intra-molecular hydrogen bonding of native cellulose.

wheat, barley straw), seed fibers (rice husk, cotton, coir, ushar etc.), bast fibers (flax, hemp, jute, ramie etc.), grasses (bagasse, bamboo etc.), leaf fibers (pineapple, oil palm, and abaca leaf), marine animals (tunicate), algae, fungi, invertebrates and bacteria (Akil et al. 2011). Bacterial cellulose has no wax, lignin, pectin, and hemicellulose compared to vegetable cellulose. Also, bacterial cellulose can be successfully controlled for repeat units and molecular weight during the fermentation process. However, production of the industrial sector was relatively expensive (Reiniati, Hrymak, and Margaritis 2016).

Regardless of its source, cellulose is characterized as a high molecular weight homopolymer of β -1,4-linked anhydro-D-glucose having the chemical formula of $(C_6H_{10}O_5)_n$, where n is the number of repeating sugar units or the degree of polymerization (DP) (Azizi, Alloin, and Dufresne 2005; Moon et al. 2011). The repeating unit in cellulose consists of two glucose molecules, anhydrocellobiose (Festucci-Buselli, Otoni, and Joshi 2007) (Fig. 1). Each monomer of cellulose contains three hydroxyl groups at positions of 2C-OH, 3C-OH, and 6C-OH. Such hydroxyl groups can form hydrogen bonds between two adjacent chains (interchain) in addition to between two glucan units within the same chain (intrachain) and subsequently formation of fibrillar packing (Nishiyama, Langan, and Chanzy 2002).

Approximately 36 glucose chains are linked to each other through van der Waals forces and intra- and intermolecular hydrogen bonds to form protofibrils and they stack together to form long fibers called microfibrils, which linked together to form cellulosic fibers (Habibi 2014) as shown in Fig. 2. Single cellulosic microfibrils have a diameter ranging from 2 to 20 nm (Azizi, Alloin, and Dufresne 2005).

Cellulose is a stable natural polymer and does not dissolve in most aqueous solvents does not exhibit a melting point (Krumm, Pfaendtner, and Dauenhauer 2016). The properties of cellulose are greatly influenced by chain length and the degree of polymerization. For example, lignocellulose contains about 10,000 glucopyranose units and about 15,000 units in cellulosic cotton (Klemm et al. 2005).

However, the DP of native cellulose is reduced from 14,000 to about 2,500 after the separation process (Bledzki and Gassan 1999). Native cellulose consists of both crystalline (ordered) and amorphous (less ordered) regions. The degree of crystallinity of native cellulose usually ranges from 40% to 70% depending on the source of cellulose and the isolation method (Schenzel, Fischer, and Brendler 2005).

There are six polymorphs of cellulose, i.e., cellulose I, II, III_I, III_{II}, IV_I, and IV_{II}, which can be converted from one to another by chemical or thermal treatments as shown in Fig. 3 (O'Sullivan 1997). Cellulose I is known as native cellulose with crystal structures I _{α} and I _{β} (Nishiyama, Langan, and Chanzy 2002). Most native cellulose contains a mixture of crystal structures I _{α} and I _{β} depending on the origin of cellulose (Attala and van der Hart 1984). The I _{α} and I _{β} lattices have the same structure of the polysaccharide chain but different hydrogen bonding patterns (Lima and Borsali 2004). The I _{α} polymorph is a rare form and consists of a chain of trinuclear structures with alternating glucosyl residues of slightly different in the conformation and hydrogen bonds (Moon et al. 2011). On the other hand, cellulose I _{β} has two chains in a monocyclic structure in which all the glucosyl residues are the same but are alternately directed in opposite directions (Dufresne 2008). The intra-chain bond of O2-H-O6 is shorter in I _{α} than in I _{β} . Also, I _{α} is metastable and can be converted to I _{β} by hydrothermal treatment in alkaline solution (Nishiyama, Langan, and Chanzy 2002). Cellulose I is crystalline cellulose consisting of parallel chains, but it is thermodynamically metastable and converted to either cellulose II or III (Siqueira, Bras, and Dufresne 2010).

Cellulose II is obtained by regeneration and mercerization of cellulose I in concentrated sodium hydroxide (O'Sullivan 1997). Cellulose II has an antiparallel crystal structure and is known as the most thermodynamically stable form of cellulose (Saxena and Brown 2005). The characteristic distinction between these two forms of cellulose lies in the arrangement of the atoms, i.e., the chains in cellulose I are parallel, but antiparallel in cellulose II (Nishiyama et al. 2003; Nishiyama, Langan, and Chanzy 2002). Cellulose III_I and III_{II} can be obtained by cellulose I and II, respectively, whereas cellulose IV is derived from the modification of cellulose III by heat treatment (260 °C).

Isolation methods of nanocellulose

Several methods have been used to separate nanocellulose from the lignocellulosic sources, including mechanical method (Chakraborty, Sain, and Kortschot 2005; Uetani and Yano 2011), acid hydrolysis (Li et al. 2012; Liu et al. 2014), chemical/TEMPO-mediated oxidation (Isogai, Saito, and Fukuzumi 2011), ammonium persulfate (Leung et al. 2011; Oun and Rhim 2017b), and cellulose regeneration method (Shankar and Rhim 2016a; Wang, Lu, and Zhang 2016). The characteristics of the separated nanocellulose are mainly dependent on the source of cellulose (i.e., a chemical structure of cellulose) and the methods for the isolation of nanocellulose (Liu, Dong, and Sui 2016). Nanocellulose can be directly isolated from pure cellulose such as cotton fibers

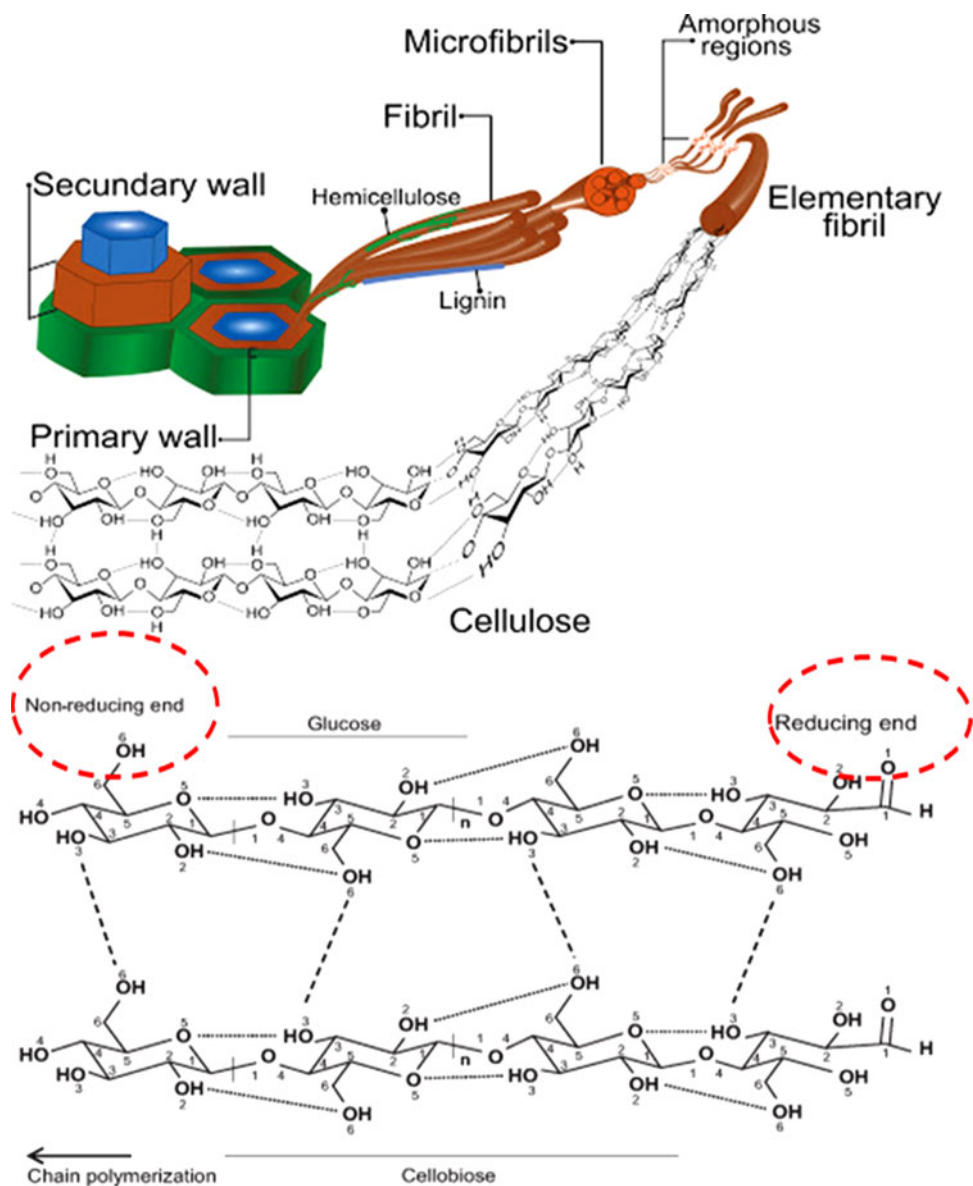


Figure 2. The structural arrangement of fibers and microfibrils of cellulose.

and bacterial cellulose or other lignocellulosic sources such as wood and plant grass, but pretreatment to remove non-cellulosic substances such as lignin, hemicellulose, pectin, wax, and other extractives materials is needed in the latter (Lu and Hsieh 2012; Oun and Rhim 2016b).

Mechanical methods

Mechanical methods are often used to decompose cellulose fibrils into their underlying nano-units, or cellulosic nano-fibers (CNF). Turbak, Snyder, and Sandberg (1983) first produced CNF with lateral dimensions in the nanometer range from a softwood pulp aqueous suspension using a high-pressure homogenizer. The CNF produced by the mechanical method showed a strongly entangled network with crystalline and amorphous domains and showed gel characteristics in water (Nechyporchuk, Belgacem, and Bras 2016). Mechanical decomposition methods include homogenization (homogenization and microfluidization), grinding, refining,

extrusion, high-speed blending, high-intensity ultrasonication, cryocrushing, steam explosion, ball milling, and ultrasonication (Chakraborty, Sain, and Kortschot 2005; Li et al. 2014; Chen et al. 2011; Uetani and Yano 2011). The homogenization, purification and grinding methods are most effective for the mechanical production of CNF (Nechyporchuk, Belgacem, and Bras 2016).

The morphology, dimensions, yield, surface chemistry and crystallinity of the CNF vary according to the method used and the reaction conditions. For example, the CNF of 20–100 nm in diameter and several tens of micrometers in length were produced by the homogenization process (Zimmermann, Pöhler, and Geiger 2004). Ultra-fine friction grinding method produced CNF with a diameter of 20–90 nm (Taniguchi and Okamura 1998). After the refining process, the fiber diameter decreased from 25 μm to 242 nm (Karande et al. 2011). CNF of uniform diameter 15–20 nm was obtained through a high-speed blending process (Uetani and Yano 2011).

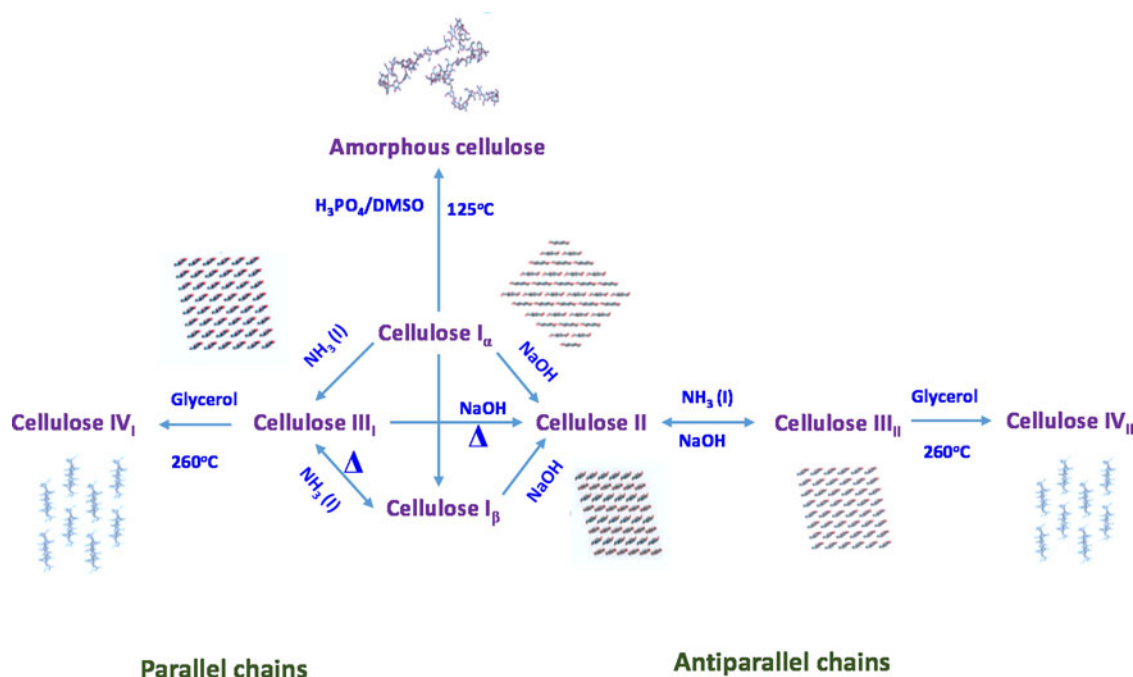


Figure 3. Polymorphs of crystalline cellulose (adapted from O'Sullivan 1997).

Ultrasonic processing technology consists of exposing aqueous media of cellulose to ultrasound (>20 kHz), creating a small vacuum bubble, and powerful hydrodynamic shear forces can be used to break down fiber cell walls (Kaboarani, Riedl, and Blanchet 2013). Ultrasonication processes are generally used after biochemical pre/post treatments such as TEMPO-mediated oxidation (Saito et al. 2013). The cryocrushing approach relies on freezing and high shear of cellulose using liquid nitrogen to further crush the cell wall to pressurize ice crystals and release cell wall fragments (Dufresne, Cavaillé, and Vignon 1997). The steam explosion process depends on exposure of the cellulosic cell wall to steam pressure for a short time, but rapid pressure release causes rupture of the fibrous cell wall. The steam explosion method is also used for the extraction of cellulose by hydrolysis of a significant amount of hemicellulose depolymerization of some lignin (Fernández-Bolaños et al. 2001; Sun et al. 2005).

Acid hydrolysis method

Acid hydrolysis is the commonly used method for the separation of cellulose nanocrystals (CNCs) (Liu, Dong, and Sui 2016). CNCs were first isolated by Rånby, Banderet, and Sillén (1949) using concentrated sulfuric acid. Various acids such as sulfuric acid, hydrochloric acid, phosphoric acid, bromic acid, and maleic acid were then used for the separation of CNC (Liu et al. 2014; Lu and Hsieh 2012). Among those acids, sulfuric acid is usually selected for the isolation of CNCs due to its ability to provide a stable suspension, which is predominantly caused by the electrostatic repulsion between the negative charges generated on the surface of the CNC (Jiang and Hsieh 2013). Other acids, such as hydrochloric acid, hydrobromic acid, can hydrolyze cellulose to CNC without esterifying the surface (Sadeghifar et al. 2011).

CNCs hydrolyzed from these acids tend to agglomerate because there is no negative charge on the surface (Yu et al. 2013). The separation of CNC by acid hydrolysis depends on the removal of the amorphous region, which is less resistant to acid attack than the crystalline region (Anglès and Dufresne 2000). The CNC produced by acid hydrolysis showed needlelike structure, high crystallinity, and low aspect ratio as compared with nanocellulose materials separated by mechanical or TEMPO-oxidation methods (Xu et al. 2013; Sun et al. 2015; Oun and Rhim 2016a). The difference between CNCs and CNFs isolated from bacteria, tunicate, and wood using acid hydrolysis, enzymatic, mechanical, and TEMPO-mediated oxidation methods have been reported (Sacui et al. 2014).

The morphology of the isolated CNCs depends on the cellulose source and the hydrolysis conditions. For example, CNCs obtained from cotton or wood are 100–300 nm in length and 5–20 nm in width, while CNCs obtained from tunic, and bacterial cellulose are reported to be several micrometers long and 5–50 nm wide (Martínez-Sanz, Lopez-Rubio, and Lagaron 2011). Hydrolysis conditions such as acid concentration, temperature, cellulose/acid ratio, and hydrolysis time are key factors in determining morphology and reinforcing the capacity of the CNC (Eichhorn et al. 2010). At high sulfuric acid concentrations (>65%), cellulose can break down and decompose into sugar molecules, but at low concentrations, the fibers are not well dispersed, and it takes more time to remove the amorphous portion of cellulose.

TEMPO-oxidation method

Oxidation of cellulose by TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl)-mediated oxidation method is considered as one of surface modification methods by converting the

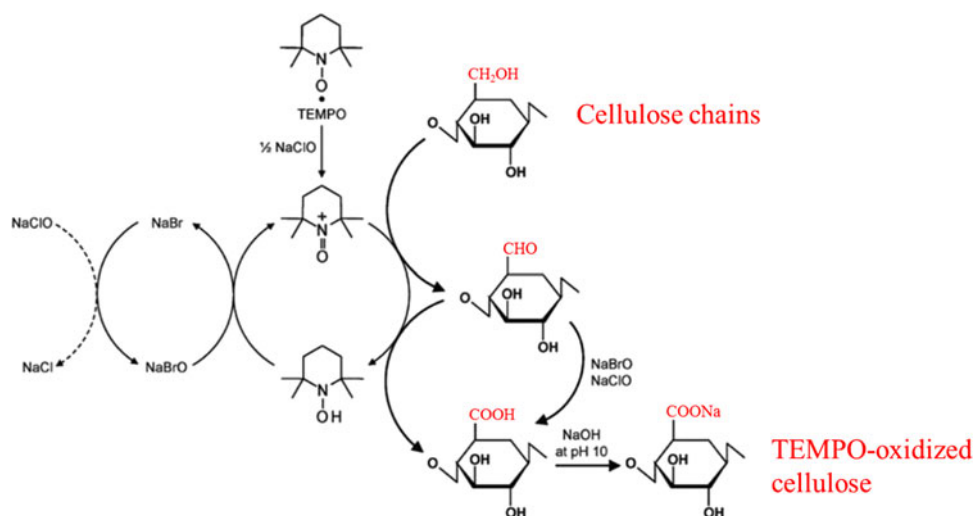


Figure 4. TEMPO-mediated oxidation of cellulose.

hydroxymethyl groups present on the cellulose surface to carboxylic form. It was initially applied with polysaccharides such as starch, amylopectin, and pullulan (Nooy, Besemer, and van Bekkum 1995). It has been reported that oxidation occurs only in the hydroxymethyl group (C6 primary hydroxyl) of the polysaccharide, while the other hydroxyl groups are not oxidized. Indeed, due to the topological structure of the cellulose chains, oxidation only occurred on the surface of the cellulose chains (Saito et al. 2005). Only half of the hydroxymethyl group can react, and the other half is buried in the crystalline particles (Habibi, Lucia, and Rojas 2010). TEMPO-oxidation mechanism occurs by dissolving the catalytic amounts of TEMPO and NaBr in the polysaccharide solution at high pH 10–11, and oxidation begins after the addition of the NaClO solution as the primary oxidant as shown in Fig. 4 (Isogai, Saito, and Fukuzumi 2011).

Over the last decade, oxidized nanocellulose materials have been reported by several researchers. TEMPO-mediated oxidation methods have been used with a variety of cellulosic resources such as softwood and hardwood celluloses (Fukuzumi et al. 2009), cotton (Saito et al. 2006), tunicate (Habibi, Chanzy, and Vignon 2006; Saito et al. 2006), hemp bast holocellulose, commercial bamboo and bagasse bleached kraft pulps (Puangsin et al. 2013), Ushar seed fiber (*Calotropis procera*) (Oun and Rhim, 2016a), rice straw (Jiang and Hsieh 2013), and jute fibers (Cao et al. 2012).

Generally, TEMPO-oxidation process is combined with other methods such as mechanical disintegration, sonication, enzymatic, or acid hydrolysis method to obtain oxidized cellulose nanocrystals or nanofibers. TEMPO-oxidized CNCs was obtained by a combination of HCl hydrolysis method and TEMPO-oxidation method (Habibi, Chanzy, and Vignon 2006). While oxidized cellulose nanofibers have been achieved by using TEMPO-oxidation method combined with moderate mechanical disintegration (Saito et al. 2007; Saito et al. 2006). The TEMPO-oxidation with mild disintegration method produced individual nanofibers 3–5 nm width and several microns in length with aspect ratios >100, high yield without significant change in their

crystallinity and crystal width. The negatively surface charged introduced from TEMPO-mediated oxidation process, formed strong electrostatic repulsion between cellulose nanofibers in water (Isogai, Saito, and Fukuzumi 2011). While other properties such as the thermal stability of TEMPO-oxidized cellulose significantly reduced from that of the original cellulose (Oun and Rhim 2016a). The thermal stability of TEMPO-oxidized cellulose could be improved by methyl esterification of carboxyl groups with trimethylsilyl diazomethane or with some metal salt solutions like CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{OAc})_2$, and CaI_2 (Fukuzumi et al. 2010). It was found that the degree of polymerization, length, and viscosity of TEMPO-oxidized cellulose nanofibrils was decreased with increasing addition of NaClO, and the further decrease was observed by sonication or mechanical fibrillation in water (Hiraoki et al. 2015). Such properties play a key role in the mechanical, optical and gas barrier properties of the TEMPO-oxidized film, which improved with increasing the length of nanofibril (Fukuzumi, Saito, and Isogai 2013; Sun et al. 2015). A comparison between nanocellulose materials prepared by TEMPO-oxidation method and sulfuric acid hydrolysis has been reported, that showed differences in morphology, length, thermal stability, and crystallinity properties (Jiang and Hsieh 2013; Sun et al. 2015; Oun and Rhim 2016a). Also, the effect of various isolation methods like acid hydrolysis, enzymatic, mechanical, and TEMPO-mediated oxidation on the properties of bacterial cellulose, tunicate, and wood has been studied (Sacui et al. 2014).

Ammonium persulfate (APS) method

In recent years, attention has been paid to expanding applications by adding surface modification or functional groups as well as separation of nanocellulose materials. Oxidation of cellulose is one of the approaches to add functional groups on the surface of nanocellulosic materials. Previously, oxidized-nanocellulose materials were prepared by TEMPO-oxidation method via oxidation of C6 primary alcohol (Isogai, Saito, and Fukuzumi 2011) or oxidation of C2 and C3 positions on the surface of cellulose fiber using

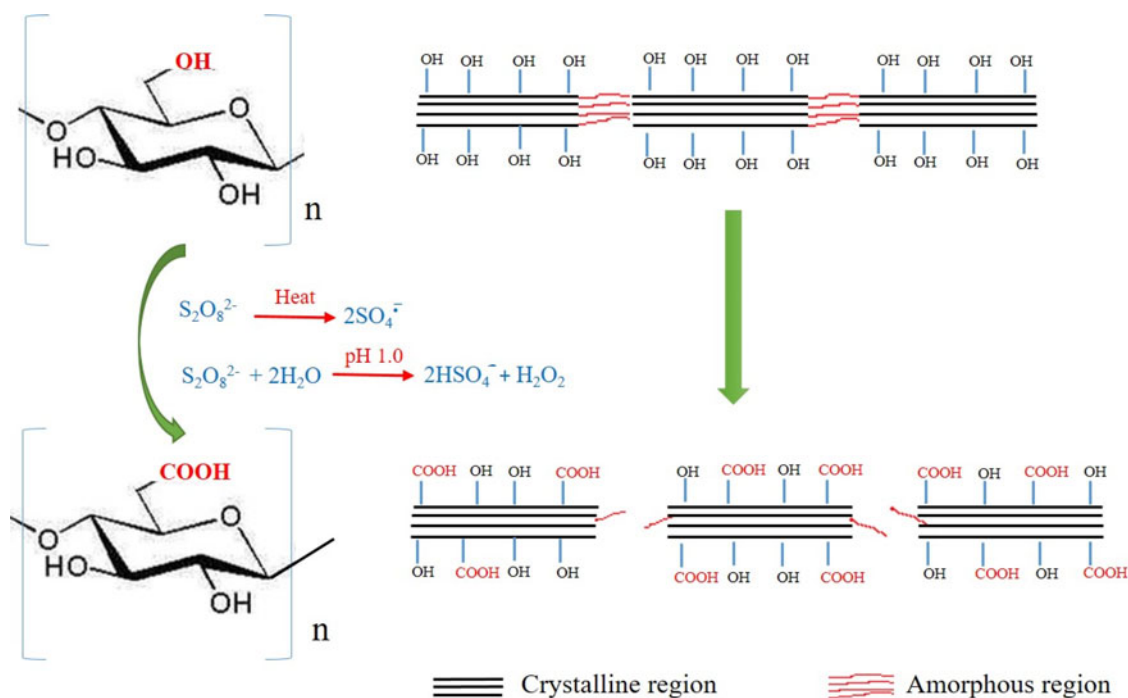


Figure 5. The principal mechanism of oxidized cellulose by ammonium persulfate (APS) method (Oun and Rhim2017b).

potassium periodate followed by sodium chlorite (Fras et al. 2005). However, this method requires additional mechanical or chemical pre-/post-treatment to produce oxidized nanocellulose, which has disadvantages in some of the nanocellulosic properties (Puangsin et al. 2013).

Recently, the ammonium persulfate (APS) method has been used as a one-step oxidation method instead of the TEMPO-oxidizing and acid hydrolysis-oxidizing methods (Leung et al. 2011). Also, it has strong oxidative properties, low long-term toxicity, low cost and high water solubility (Leung et al. 2011; Zhang et al. 2016). The APS method can generate CNC from the cellulosic material by removing the amorphous region and provide the carboxyl group at the C6 position (Leung et al. 2011). APS-based CNC manufacturing is a less harmful sustainable process than acid hydrolysis and can be made in-situ to remove some of the lignin, hemicellulose, pectin, and other plant components to make CNC production a single-step process.

As shown in Fig. 5, the main mechanism of the APS method depends on the hydrolysis and oxidation of cellulosic fibers by decomposing the amorphous region of the cellulose through the formation of free radicals ($SO_4^{\bullet-}$), hydrogen peroxide (H_2O_2), and HSO_4^- (Leung et al. 2011; Mascheroni et al. 2016). The presence of active carboxyl groups on the CNC surface provides a high possibility for CNC surface functionalization (Ifuku et al. 2009). It can also improve the dispersibility of CNC in water and can participate in cross-linking to form hydrogels in the presence of some metal cations (Dong et al. 2013). In addition, cellulose nanofibers functionalized with carboxyl groups showed high potential in removing heavy metals from wastewater (Liu, Dong, and Sui 2016).

The APS method has been used for producing carboxylated cellulose nanocrystals separated from other cellulosic

sources such as flax, flax shives, hemp, triticale, MCC, Whatman CF1 and wood pulp by the same isolation conditions (1M APS at 60 °C for 16h) and the results showed that the yields, crystallinity index, dimensions, and degree of oxidation varied with the cellulose source (Leung et al. 2011). The effects of hydrolysis conditions such as reaction time, temperature and APS concentration on morphology, microstructure and thermal stability of lyocell fibers have been reported (Cheng et al. 2014). The carboxylated cellulosic nanocrystals were separated from the bleached sugar cane gas pulp using a one-step APS method and an ultrasonic/TEMPO-oxidation method. The APS method exhibited higher crystallinity and improved the thermal stability than the TEMPO-oxidation method (Zhang et al. 2016). The APS method has also been compared with the acid hydrolysis for the extraction of microfibrillated cellulose from oil palm empty fruit bunch (Goh et al. 2016) and isolation of cellulose nanocrystals from cotton linter (Mascheroni et al. 2016). Also, the APS method has been used for the isolation of oxidized-cellulose nanocrystals (CNCs) from cotton linter and microcrystalline cellulose (Oun and Rhim 2017b) and oxidized-chitin nanocrystals (ChNCs) (Oun and Rhim 2017c) with different crystallinity index, size, zeta-potential, and degree of oxidation values.

Regenerated cellulose

Cellulose regeneration is a simple, green, and cheap technology that is used to convert natural cellulose into soluble cellulose derivatives through physical dissolution without involving chemical reactions (Cai and Zhang 2005). Due to the formation of a strong cellulose chain packing through intermolecular and intramolecular hydrogen bonding, it is not soluble in common solvents (Medronho and Lindman

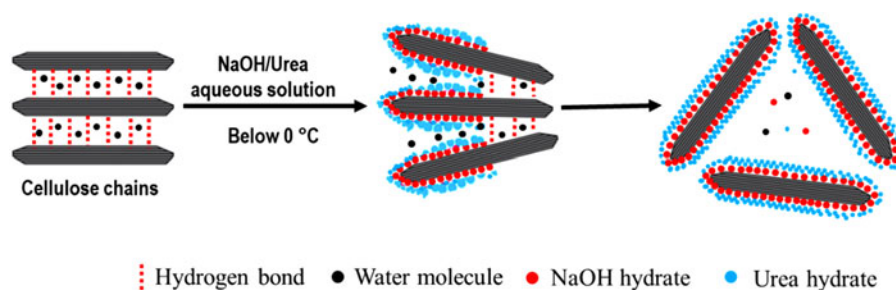


Figure 6. Schematic presentation for dissolution of cellulose in NaOH/urea solution.

2015). Several solvents have been used for dissolving cellulose such as NaOH aqueous solution (Isogai and Atalla 1998), alkali/urea and NaOH/thiourea aqueous solution (Li et al. 2014; Qin, Lu, and Zhang 2013), ionic liquids (Pinkert et al. 2009), N-methylmorpholine-N-oxide (NMMO) (Dogan and Hilmioğlu 2009), LiCl/N,N-dimethylacetamide (LiCl/DMAc) (Raus et al. 2012), metal complex solutions (Wang, Lu, and Zhang 2016), and molten inorganic salt hydrates (Yang et al. 2014).

The mechanism of cellulose dissolution depends on the removal of intermolecular hydrogen bonds and intermolecular hydrogen bonds between the cellulose molecules to form a cellulose polymer solution. For example, when cellulose dissolved in NaOH/urea system, NaOH “hydrates” create new hydrogen-bonded networks of cellulose chains with relatively stable at low temperatures, while urea hydrates as shell surrounded the NaOH hydrogen-bonded cellulose to form an inclusion complex with sheath-like structure (Cai et al. 2008). Jiang et al. (2014) reported that the OH-ion of NaOH and the amino group of urea interact directly via hydrogen bonding, but there is no direct interaction between urea and cellulose as shown in Fig. 6.

Application of nanocellulose

The inherent mechanical properties of CNCs such as high stiffness (135–155 GPa) and high strength (estimated at 7500 MPa) have increased application for the reinforcement of different polymer such as poly(lactic acid) (Dhar et al. 2016), polypropylene (Lee, Kim, and Yu 2009), agar (Oun and Rhim 2015a), and carboxymethyl cellulose (Oun and Rhim 2015, 2016b), and for the food packaging applications (Azeredo, Rosa, and Mattoso 2017; Khalil et al. 2018). It is well known that isolated crystalline cellulose is stronger and harder than amorphous cellulose or the original cellulose. As a result, the incorporation of nanocrystalline cellulose led to improving the mechanical properties, thermal stability, water vapor and gas barrier properties of biopolymers films. On the other hand, nanocellulose materials have also been used in the electronics filed due to its high thermal conductive properties (Uetani, Okada, and Oyama 2015), in support of metal nanoparticles in catalysis (Kaushik and Moores 2016), and in the biomedical applications (Jorfi and Foster 2015; Lin and Dufresne 2014). The use of nanocellulose materials as reinforcing agents to improve the properties of bio-nanocomposite films is summarized in Table 2.

TEMPO-oxidized nanofibers were used in the manufacture of transparent cellulose film with high tensile strengths of 200 - 300 MPa, modulus of elasticity of 6–7 GPa, high transparency and low oxygen permeability (Isogai, Saito, and Fukuzumi 2011). Sun et al. (2015) produced transparent cellulose films from TEMPO-oxidized cellulose nanocrystals and found a higher optical transmittance (98.4% at 900 nm) and a higher tensile strength (236.5 MPa) compared to films made from sulfuric acid treated cellulosic nanocrystals. TEMPO-oxidized fibrillated cellulose was also used as a reinforcing agent in chitosan film (Soni et al. 2016), polyurethane (Cheng et al. 2016), poly(lactic acid) (PLA) (Bulota et al. 2012), and for the preparation of a high gas barrier film (Fukuzumi et al. 2009; Wu et al. 2012), a crosslinking aid for alginate-based sponges (Lin, Bruzzese, and Dufresne 2012), a highly transparent all-cellulose nanopaper (Sun et al. 2015), a conductive composite (Koga et al. 2013), and a carrier for bioactive molecules (Weishaupt et al. 2015), as well as being used for selective CO₂ and NH₃ gases adsorption (Shah and Imae 2016) and Cu(II) removal (Zhang et al. 2016).

Cellulose regeneration is a simple route to the conversion of natural cellulose to various forms such as cellulose fibers, cellulose bioplastics, films, membranes, hydrogels, aerogels, microspheres and beads (Wang, Lu, and Zhang 2016). Industrially, regenerated cellulose fibers, such as rayon, are made by soaking the cellulose by dissolving the pulp in NaOH (Müller, Gebert-Germ, and Russler 2012). For example, Tencel® fiber was obtained by regeneration of Lyocell® cellulose in NMMO-solutions (Fink et al. 2001), and cuprammonium rayon was made by dissolving rayon cellulose in cuprammonium solution (trade name “Bemberg”) (Wang, Lu, and Zhang 2016). Regenerated cellulose was used in the production of transparent films, which plays an important role in cosmetics, pharmaceutical, and food packaging, and pressure-sensitive tapes. Recycled cellulose was used in the production of transparent films, which play an important role in cosmetics, pharmaceutical packaging, food casting and pressure-sensitive tapes Isogai and coworkers prepared a transparent regenerated cellulose film with high oxygen barrier properties (0.003–0.03 mL $\mu\text{m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ at 0% relative humidity) (Yang et al. 2011). Regenerated cellulose film with a high tensile strength (100 MPa), the excellent light transmittance (90% at 800 nm), and completely biodegradable within one month was prepared using NaOH (or LiOH)/urea solvent. The tensile strength of cellulose film regenerated from alkali/urea

Table 2. Examples of using nanocellulose as a reinforcing agent for nanocomposite films.

Polymer	Type/source of cellulose	Effects	Ref.
PLA	Cellulose nanofibers (CNF) from oil palm mesocarp fiber (W = 80–100 nm)	Improved mechanical and wettability properties	Ariffin et al. 2018
PLA	CNC from Whatmann filter paper	Improved thermomechanical, water vapor and oxygen barrier properties	Dhar et al. 2017
PLA	Lyocell fibers and microcrystalline cellulose nanospheres (CNS) (W = 27), cellulose nanocrystals (CNC) (L = 270, W = 16), and cellulose nanofibers (CNF) (L = 589, W = 25)	Mechanical, thermal stability, water barrier, and crystallinity of PLA were improved depending on the type of nanocellulose	Yu et al. 2017
PLA	Microfibrillated cellulose (W = 30–50 μ m)	Increased the tensile strength and Young's modulus of the film	Iwatake, Nogi, and Yano 2008
PLA	CNCs from Whatmann® filter paper using different acids (L = 198–1290 nm, W = 12–26 nm)	Mechanical and thermal properties of PLA films significantly influenced by the type of acid and aspect ratio of CNCs.	Dhar et al. 2016
PLA	Cellulose nanofibrils from bleached wood	Increased tensile strength by 56.7% and elongation by 60%.	Qu et al. 2010
PVA	TEMPO-oxidized cellulose nanofibril (L = 110–600 nm, W = 10–40 nm)	Increased Young's modulus and tensile strength	Hamou et al. 2018
Chitosan	Cellulose nanofibers (L = 98.1 nm, W = 8.0 nm)	Improved the mechanical properties.	Azeredo et al. 2010
Starch-gelatin	Recycled cellulose (W = 16–25.9 μ m)	Increased hardness and elastic modulus by 163% and 123%, respectively by mixing 5wt% of cellulose.	Rodríguez-Castellanos et al. 2015
CMC	Oxidized-CNCs from cotton linter (L = 120–150 nm, W = 10.3 nm) and microcrystalline cellulose (L = 103–337 nm, W = 11.4 nm)	Increased tensile strength by 102% and 73%, and elastic modulus by 228% and 166% by mixing 10 wt% of CNCs from cotton linter and microcrystalline cellulose, respectively.	Oun and Rhim 2017b
CMC	CNCs isolated from rice straw (RS), wheat straw (WS), and barley straw (BS) with L = 120–800 nm and W = 10–25 nm	Increased tensile strength by 45.7%, 25.2%, and 42.6%, and decreased water vapor permeability by 26.3%, 19.1%, and 20.4% by mixing 5% of RS, WS, and BS, respectively.	Oun and Rhim 2016b
CMC	Cellulose nanofibrils with L = 125–217 nm and W = 23–38 nm isolated from cotton linter using acid hydrolysis.	Increased tensile strength and elastic modulus by 23% and 27%, respectively.	Oun and Rhim 2015b

solution reached to 124 MPa when reinforced with cellulose whiskers (Qi et al. 2009). On the other hand, the cellulose nanofibrils were prepared by pretreating cellulose with NaOH/urea/thiourea solution and then defibrillating the fibers using ultrasonic waves. The resulting cellulose nanofibers exhibited high thermal stability (270 °C of onset of thermal degradation and 370 °C of a maximum degradation temperature) and high yield (85.4%) (Li et al. 2014).

The cellulose bioplastic films made of cellulose by dissolving cellulose using NaOH/urea solution and using simple hot-pressing were excellent in mechanical properties (tensile strength of 240 MPa and modulus of 3.7 GPa), good thermal stability, and environmental friendliness (Wang et al. 2013). An optically transparent paper has been prepared after the dispersion of fibrillated cellulose fibers (diameter 15 nm) in water and followed by vacuum filtration and hot-pressing (Nogi et al. 2009). Regenerated cellulose films have promising potential for packaging materials.

Cellulose and cellulose derivatives have been used for the preparation of hydrogels. Hydrogels produced from cellulose have recently become of increasing importance due to their low cost, safety, hydrophilicity, biodegradability, and biocompatibility (Chang and Zhang 2011). A transparent cellulose hydrogel having an equilibrium swelling ratio of 30–60 g of water/g dry hydrogel at 25 °C was prepared (Zhou et al. 2007). Zhang and coworkers used epichlorohydrin (ECH) as a crosslinking agent to produce a series of hydrogels from cellulose in heated or frozen NaOH/urea

solutions with different porosity structures, mechanical and equilibrium swelling ratios (Qin, Lu, and Zhang 2013).

To add more functionality and increase the application of cellulose, Qi, Mäder, and Liu (2013) blended carbon nanotubes to produce functionalized regenerated cellulose. The results showed excellent thermal stability, conductivity (2.3×10^{-4} – 2.2×10^{-2} S cm⁻¹) and excellent mechanical properties indicating promising applications in detectors, energy storage, catalysts, and biotechnology. The regenerated cellulose was functionalized by making a composite with other functional materials such as silver, gold, and platinum nanoparticles, in addition to carbon nanotubes and cellulose nanowhiskers (Cai et al. 2009).

Metal and metal oxide nanoparticles

In recent years, research on metal and metal oxide nanoparticles have attracted great interest due to their optical, electronic, catalytic and antibacterial properties (Tian et al. 2013). Among them, ZnO, CuO and Ag NP are considered more attractive because they have many potential applications in the fields of polymers, medical, biosensors, electronics, catalysts, ceramics, inks, biocides, biomedical and healthcare products (Shankar and Rhim 2015; Maruthupandy et al. 2017; Maleki and Kamalzare 2014). In particular, ZnO, CuO, and Ag NP have been used as antibacterial and UV barrier properties in food packaging and biomedical applications.

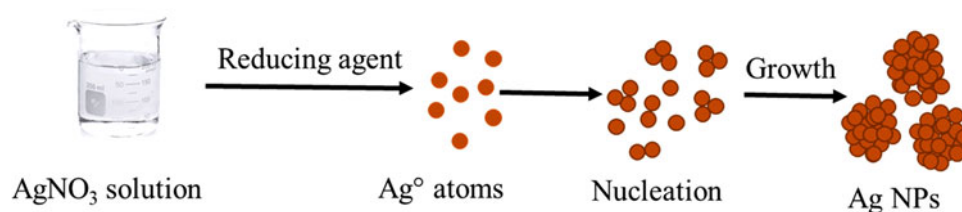


Figure 7. Illustration of silver nanoparticles formation.

Silver nanoparticles (Ag NP)

The unique properties of silver nanoparticles (Ag NP) such as strong antibacterial, antifungal, antiviral, anti-inflammatory, anti-angiogenic, and anti-cancer activity (Li et al. 2010; Zhang et al. 2016) has increased its applications in a variety of fields including medical device coatings, cosmetics, pharmaceutical industry, drug delivery, wound dressings, food packaging, and textiles (Li et al. 2010). Ag NP have been synthesized by physical methods (Rhim et al. 2014) and chemical methods using reducing agents such as sodium borohydride, triethanolamine, dimethylformamide, and hydrazine (Yoksan and Chirachanchai 2010), amino acids (Shankar and Rhim 2015), as well as a biological method using microorganisms and plants extracts (Awwad, Salem, and Abdeen 2013; Borase et al. 2014; Thatoi et al. 2016). Among those methods, a biological method using plant extracts have several advantages over the use of physical, chemical, and microbial methods for synthesis of Ag NP. Plant extracts can serve as safe reducing and capping agents and do not require specific reaction conditions such as toxic chemicals, high temperatures, radiation, and costly media for nanoparticle production (Borase et al. 2014). Such advantages facilitate its application in biomedical applications, tissue engineering, drug delivery, bio-insecticide and water purification (Awwad, Salem, and Abdeen 2013; Borase et al. 2014; Wei et al. 2015). The size and morphology of Ag NP are strongly influenced by reaction conditions such as the concentration of precursor (AgNO_3), type and concentration of reducing agent, reaction time, temperature and pH (Borase et al. 2014; Wei et al. 2015).

The mechanism of formation of Ag NP by chemical reduction process proceeds in two steps (Fig. 7). The first is to reduce the Ag ion form (Ag^+ ion) to the metal form (Ag° atom) and form nucleation nuclei, and the second is the adhesion of some nuclei to form Ag NP (García-Barrasa, López-de-Luzuriaga, and Monge 2011). Surfactants such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVOH) are commonly used to control the growth of Ag NP, including nucleophilic electron donor groups capable of donating electrons to Ag NP (Wiley et al. 2005).

Zinc oxide nanoparticles (ZnO NP)

Zinc is an essential element, and ZnO nanoparticles are nontoxic, environmentally friendly, low cost with abundant availability, and have excellent photocatalytic properties (Yoon et al. 2015). Interestingly, ZnO NP is not toxic to human cells and have been reported in several studies, exhibiting antibacterial activity and UV blocking properties

(Talebian, Amininezhad, and Doudi 2013). ZnO NP showed high photocatalytic efficiency among all inorganic photocatalytic materials (Nirmala et al. 2010). The high photocatalytic efficiency of ZnO NP leads to a photo-induced oxidation process that can destroy and inhibit organisms by producing ROS species such as H_2O_2 and superoxide ions $\text{O}_2^{\cdot-}$ (Baruah et al. 2010). The intrinsic properties of ZnO NP are strongly influenced by the synthesis methods and conditions, resulting in ZnO NP of different nanostructured forms, and each nanostructure has specific structural, optical, electrical, physicochemical and antimicrobial properties (Conde et al. 2011). For example, the microwave-assisted method produced spherical ZnO NP whereas ZnO NP produced by wet chemical route have different forms, such as nano and micro-flowers, dumbbell-shaped, rice flakes, and ring. Forms of ZnO synthesized through the deposition process showed rod and dumbbell-shaped ZnO, simple precipitation method (nano-flake), hydrothermal synthesis (hexagonal prismatic rods), solvothermal method (nano-flowers, nanorods, nano-spheres), and hydrothermal technique (nanorods). The antimicrobial activity is strongly influenced by the shape and size of ZnO NP (Talebian, Amininezhad, and Doudi 2013). The shape of the ZnO NPs depends on the growth surface, whereas the spherical nanostructure mainly has the (100) plane and the rod structure has the (111) and (100) planes (Ramani et al. 2014). Yang et al. (2009) reported that rod-shaped and wire-shaped ZnO could penetrate more easily into bacterial cell walls than spherical ZnO NP. Talebian, Amininezhad, and Doudi (2013) reported that the photocatalytic activity of flower-shaped ZnO NP was significantly higher than that of rod-shaped or spherical ZnO NP, and also found that ZnO NP showed stronger antibacterial activity against *E. coli* than *S. aureus* and the antimicrobial activity increased with a decrease in their crystallite size. Although the antimicrobial mechanism of ZnO NP is not yet known, a possible mechanism of antimicrobial activity of ZnO NP has been proposed (Liu et al. 2009). The unique antibacterial and UV barrier properties of ZnO NP have encouraged the use of antimicrobial fabric preparation (Petkova et al. 2014) and poly(vinyl chloride) coatings for antimicrobial packaging preparation (Li et al. 2009).

Copper oxide nanoparticles (CuO NP)

Copper oxide nanoparticles (CuO NP) are interesting class of materials with versatile properties with promising applications in photoconductive applications, gas sensors,

biosensors, biomedicine, magnetic storage media, batteries, solar energy and superconductivity (Etefagh, Azhir, and Shahtahmasebi 2013; Oun and Rhim 2017a). Various active food packaging films were prepared by incorporation of CuO NP into polypropylene (Delgado et al. 2011) and polyethylene (Cushen et al. 2014) to increase the shelf life of the packaged foods (Beigmohammadi et al. 2016). In addition to the presence of CuO NPs in the oxidized form, CuO NP is considered a cheap substitute for silver nanoparticles that can easily mix with petrochemical-based plastics or biological macromolecules without changing the chemical and physical properties (Usman et al. 2012). CuO NP has been used as an antimicrobial against yeast, fungi and numerous bacterial species (Ramyaadevi et al. 2012). CuO NP was also used to produce antimicrobial fabrics by coating cotton fabrics using sonochemical methods (Perelshtein et al. 2013). The antimicrobial hydrogel beads formed by in situ synthesis of CuO NP during the formation of the chitosan hydrogel showed excellent antibacterial activity and pH-sensitive swelling behavior (Farhoudian, Yadollahi, and Namazi 2016). On the other hand, CuO NP has been used in the production of antibacterial bio-nanocomposite films that can be used in antimicrobial hydrogels and biomedical and active food packaging (Arfat et al. 2017; Oun and Rhim 2017a). The possible mechanisms of antimicrobial action and cytotoxicity of CuO NP have been discussed by Ingle, Duran, and Rai (2014). The effect of particle size on the antimicrobial activity has been reported, and as a result, the higher antibacterial activity of CuO NP has been obtained with a smaller particle size (Azam et al. 2012).

CuO NP of various size and shape were synthesized by various methods such as a chemical procedure (Mahapatra et al. 2008; El-Trass et al. 2012), chemo-thermal method (Shankar, Wang, and Rhim 2017), gel combustion method (Azam et al. 2012), sol-gel and spray pyrolysis method (Etefagh, Azhir, and Shahtahmasebi 2013), microwave method (Blosi et al. 2011), using plant extract (Naika et al. 2015) and other biological method (Usha et al. 2010).

Iron oxide nanoparticles

Iron oxide is present in many forms, with magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) being the most common. Magnetite is also known as black iron oxide, magnetic iron ore, loadstone, ferrous ferrite or Hercules stone and has the strongest magnetism of all transition metal oxides (Maleki, Hajizadeh, and Firouzi-Haji 2018). In recent decades, the synthesis and utilization of Fe_3O_4 NP with novel properties and functions have been extensively studied due to their size in nano-range, high surface area to volume ratios, and superparamagnetism (Maleki, Hajizadeh, and Firouzi-Haji 2018). In particular, easy synthesis, coating or modification, and the ability to control or manipulate shape and size can provide unparalleled versatility. In addition, Fe_3O_4 NP with low toxicity, chemical inertness and biocompatibility show tremendous potential in a variety of applications (Maleki, Movahed, Ravaghi 2017). Synthesis of magnetic nanoparticles of

custom size and shape has long been a science and technology challenge. Physical methods such as vapor deposition and electron beam lithography are elaborate procedures that suffer from the inability to control the size of particles in the nanometer size range. The wet chemical routes to magnetic nanoparticles are simpler, easier to handle, and more efficient in controlling the size, composition and even shape of the nanoparticles. Iron oxides (either Fe_3O_4 or others) can be synthesized by coprecipitation of Fe^{2+} and Fe^{3+} aqueous salt solutions by the addition of a base. Control of nanoparticle size, shape, and composition depends on the type of salts used such as chlorides, sulfates, nitrates, perchlorates, etc., as well as Fe^{2+} and Fe^{3+} ratio, pH and ionic strength of the media (Maleki, Zand, and Mohseni 2016). Typically, the magnetite is prepared by adding a base at a 1:2 molar ratio to an aqueous mixture of Fe^{2+} and Fe^{3+} chloride (Maleki, Zand, and Mohseni 2016).

Hybrid metal and metal oxide NP

The combination of metal and metal oxide NPs is becoming increasingly important to make the most of the nanocomposite technology characteristics. Dizaj et al. (2014) suggested that the combination of metal NP is one way to overcome bacterial resistance to antimicrobial agents. The synthesized ZnO/Ag NP heterostructures showed stronger antimicrobial activity, and photocatalytic properties than single NP (Trandafilovic et al. 2014; Jaramillo-Páez et al. 2017), and the photocatalytic activity of ZnO was improved after incorporation of CuO (Xu et al. 2017).

Hybrid nanoparticles were prepared using numerous metal and metal oxide nanoparticles with different shapes for a variety of applications. For example, Ag/ZnO NP was used to produce antimicrobial fabrics (Buşilă et al. 2015). Nanocomposites of ZnO/CuO/ TiO_2 showed the ability to remove phenol from wastewater (Mohammadi et al. 2014), and the Fe_3O_4 /ZnO/CuO nanocomposites showed organic dye removal capacity (Taufik and Saleh 2017). Spherical CuO/ZnO NP showed a potential use as an optical sensor for the detection of metal ions (Maruthupandy et al. 2017). ZnO/CuO nanocomposite was used as a humidity sensor (Ashok, Rao, and Chakra 2016), ZnO-SnO₂ was used as a gas sensor (Mondal et al. 2014), and Zeolite/ZnO-CuO nanocomposite was used as antimicrobial agents (Alswat, Ahmad, and Saleh 2017). Recently, Maleki, Hajizadeh, and Firouzi-Haji (2018) prepared a green composite nanostructure of Fe_3O_4 /PEG-SO₃H that served as a catalyst for the preparation of biologically active aminocarbonyl compounds. Varaprasad et al. (2017) used ZnO/CuO NP as a nanofiller in PCL (poly- ϵ -caprolactone) and PET (poly(ethylene terephthalate)) polymer films. The results show that the polymer nanocomposite films using ZnO/CuO hybrid NP have higher mechanical properties than the nanocomposite films using ZnO or CuO alone. Ahmed et al. (2016) reported that the mechanical properties and glass transition temperature (T_g) of poly(lactic acid) (PLA) film were improved after the incorporation of Ag/Cu alloy. The Ag/Cu hybrid nanomaterial showed significant reinforcement, antibacterial and UV barrier

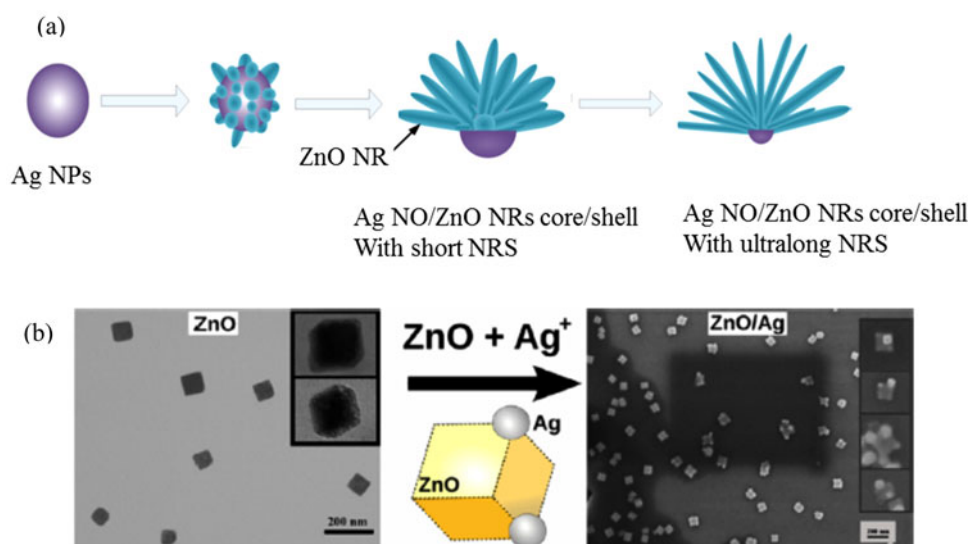


Figure 8. (a) growth of ZnO nanorods on the surface of the Ag nanoparticles (Yin et al.2012), (b) formation of spherical Ag nanoparticles on the surface of ZnO nanocubes (Trandafilovic et al.2014).

properties when added to the gelatin film (Arfat, Ahmed, et al. 2017).

Various approaches such as microwave irradiation (Roberson et al. 2014), laser ablation (Murzin and Kryuchkov 2017), electrochemical method (Das and Srivastava 2017), electrospinning (Lin et al. 2009; Zhou et al. 2014), mechanical method (Yin et al. 2012), chemical method (Alswat et al. 2017), and biological methods (Azizi et al. 2016; Maruthupandy et al. 2017; Thatoi et al. 2016) have been used for the synthesis of different hybrid nanomaterials. The morphology and size of ZnO/Ag NP were significantly changed according to the synthesis method and reaction conditions. For example, hybrid metal Ag NP/ZnO nanorods with a core/shell structure were prepared, and ZnO nanorods could be grown directly on the surface of spherical Ag nanoparticles (Yin et al. 2012), which was illustrated in Fig. 8a. Trandafilovic et al. (2014) synthesized ZnO/Ag heterostructure using a microwave-assisted process in the presence of alginate biopolymer and found that spherical Ag NP was formed at the edge and apex of ZnO nanocubes (Fig. 8b). During the use of microwave chemical reactor, glucose act as a reducing agent and a hybrid nanometal of ZnO in nanorods and Ag NP in nano-spherical shapes were formed (Saoud et al. 2015).

Nanocellulose/metal or metal oxide hybrid NP

Nanocellulose has an excellent mechanical and barrier properties, and metal and metal oxide nanomaterials such as Ag NP, ZnO NP, and CuO NP have antimicrobial activity, UV-barrier properties, and excellent thermal stability. To this end, prepared nanocellulose/nanometal (organic/inorganic) nanohybrid with multifunctional properties has attracted much attention in academia and industry recently. Hybrid nanocellulose/metallic NPs have been applied in the fields of electronics and sensors (Liu et al. 2010; Khalil, Hassan, and Ward 2017), catalysis applications (Kaushik and Moores 2016; An, Long, and Ni 2017), biomedical (Singla

et al. 2017), detection of pesticides (Liou et al. 2017), and multifunctional nanocomposite films (Ahmed et al. 2016; Arfat et al. 2017). Various physical and chemical methods have been developed to synthesize metal and metal oxide NPs (Lin et al. 2009; Saoud et al. 2015; Zhang et al. 2016). However, most of these methods require hazardous chemicals or expensive equipment under certain reaction conditions (Wiley et al. 2005). Furthermore, concerns over the safety of nanotechnology products used in related food and food packaging have increased interest in using a greener approach to metal NP synthesis (Thatoi et al. 2016). To this end, a green method using biological systems have emerged as the best alternative way to synthesize metal NPs in a simple, rapid, nontoxic and environmentally friendly method (Naika et al. 2015). For example, ginger oil has been used in synthesizing ZnO/Ag core-shell nanocomposite (Azizi et al. 2016). Salem et al. (2015) produced silver and zinc nanoparticles using aqueous extracts of *Caltropis procera* fruit or leaves, and they applied the NP as an antimicrobial in the biomedical and pharmaceutical fields. Metal or metal oxide NP are generally thermodynamically unstable and tend to lose the advantages of nanostructures in the absence of capping agents. Recently, nanocellulose has been used as a template, stabilizer and reducing agent in the synthesis of various inorganic nanoparticles. The presence of a large surface area and a highly reactive primary OH group on the surface of nanocellulose is believed to play an essential role in the synthesis and capping of inorganic NP (Drogat et al. 2011; Azizi et al. 2013b).

Several approaches have been developed to attach inorganic NP on the surface of nanocellulose which can be classified as following four methods (Fig. 9)

1. Simple blending of cellulose and inorganic NP components.
2. Synthesis of NP using an external reducing agent.
3. Synthesis of NP via surface modification of nanocellulose.
4. Synthesis of NP using cellulose materials without any external reducing or capping agents.

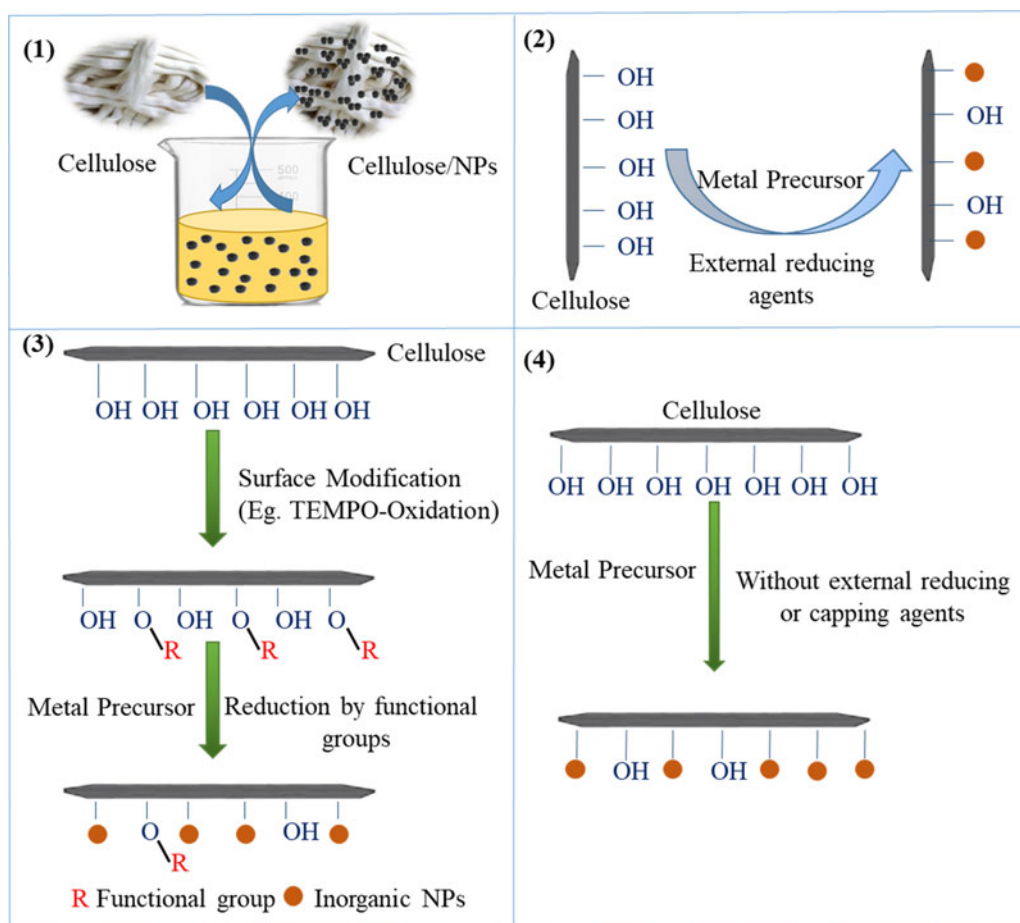


Figure 9. Schematic presentation for the synthesis of metal NPs/nanocellulose hybrid composite. (1) Simple blending of cellulose source and prepared inorganic NPs, (2) Synthesis of NPs using an external reducing agents, (3) Synthesis of NPs via nanocellulose surface modification, and (4) Synthesis of NPs using nanocellulose itself without external reducing agents.

The first approach is based on immersing or blending a cellulose material such as paper sheet, cellulosic fibers or CNC into a previously prepared inorganic NP suspension (Varaprasad et al. 2016; Khalil, Hassan, and Ward 2017). In this method, the cellulosic material was used as a template or carrier for the inorganic NP. Although this technique is simple to apply, it does not produce a uniform NP distribution in cellulose with some aggregates during the drying process (Ul-Islam et al. 2014).

The second approach is the most commonly used method of reducing metal ions to metallic NPs in the presence of cellulosic materials using external reductants (Wang et al. 2014). In this method, metal ions (precursors) are captured using a cellulosic material, and then metal ions are reduced to NP using an external reducing agent such as sodium borohydride, ascorbic acid, sodium citrate, triethanolamine or plant extracts (Kaushik and Moores 2016). Here, the cellulose material serves as an auxiliary stabilizer to avoid aggregation of the metal NP (Jiang and Hsieh 2014; Hu and Hsieh 2015).

In a third approach, the cellulose material was used as a template and capping agent through the modified surface to attach functional groups capable of reducing and stabilizing the metal precursor to metal NP on the surface of the cellulosic material. Several methods have been developed for modifying the surface of cellulose by loading negatively

charged groups that can reduce metal ions to NPs through electrostatic interactions and produce homogeneously dispersed NPs (Hoeng et al. 2015). Sulfonation is one of the ways to introduce a negatively charged group onto the surface of the nanocellulose through the esterification of hydroxyl groups (Nechyporchuk, Belgacem, and Bras 2016). Sulfonation of nanocellulose occurs in the hydrolysis of sulfuric acid, which generates sulfuric acid ester groups on the surface of CNC (Lokanathan et al. 2014). The presence of a negative charge on the surface of the nanocellulosic material induces excellent colloidal stability through electrostatic repulsion, resulting in an excellent dispersion of the nanocellulose/nanomaterial complex in suspension form for a long time. Sulfuric acid hydrolysis produces negative charge density in the range of 130–200 $\mu\text{moles/g}$, and lower or higher values lead to CNCs aggregation (Lokanathan et al. 2014). On the other hand, the negative charge density of the CNC produced in the TEMPO-oxidation process can be up to 1500 $\mu\text{mole/g}$ (Saito et al. 2007).

Carboxylation is often used for surface modification of cellulosic materials by the introduction of negatively charged carboxy or carboxymethyl groups through oxidation of the primary alcohol group on the surface of the nanocellulosic material (Soni et al. 2016). TEMPO-mediated oxidation is the most commonly used method for introducing carboxyl groups with a negative charge on the nanocellulose surface

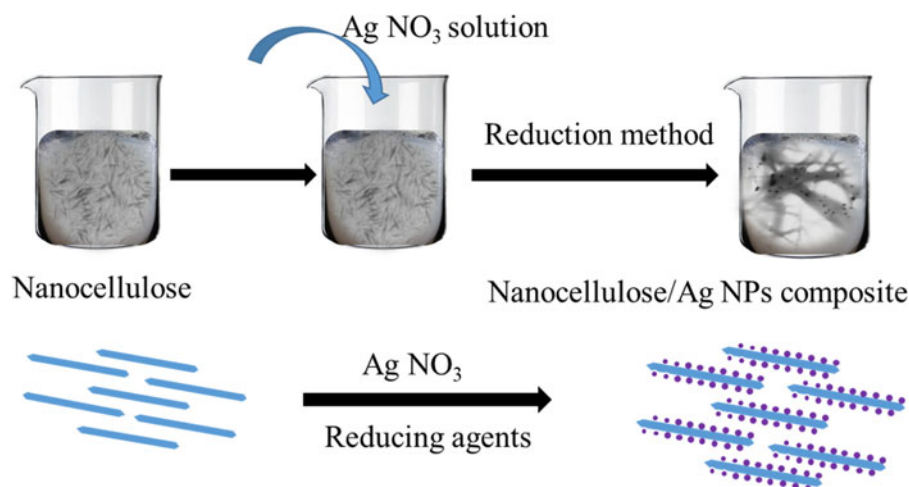


Figure 10. Illustrated presentation of the synthesis of CNC/Ag hybrid NP nanocomposite.

(Yan et al. 2016). TEMPO oxidation of cellulose converted OH group at C6 to COO^-Na^+ , which is used to convert the metal salt (AgNO_3) to COO^-Ag^+ and to form Ag NP by thermal reduction (Ifuku et al. 2009). Carboxylation of cellulose can also occur via periodate-oxidizing oxidation, which converts the secondary alcohol of cellulose into a carboxyl group (Kim and Kuga 2001). The reaction mechanism first oxidizes the secondary alcohol of the cellulose to the aldehyde group and then converts it into the carboxyl group by sodium chlorite to produce 2,3-dicarboxylic acid cellulose (Nechyporchuk, Belgacem, and Bras 2016). Drogat et al. (2011) synthesized Ag NP using surface modified CNC with periodate oxidation using the presence of an aldehyde group on the CNC surface as a reducing agent. Recently, cellulose has been carboxylated through an ammonium persulfate (APS) method to simultaneously isolate and oxidize nanocellulose (Leung et al. 2011; Oun and Rhim 2017b; Zhang et al. 2016).

The non-covalent surface modification is one of the types of nanocellulose modifications obtained through the adsorption of surfactants. These surfactants are oppositely charged or polyelectrolytes and interact with the CNC surface through electrostatic attractions such as hydrogen bonding and van der Waals forces (Habibi 2014). To increase the interaction between hydroxyl groups of cellulose and metal ions, the surface of the cellulosic materials was treated with different materials like sodium alginate (Varaprasad et al. 2016), lignin (Hu and Hsieh 2015), terpyridine (Hassan and Hassan 2016), and polydopamine (Shi et al. 2015).

In the fourth approach, cellulose materials and thermal process were used for the synthesis of inorganic metals without any external reducing or capping agents that are predominantly dependent on the abundant hydroxyl groups of the cellulose surface. In this process, the surface OH group itself can be used as a template for metal precursors through ion-dipole interactions and stabilize the NPs generated through nucleophilic interactions to produce well-dispersed NPs on the nanocellulose surface. For strong reduction and binding of metal precursor (metal ions) on the surface of cellulose materials, surface hydroxyl groups were activated using various methods such as hydrothermal process (Cai

et al. 2009; Li, Mascheroni, and Piergiovanni 2015), UV-irradiation (Yao et al. 2015), and microwave radiation (Li et al. 2011; Ma et al. 2013). Recently, dissolved cellulose using an ionic liquid (NaOH-urea) has been used as a green strategy for the production of cellulose/inorganic nanohybrids such as cellulose/ZnO NPs and cellulose/CuO NPs (Shankar, Wang, and Rhim 2017). This method has been used for the production of functional textiles with antibacterial activity.

Nanocellulose/Ag NP

Ag NP is generally prepared by the reduction of AgNO_3 (precursor) and stabilizing with capping agents to minimize the aggregation of nanoparticles. For this purpose, CNC has been used as an environmentally friendly method to immobilize and stabilize Ag NP in aqueous solutions as illustrated in Fig. 10 (Peng et al. 2011). Evans et al. (2003) first used bacterial cellulose as a template for the synthesis of Ag NP as well as palladium and gold nanoparticles. The preparation of multifunctional nanocellulose/Ag NP nanocomposites using external reducing agents such as sodium borohydride, triethanolamine, hydroxylamine, and ascorbic acid is the most commonly used method (Kaushik and Moores 2016). The Ag NP was also prepared using other external reducing agents such as triethanolamine, NH_2NH_2 , NH_4OH , and ascorbic acid (Barud et al. 2011). In the case of the preparation of nanocellulose/Ag NP nanocomposites, the nanocellulose acts as a template for reducing silver nitrate (AgNO_3) to Ag NP and as an external reducing agent (Dong et al. 2013; Lokanathan et al. 2014; Wang et al. 2014).

The second method of synthesizing nanocellulose/Ag NP is by surface modification of nanocellulose itself. The surface of the nanocellulose is modified by TEMPO or periodate-oxidation to form a negative charge on the surface of the CNC to improve the surface reactivity for binding with Ag^+ and increase the amount of Ag NP (Drogat et al. 2011). The size, morphology, concentration, stability, dispersibility, and antimicrobial activity of Ag NP were significantly influenced by the surface charge of CNC (Hoeng et al. 2015), CNC concentration (Lokanathan et al. 2014), carboxyl surface

density (Uddin et al. 2014), CNC size (Yan et al. 2016), reaction time (Cao et al. 2013), reaction pH (Khandanlou et al. 2016), AgNO₃ concentration and type of reducing agents (Li, Mascheroni, and Piergiovanni 2015).

Hoeng et al. (2015) studied the effect of charge density of TEMPO-oxidized CNC on the size and suspension stability of Ag NP and found that small Ag NPs well dispersed on the surface of CNC can be obtained using CNC with high carboxylate group and surface charge contents. This was probably due to the introduction of a new active site after the oxidation process, which acts as a nucleation promoter by the strong electrostatic interaction between the anion carboxyl group and the cation. As a result, silver ions would prefer to react with this active site and increase the size of Ag NP instead of the growth phase (Hoeng et al. 2015). Uddin et al. (2014) also investigated the role of carboxyl surface density and concentration of TEMPO-oxidized CNC on the size distribution and agglomeration of AgNPs. They showed that the stability and percentage of small Ag NP increase with increasing both carboxyl content and CNC concentration. They assumed a steric hindrance that could limit the growth phase of Ag NP and limit better nucleation control.

On the contrary, as the carboxyl content and concentration of CNC increased, the rate of Ag NP nucleation decreased, and the hydroxyl-based interaction was believed to have a greater effect on the nucleation stage than the electrostatic effect during Ag NP synthesis.

On the other hand, the effect of sulfate ester content and CNC concentration on the nucleation of Ag NP was also studied (Lokanathan et al. 2014). They found that as the concentration of CNC increased, the ratio of small Ag NP (1–5 nm) and the formation rate of Ag NP increased so that CNC could act as a nucleation regulator. Also, partially desulfated CNC (treated with 0.1 M NaOH) showed the highest percentage of small Ag NP in the range of 1–5 nm compared to unmodified and CNC.

The shape of silver was also affected by the concentration and surface charge of nanocellulose. Jiang and Hsieh (2014) synthesized Ag NP with nanospheres and nanoprisms form using TEMPO-oxidized cellulose nanofibers as capping and shape regulators. Ag NP with flower-like structure was obtained by the synergistic action of TEMPO-oxidized nanocellulose and trisodium citrate (Nabeela et al. 2016). Shi et al. (2015) reported that the antimicrobial activity of Ag NP was increased four-fold using CNC coated with polydopamine compared to Ag NP alone. Yan et al. (2016) studied the effect of size of cellulose on the morphology and antimicrobial activity of Ag NP and found that Ag NP loaded on the surface of TEMPO-oxidized nanofibrillar, microfibrillar celluloses showed stronger antimicrobial activity against *E. coli* than filter paper, however, nano-fibrillar cellulose showed higher concentration of Ag NP with smaller size than microfibrillar and filter paper.

Recently, cellulose nanocrystals (CNC) have been used as a facile and environmentally friendly method for synthesis of well-dispersed and stable Ag NP without additional reducing, capping or dispersing agents (Ifuku et al. 2009;

Xiong et al. 2013). Ag NP has been synthesized without external reducing or capping agents using TEMPO-oxidized jute fibers (Cao et al. 2013), TEMPO-oxidized bacterial cellulose (Elayaraja et al. 2017), regenerated cellulose fibers (Li, Mascheroni, and Piergiovanni 2015), and CNC isolated from microcrystalline cellulose (Xiong et al. 2013).

Multifunctional CNC/Ag NP nanocomposites were used to improve the mechanical properties, thermal stability, and antimicrobial activity of biopolymer films such as poly(lactic acid) and poly(3-hydroxybutyrate-co-3-hydroxy valerate) (Fortunati et al. 2013; Yu et al. 2014; Yu et al. 2014) and polyurethane (Liu et al. 2012). The CNC/Ag NP nanocomposites have been shown to be effective against shrimp pathogens (Elayaraja et al. 2017), antibacterial activity and fluorescence properties (Khandanlou et al. 2016; An, Long, and Ni 2017), and catalyst properties (Kaushik and Moores, 2016; Khandanlou et al. 2016). In addition, CNC/Ag NP nanocomposites have been used in the production of functionalized hydrogels, aerogels and films (Cai et al. 2009; Dong et al. 2013), flexible films with electrical conductivity properties (Khalil, Hassan, and Ward 2017), detection of pesticides in apples (Liou et al. 2017), antimicrobial absorbent pads to extend the shelf life of fresh-cut melon pieces (Fernández, Picouet, and Lloret 2010), antimicrobial wound healing (Kim, Cha, and Gong 2017), functional wound dressings for skin repair (Singla et al. 2017), and DNA biosensor (Liu et al. 2011).

Nanocellulose/ZnO NP

Since ZnO NP is aggregated due to its high surface energy and large surface area, the capping agent should be used to improve its dispersion. Recently, nanocellulosic materials have been used as templates during the manufacture of ZnO NP using their abundant hydroxyl groups. Nanocellulose-hosted ZnO nanostructures have become a prominent area of material science, engineering, biomedical, catalysis, packaging and electronics (Ul-Islam et al. 2014; Fu et al. 2016). Hybrid CNC/ZnO NP showed better antibacterial and photocatalytic activity than pure ZnO NP (Azizi et al. 2014; Yu et al. 2015). Using CNC in the synthesis of ZnO NP led to improving the antibacterial activity and photocatalytic efficiency of ZnO NP by the role of CNC in reducing the size of ZnO NP (Lefatshe, Muiva, and Kebaabetswe 2017). Hybrid nanocellulose/ZnO NP has been used in the manufacture of multifunctional films with excellent mechanical properties, UV-blocking, photocatalytic properties, thermal stability, hydrophobicity, and antimicrobial activity (Hassan and Hassan 2016; Varaprasad et al. 2016), and in the production of antibacterial paper (Martins et al. 2013).

Different cellulose and cellulose derivatives such as regenerated cellulose (Fu et al. 2014), cellulose nanocrystals (Lefatshe, Muiva, and Kebaabetswe 2017), spherical cellulose nanocrystals (Yang et al. 2016), cellulose fibers (Khatri et al. 2014; Varaprasad et al. 2016), and cellulose acetate (Anitha et al. 2013) have been used for the preparation of multifunctional cellulose/ZnO NP. During the synthesis of ZnO NP and nanocellulose, NaOH concentration and reaction

temperature played a crucial role in the morphology and properties of ZnO NP (Conde et al. 2011; Azizi et al. 2013b; Fu et al. 2016; Shankar, Wang, and Rhim 2017). Recently, there have been studies on the effect of CNC concentration and manufacturing conditions on the morphology, morphology, dispersibility and antibacterial activity of ZnO NP by preparing CNC/ZnO nanocomposites (Azizi et al. 2014a; Yu et al. 2015; Fu et al. 2016). Azizi et al. (2013b) studied the effect of cellulose nanocrystal (CNC) ratio on ZnO NP size and demonstrated the ability of CNC as a new stabilizer. They showed that the average size of ZnO NP increased with increasing molar ratio of zinc precursor (zinc acetate) to CNC. Moreover, CNC/ZnO NP showed stronger antimicrobial activity against Gram-positive and Gram-negative bacteria than ZnO NP alone. Azizi and coworkers synthesized ZnO-Ag heterostructure NP using cellulose nanocrystals (CNC) as a stabilizer to improve its bactericidal activity (Azizi et al. 2013a). They used both CNC/ZnO NP and CNC/ZnO-Ag heterostructure NP as multifunctional nanofillers to improve the mechanical properties, crystallinity, UV-barrier, and antibacterial activity of in poly(vinyl alcohol)/chitosan film (Azizi et al. 2014a,b).

Nanocellulose/CuO NP

Since self-aggregation of CuO NP has limited its application and efficiency, cellulose as a green, safe and sustainable material has been used as novel support and stabilizer during the synthesis of CuO NP. The incorporation of cellulose prevented the agglomeration of CuO NP through electrostatic interaction between OH groups of CNC and copper ions, thereby improving dispersibility and catalytic activity (Zhou et al. 2013).

Compared to CNC/ZnO NP and CNC/Ag NP nanocomposites, there are few reports on cellulose/CuO NP nanocomposites. A simple blending method was used to adsorb CuO NP on the surface of the cotton fiber by immersing the cellulose fibers in a CuO NP suspension and stirring (Shankar and Rhim 2017). Zhou et al. (2013) used external reducing agents and cellulose as a template for the fabrication of CuO NP. The shape and size of the CuO NP were controlled by the synthesis conditions and the type of external reductant (Vainio et al. 2007). Cotton fabrics were oxidized by the TEMPO-oxidation method (Hassan and Hassan 2016) or periodate-oxidation method to increase the binding of copper ions on the cellulose surface (Mary, Bajpai, and Chand 2009). Surface modified cellulose produced hybrid cellulose/copper NP with strong antimicrobial properties and increased ionic bonding on the cellulose surface through electrostatic interactions. The ionic liquid as an environmentally friendly method was used for CuO NP synthesis by dissolving cellulose into the ionic liquid, then added with a copper salt, heated using a microwave for thermal reduction at 800 °C (Ma et al. 2013). Here, the morphology of CuO NP was affected by the reaction conditions such as heating time and cellulose/ionic liquid ratio. As the microwave heating time increased, the shape of the CuO turned from nanosheets into bundles and particles.

Hybrid cellulose/CuO NP has been used for the production of multi-functional films and coated paper with excellent antibacterial, mechanical, water vapor permeability and absorbency properties (Hassan and Hassan 2016). The excellent antimicrobial activity of cellulose/CuO NP hybrid nanocomposites for a wide range of microorganisms encouraged application in the textile and medical fields (Shao et al. 2016).

The characteristics of Ag, ZnO and CuO NP synthesized in the presence of cellulose were affected by various factors. Shankar, Wang, and Rhim (2017) compared the characteristics of hybrid ZnO, CuO, and Ag NP using two types of regenerated cellulose and found that the source of cellulose influenced the shape and size of NP. Shankar and Rhim (2017) prepared hybrid cotton pads with Ag NP, ZnO NPs, and CuO NP using simple blending method, and found that the amount of NP attached to the surface of cotton fiber varied with the type of NP. AgNP showed the highest amount attached to the fiber surface, followed by CuO NP and ZnO NP, which was probably due to the initial size difference. Among them, the fiber-Ag nanocomposite showed the highest antimicrobial activity and the lowest release amount followed by CuO NP and ZnO NP.

Applications of nanocellulose/metal or metal oxide hybrid NP

Nanocellulose/metal or metal oxide hybrid NP has been applied in various fields such as catalytic applications, electronics, wastewater treatment, biomedical, antibacterial and biosensors (An, Long, and Ni 2017; Elayaraja et al. 2017). Recently, more attention has been paid to nanocellulose/metal nanohybrid for use as a multifunctional nanofiller in food packaging materials. Packaging materials are used to protect food from chemical, physical, and microbiological hazards, extending the shelf life of packaged foods during storage and distribution. In recent years, there has been a growing interest in replacing conventional plastics with biodegradable materials to reduce environmental problems (Khalil et al. 2018). Due to the inherent properties of cellulose, such as biodegradability, low cost, barrier properties, and nontoxicity, interest in the use of cellulose as an eco-friendly packaging material is increasing (Abdul Khalil et al. 2012). Cellulose fibers are already used in commercial packaging products in the form of paper, paperboard, corrugated fiberboard and pulp containers (Imam, Glenn, and Chiellini 2012). Cellophane (regenerated cellulose) and cellulose acetate (acetylated cellulose) are examples of commonly used cellulose-based food packaging materials (Abdul Khalil et al. 2016). Paperboard coated with polyethylene (PE) is used commercially for the packaging of liquid foods such as milk and fruit juice (Abdul Khalil et al. 2016).

Sometimes, hydrophilicity, weak mechanical properties, low gas barrier, and thermal stability properties of biopolymers are limited to food packaging application. Nanocellulose materials have been used as reinforcing agents to improve the mechanical and barrier properties of in biopolymers and papermaking materials (Jawaid, Boufi, and

Table 3. Application of biodegradable packaging films reinforced with nanocellulose/metal or metal oxide nanoparticles.

Matrix	Reinforcement	Application	Ref.
PHBV	CNC/Ag NP	Food packaging	Zhang et al. 2017
PHBV	CNC/Ag NP	Food packaging, beverage packaging and disposable overwrap film	Yu et al. 2014
PLA	CNC/Ag NP	Food packaging	Yu et al. 2016
PLA	CNC/Ag NP	Fresh food packaging	Fortunati et al. 2014
PLA	CNC/Ag NP	Active food packaging	Fortunati et al. 2013
PLA	CNC/Ag NP	Food packaging	Fortunati et al. 2012a,b
PLA	CNC/Ag NP	Food packaging	Cacciotti et al. 2014
PLA/PBAT	CNC/Ag NP	Packaging and textile	Ma et al. 2016
PVOH	CNC/Ag NP	Antibacterial and carbon dioxide balancing material for vegetable packaging	Fortunati et al. 2013
PU	CNC/Ag NP	Coating, binding, adhesive, sealants, and foam	Liu et al. 2012
PVOH	CNC/Ag NP	Improved mechanical and antibacterial properties	Xu et al. 2013
PVOH/Chitosan	CNC/ZnO/Ag NP	Medical, textile, and packaging	Azizi, Ahmad, Hussein, et al. 2014
PVOH/Chitosan	CNC/ZnO NP	High mechanical, UV-light barrier and antibacterial for packaging and medical	Azizi, Ahmad, Hussein, et al. 2014
PLA	CNC/ZnO NP	High strength and antibacterial packaging	Luzi et al. 2017
LDPE	CNC/CuO NP	Antimicrobial and cheese packaging	Beigmohammadi et al. 2016
Bacterial cellulose	CuO	Water purification and food packaging	Almasi, Jafarzadeh, and Mehryar 2018
PLA	CNF/Ag	Food packaging	Yu et al. 2016
Nanocellulose	ZnO	Photocatalyst and antibacterial	Lefatshe, Muiva, and Kebaabetswe 2017
Regenerated cellulose	Ag NP/CuO NP/ZnO NP	Antibacterial food packaging	Shankar, Oun, and Rhim 2018

Abdu 2017). For example, modified cellulosic nanocrystals have been used as nanofillers to improve the water vapor and oxygen gas barrier properties of PLA films (Fortunati et al. 2012). Addition of surface acetylated cellulose nanocrystals increased the mechanical and thermal properties of PLA films (Lin et al. 2011). The mechanical properties, dynamic viscosity, glass transition temperature and crystallization temperature of PBAT [poly (butylene adipate-co-terephthalate)] films were also improved by the mixing of nanofibrillated cellulose (Mukherjee et al. 2014), and the film was applied in the food packaging and agricultural mulching film (Dhar et al. 2016). Because cellulose is essentially hydrophilic, it cannot easily bind hydrophobic polymers, but there is no problem using nanocellulosic nanofillers in hydrophilic fillers. Surface modification of cellulosic materials is one of the ways to increase the interaction and dispersibility of cellulose in non-polar solvents and hydrophobic polymers (Peltzer et al. 2014). Surface modified nanoclusters have been incorporated into nanocomposite bioplastic films based on poly(lactic acid)/poly(-hydroxybutyrate) (PLA/PHB) blends to improve mechanical performance, water vapor and oxygen gas barrier properties of the film (Arrieta et al. 2015).

Antimicrobial packaging materials are usually prepared by adding antimicrobial agents to the packaging material (Díez-Pascual and Díez-Vicente 2014). For example, Ag, ZnO, and CuO NP were added to PLA (Ahmed et al. 2016), PBAT (Shankar and Rhim 2016b), LDPE (Tankhiwale and Bajpai 2012), PHBV (Díez-Pascual and Díez-Vicente 2014), PVC (Li et al. 2009), alginate (Trandafilovic et al. 2014), gelatin (Arfat, Ahmed, et al. 2017), papers (Martins et al. 2013), and different carbohydrate-based biopolymers (Shankar, Wang, and Rhim 2017) to prepare antimicrobial packaging films. In most cases, however, the mechanical properties of the film were reduced by the addition of metal or metal oxide NP (Castro-Mayorga et al. 2017). For this reason, multifunctional nanofillers prepared by combining nanocellulose and inorganic NP have been used to improve

the mechanical and antibacterial properties of packaging films. Fu et al. (2017) used regenerated cellulose for the production of cellulose/ZnO-Ag hybrid NP film without any toxic chemicals. The regenerated cellulose/ZnO-Ag hybrid NP exhibited excellent antimicrobial activity and opened the door for mass production of antibacterial film for food packaging.

The effects of multifunctional nanocellulose/inorganic nanohybrid on the physical, chemical and antimicrobial properties of bioplastic films have been studied (Fortunati et al. 2013). The nanocellulose-inorganic/biopolymer composite films exhibited high mechanical properties, the barrier to water and gas, thermal stability, antimicrobial activity, and biodegradability (Fortunati et al. 2013; Zhang et al. 2017). Yu et al. (2014) successfully prepared an active packaging film using poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV)/CNC-Ag hybrid nanocomposite. The tensile strength and Young's modulus of PHBV films improved by 140% and 200%, respectively, when 10 wt% of CNC-Ag NP was incorporated. Moreover, the PHBV/CNC-Ag composite film showed high thermal stability, gas barrier property, and potent antibacterial activity. As the Ag NP content of CNC-Ag nanohybrid increased, antibacterial activity, mechanical and barrier properties were improved. Even at a high content of Ag NP, PHBV/CNC-Ag nanocomposite film showed negligible cytotoxicity to human cells, suggesting the possible use of the food packaging application (Zhang et al. 2017). The PLA-based films with CNC-Ag NP nanohybrid bonded showed good biodegradability and antibacterial activity as well as reduced oxygen and water vapor permeability. Moreover, the migration level of the nanoparticles was below the permitted limits, suggesting it suitable for the food packaging applications (Fortunati et al. 2013; Fortunati et al. 2014). The CNC-Ag nanohybrid was also used with biopolymers such as polyvinyl alcohol (PVOH) (Fortunati et al. 2013) and polyurethane (PU) (He et al. 2012).

Table 3 summarizes some examples of nanocellulose/metal or metal oxide nanomaterials as multifunctional

nanofillers for the production of active packaging materials. Most of the previous studies have used CNC-Ag hybrid NP as a multifunctional nanofiller, while only a few papers have reported CNC-ZnO or CNC-CuO hybrid NP. Azizi and her colleagues prepared CNC/ZnO NP and CNC/ZnO-Ag hybrid NP and showed the effect of nanocellulose as a stabilizer on the antimicrobial activity of ZnO-Ag NP (Azizi, Ahmad, Hussein, et al. 2013; Azizi, Ahmad, Mahdavi, et al. 2013). They also studied the influence of CNC/ZnO NP and CNC/ZnO-Ag NP as a bifunctional reinforcing material on the properties of polyvinyl alcohol (PVOH)/chitosan blend films. Their results showed that the incorporation of CNC/ZnO NP improved the tensile strength and modulus of the blend films from 55 to 153 MPa and 395 to 932 MP, respectively. Also, the thermal stability, UV-barrier property and antimicrobial activity were improved by a load of CNC/ZnO hybrid NP (Azizi, Ahmad, Hussein, et al. 2014). The addition of CNC/ZnO-Ag hybrid NP to PVOH/chitosan films increased the tensile strength from 55 to 205 MPa and modulus from 395 to 1200 MPa, respectively. Also, the nanocomposite films exhibited excellent antimicrobial activity and UV-barrier properties (Azizi, Ahmad, Ibrahim, et al. 2014). Poly(lactic acid) (PLA) as biodegradable polymers was supported by cellulose nanocrystals and ZnO NP to improve its water and gas barrier properties, as well as mechanical and thermal properties. In addition, a variety of studies, have been conducted to improve the mechanical and thermal properties as well as the water vapor and gas barrier properties by preparing a composite film with cellulose nanocrystals and ZnO NP using a biodegradable polymer, poly(lactic acid) (PLA) (Luzi et al. 2017).

Luo and Zhang (2009) prepared magnetic cellulose beads by blending cellulose/NaOH/urea solution and Fe_2O_3 NP in a submerged circulative impinging stream reactor. The Fe_2O_3 /cellulose magnetic beads exhibited a sensitive magnetic response and their recovery could be facilitated by applying a magnetic field. Moreover, the magnetic beads could efficiently adsorb organic dyes in the wastewater and the sorbents could be completely recovered and applied to remove hazardous materials. Liu et al. (2012) has developed magnetic hydrogel microspheres with chitosan and cellulose coating in which cellulose contributed to mechanical strength and chemical stability and chitosan stabilized Fe_3O_4 . The hybrid hydrogel microspheres had high adsorption capacity for various heavy metal ions (Cu^{2+} , Fe^{2+} , and Pb^{2+}) and could be efficiently recycled and reused, showing a promising applications in the areas of food packaging, biomedicine, healthcare, and catalysis.

In addition, a variety of polymer nanocomposites have been synthesized to study the corrosion resistance and abrasion resistance of various metal substrates. Such polymer nanocomposites have attracted interest in engineering plastics and coating materials applications due to their excellent properties such as high-dimensional stability, heat deflection temperature, reduced gas permeability, optical properties, flame retardancy, and enhanced mechanical properties. Various polymer nanocomposites have been evaluated for their various functional properties including corrosion

resistance and abrasion resistance. Barrier, adhesion, abrasion resistance and corrosion protection play an important role in extending the life of the protective coating. In recent years, much effort has been made to improve the abrasion resistance, adhesiveness and corrosion resistance of the organic coating by modifying it with hybrid binders (Madhup et al., 2015). Comparative study of epoxy-polyamide coating on hot-dip galvanized steel of micro ZnO versus nano ZnO nanoscale zinc oxide with excellent corrosion resistance and deterioration properties (Ramezanzadeh and Attar 2013). Improvement of barrier properties and corrosion prevention by incorporation of SiO_2 , ZnO, Fe_2O_3 , and halloysite clay nanomaterials was observed in the epoxy coating (Shi et al. 2009). In addition to the applications above, nanocellulose/metal or metal oxide hybrid nanomaterials can also be applied to other areas. For example, they can be used for cosmetic thickeners, food texturing agents, special fiber fillers, CO_2 adsorbents and oil recovery (Phanthong et al., 2018).

Nanocellulose-based hybrid materials have emerged as promising materials for food packaging, but there are still many challenges to be addressed for their application. In order to promote commercialization and marketability of hybrid nanocellulose/metal or metal oxide nanomaterials, they must be easily scalable, low cost, and produce valuable end products (Carpenter, de Lannoy, and Wiesner 2015). So far, most of the research on the production of hybrid nanomaterials is only laboratory scale. The challenge lies in the scalability, environmental impact and cost that comes with the choice of efficient processes to produce nanocellulose-based hybrid materials. In addition, economic and regulatory barriers to unclear toxicological problems of various modified nanocellulose and nano-cellulose hybrid materials can be the biggest obstacles in terms of application and marketability. Environmental toxicity studies on nanocellulose-based composites are still limited and in the early stages (Lin and Dufresne, 2014). Generally, inhaled nanoparticles of small size are absorbed by the cell, blood, and lymphatic circulation and reach a potentially sensitive target area, increasing the risk of nanoparticles as the particle size decreases (Shak, Pang, and Mah 2018). Most nanocellulose-based materials are not toxic, but when used at high concentrations, the toxicity of nanocellulose/metal or metal oxide-based hybrid nanomaterials must be thoroughly addressed.

8. Conclusions

Cellulose is the most abundant, renewable and environmentally friendly biopolymer on the planet and can be obtained in large quantities from plants, crops and forest waste. Recent advances in nanotechnology have enabled the successful extraction of high-performance nanocellulose materials from the lignocellulosic sources in the form of CNFs and CNCs, enabling potential applications at the industrial level. The nanocellulose has been used as a reinforcing filler of polymeric materials in a variety of fields such as food packaging, biomedical, and textile industries. Also, surface

properties of nanocellulose can be modified by oxidation of hydroxyl groups using the TEMPO-oxidation or APS method to form multifunctional hybrid nanomaterials coupled with metal or metal oxide nanoparticles such as Ag NP, ZnO NP, CuO NP, and Fe₂O₃ NP. Based on various characteristics of nanocellulose/metal or metal oxide hybrid nanomaterials, it can be concluded that they have a high potential to be used in various fields including food packaging and other biotechnological applications.

References

- Abdul Khalil, H. P. S., I. U. H. Bhat, M. Jawaid, A. Zaidon, D. Hermawan, and Y. S. Hadi. 2012. Bamboo fiber reinforced biocomposites: A review. *Materials & Design* 42:353–68.
- Abdul Khalil, H. P. S., Y. Davoudpour, M. N. Islam, A. Mustapha, K. Sudesh, R. Dungani, and M. Jawaid. 2014. Production and modification of nanofibrillated cellulose using various mechanical processes: A review. *Carbohydrate Polymers* 99:649–65.
- Abdul Khalil, H. P. S., Y. Davoudpour, C. K. Saurabh, M. S. Hossain, A. S. Adnan, R. Dungani, M. T. Paridah, M. D. Z. Islam Sarker, M. R. Nurul Fazita, M. I. Syakir, and M. K. M. Haafiz. 2016. A review on nanocellulosic fibers as new material for sustainable packaging: Process and applications. *Renewable & Sustainable Energy Reviews* 64:823–36.
- Adel, A. M., A. A. El-Gendy, M. A. Diab, R. E. Abou-Zeid, W. K. El-Zawawy, and A. Dufresne. 2016. Microfibrillated cellulose from agricultural residues. Part I: Papermaking application. *Industrial Crops and Products* 93:161–74.
- Ahmed, J., Y. A. Arfat, E. Castro-Aguirre, and R. Auras. 2016. Mechanical, structural and thermal properties of Ag-Cu and ZnO reinforced polylactide nanocomposite films. *International Journal of Biological Macromolecules* 86:885–92.
- Akil, H. M., M. F. Omar, A. A. M. Mazuki, S. Safiee, Z. A. M. Ishak, and A. Abu Bakar. 2011. Kenaf fiber reinforced composites: A review. *Materials and Design* 32(8–9):4107–21.
- Almasi, H., P. Jafarzadeh, and L. Mehryar. 2018. Fabrication of novel nanohybrids by impregnation of CuO nanoparticles into bacterial cellulose and chitosan nanofibers: Characterization, antimicrobial and release properties. *Carbohydrate Polymers* 186(15):273–81.
- Alswat, A. A., B. Ahmad, and T. A. Saleh. 2017. Preparation and characterization of zeolite/zinc oxide-copper oxide nanocomposite: Antibacterial activities. *Colloid and Interface Science Communications* 16:19–24.
- An, X., Y. Long, and Y. Ni. 2017. Cellulose nanocrystal/hexadecyltrimethylammonium bromide/silver nanoparticle composite as a catalyst for reduction of 4-nitrophenol. *Carbohydrate Polymers* 156:253–8.
- Angles, M. N., and A. Dufresne. 2000. Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules* 33(22):8344–53.
- Anitha, S., B. Brabu, D. John Thiruvadigal, C. Gopalakrishnan, and T. S. Natarajan. 2013. Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO. *Carbohydrate Polymers* 97(2):856–63.
- Arfat, Y. A., J. Ahmed, N. Hiremath, R. Auras, and A. Joseph. 2017. Thermo-mechanical, rheological, structural and antimicrobial properties of bionanocomposite films based on fish skin gelatin and silver-copper nanoparticles. *Food Hydrocolloids* 62:191–202.
- Arfat, Y. A., M. Ejaz, H. Jacob, and J. Ahmed. 2017. Deciphering the potential of guar gum/Ag-Cu nanocomposite films as an active food packaging material. *Carbohydrate Polymers* 157:65–71.
- Ariffin, H., F. Norrahim Mohd Nor, Taty-A, H. Nishida, M. A. Hassan, N. A. Ibrahim, and W. M. Z. W. Yunus. 2018. Oil palm biomass cellulose-fabricated polylactic acid composites for packaging applications. In: *Bionanocomposites for packaging applications*. Cham: Springer; p. 95–105.
- Arrieta, M. P., E. Fortunati, F. Dominici, J. López, and J. M. Kenny. 2015. Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends. *Carbohydrate Polymers* 121:265–75.
- Ashok, C., K. V. Rao, and C. S. Chakra. 2016. Facile synthesis and characterization of ZnO/CuO nanocomposite for humidity sensor application. *Journal of Advanced Chemical Sciences* 2:223–6.
- Ashori, A. 2008. Wood-plastic composites as promising green-composites for automotive industries. *Bioresource Technology* 99:4661–7.
- Awwad, A. M., N. M. Salem, and A. O. Abdeen. 2013. Green synthesis of silver nanoparticles using carob leaf extract and its antibacterial activity. *International Journal of Industrial Chemistry* 4(1):29–35.
- Azam, A., A. S. Ahmed, M. Oves, M. Khan, and A. Memic. 2012. Size-dependent antimicrobial properties of CuO nanoparticles against gram-positive and -negative bacterial strains. *International Journal of Nanomedicine* 7:3527–35.
- Azeredo, H. M. C., L. H. C. Mattoso, R. J. Avena-Bustillos, G. C. Filho, M. L. Munford, D. Wood, and T. H. McHugh. 2010. Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content. *Journal of Food Science* 75:1–7.
- Azeredo, H. M. C., M. F. Rosa, and L. H. C. Mattoso. 2017. Nanocellulose in bio-based food packaging applications. *Industrial Crops and Products* 97:664–71.
- Azizi, S., M. B. Ahmad, M. Z. Hussein, and N. A. Ibrahim. 2013a. Synthesis, antibacterial and thermal studies of cellulose nanocrystal stabilized ZnO-Ag heterostructure nanoparticles. *Molecules* 18(6):6269–80.
- Azizi, S., M. Ahmad, M. Mahdavi, and S. Abdolmohammadi. 2013b. Preparation, characterization, and antimicrobial activities of ZnO nanoparticles/cellulose nanocrystal nanocomposites. *BioResources* 8:1841–51.
- Azizi, S., M. B. Ahmad, N. A. Ibrahim, M. Z. Hussein, and F. Namvar. 2014a. Cellulose nanocrystals/ZnO as a bifunctional reinforcing nanocomposite for poly(vinyl alcohol)/chitosan blend films: Fabrication, characterization and properties. *International Journal of Molecular Sciences* 15(6):11040–53.
- Azizi, S., M. Ahmad, M. Z. Hussein, and N. A. Ibrahim. 2014b. Preparation and properties of poly(vinyl alcohol)/chitosan blend bionanocomposites reinforced with cellulose nanocrystals/ZnO-Ag multifunctional nanosized filler. *International Journal of Nanomedicine* 9:1909–17.
- Azizi, S., R. Mohamad, R. A. Rahim, A. B. Moghaddam, M. Moniri, A. Ariff, W. Z. Saad, and F. Namvab. 2016. ZnO-Ag core-shell nanocomposite formed by green method using essential oil of wild ginger and their bactericidal and cytotoxic effects. *Applied Surface Science* 384:517–24.
- Azizi, S., F. Alloin, and A. Dufresne. 2005. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* 6(2):612–26.
- Baruah, S., M. A. Mahmood, M. T. Z. Myint, T. Bora, and J. Dutta. 2010. Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods. *Beilstein Journal of Nanotechnology* 1:14–20.
- Barud, H. S., T. Regiani, R. F. C. Marques, W. R. Lustri, Y. Messaddeq, and S. J. L. Ribeiro. 2011. Antimicrobial bacterial cellulose-silver nanoparticles composite membranes. *Journal of Nanomaterials* 2011:1–10.
- Beigmohammadi, F., S. H. Peighambari, J. Hesari, S. Azadmard-Damirchi, S. J. Peighambari, and N. K. Khosrowshahi. 2016. Antibacterial properties of LDPE nanocomposite films in packaging of UF cheese. *Lebensmittel-Wissenschaft & Technologie* 65:106–11.
- Bettaieb, F., R. Khiari, M. L. Hassan, M. N. Belgacem, J. Bras, A. Dufresne, and M. F. Mhenni. 2015. Preparation and characterization of new cellulose nanocrystals from marine biomass posidonia oceanica. *Industrial Crops and Products* 72:175–82.
- Bledzki, A. K., and J. Gassan. 1999. Composites reinforced with cellulose-based fibers. *Progress in Polymer Science* 24(2):221–74.
- Blosi, M., S. Albonetti, M. Dondi, C. Martelli, and G. Baldi. 2011. Microwave-assisted polyol synthesis of Cu nanoparticles. *Journal of Nanoparticle Research* 13 (1):127–38.

- Borase, H. P., B. K. Salunke, R. B. Salunkhe, C. D. Patil, J. E. Hallsworth, B. S. Kim, and S. V. Patil. 2014. Plant extract: a promising biomatrix for ecofriendly, controlled synthesis of silver nanoparticles. *Applied Biochemistry and Biotechnology* 173 (1):1–29.
- Boufi, S., I. González, M. Delgado-Aguilar, Q. Tarrès, M. À. Pèlach, and P. Mutjé. 2016. Nanofibrillated cellulose as an additive in paper-making process: A review. *Carbohydrate Polymers* 154:151–66.
- Bulota, M., S. Tanpichai, M. Hughes, and S. J. Eichhorn. 2012. Micromechanics of TEMPO-oxidized fibrillated cellulose composites. *ACS Applied Materials & Interfaces* 4 (1):331–7.
- Buşilă, M., V. Muşat, T. Textor, and B. Mahltig. 2015. Synthesis and characterization of antimicrobial textile finishing based on Ag:ZnO nanoparticles/chitosan biocomposites. *RSC Advances* 5 (28): 21562–71.
- Cacciotti, I., E. Fortunati, D. Puglia, J. M. Kenny, and F. Nanni. 2014. Effect of silver nanoparticles and cellulose nanocrystals on electrospun poly(lactic) acid mats: Morphology, thermal properties and mechanical behavior. *Carbohydrate Polymers* 103:22–31.
- Cai, J., S. Kimura, M. Wada, and S. Kuga. 2009. Nanoporous cellulose as metal nanoparticles support. *Biomacromolecules* 10 (1):87–94.
- Cai, J., and L. Zhang. 2005. Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. *Macromolecular Bioscience* 5 (6): 539–48.
- Cai, J., L. Zhang, S. Liu, Y. Liu, X. Xu, X. Chen, X. Chu, X. Guo, J. Xu, H. Cheng, et al. 2008. Dynamic self-assembly induced rapid dissolution of cellulose at low temperatures. *Macromolecules* 41(23): 9345–51.
- Cao, X., B. Ding, J. Yu, and S. S. Al-Deyab. 2012. Cellulose nanowhiskers extracted from TEMPO-oxidized jute fibers. *Carbohydrate Polymers* 90 (2):1075–80.
- Cao, X., B. Ding, J. Yu, and S. S. Al-Deyab. 2013. In situ growth of silver nanoparticles on TEMPO-oxidized jute fibers by microwave heating. *Carbohydrate Polymers* 92 (1):571–6.
- Carpenter, A. W., C. F. de Lannoy, and M. R. Wiesner. 2015. Cellulose nanomaterials in water treatment technologies. *Environmental Science & Technology* 49 (9):5277–87.
- Castro-Mayorga, J. L., M. J. Fabra, A. M. Pourrahimi, R. T. Olsson, and J. M. Lagaron. 2017. The impact of zinc oxide particle morphology as an antimicrobial and when incorporated in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) films for food packaging and food contact surfaces applications. *Food and Bioprocess Technology* 101: 32–44.
- Chakraborty, A., M. Sain, and M. Kortschot. 2005. Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing. *Holzforschung* 59 (1):102–7.
- Chang, C., and L. Zhang. 2011. Cellulose-based hydrogels: Present status and application prospects. *Carbohydrate Polymers* 84 (1):40–53.
- Chen, W., H. Yu, and Y. Liu. 2011. Preparation of millimeter-long cellulose I nanofibers with diameters of 30–80nm from bamboo fibers. *Carbohydrate Polymers* 86 (2):453–61.
- Chen, W., H. Yu, Y. Liu, P. Chen, M. Zhang, and Y. Hai. 2011. Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. *Carbohydrate Polymers* 83 (4):1804–11.
- Cheng, D., Y. Wen, X. An, X. Zhu, and Y. Ni. 2016. TEMPO-oxidized cellulose nanofibers (TOCNs) as a green reinforcement for waterborne polyurethane coating (WPU) on wood. *Carbohydrate Polymers* 151:326–34.
- Cheng, M., Z. Qin, Y. Liu, Y. Qin, T. Li, L. Chen, and M. Zhu. 2014. Efficient extraction of carboxylated spherical cellulose nanocrystals with narrow distribution through hydrolysis of lyocell fibers by using ammonium persulfate as an oxidant. *Journal of Materials Chemistry A* 2 (1):251–8.
- Conde, M. N., K. Dakhsi, H. Zouhri, K. Abdelouahdi, L. Laanab, M. Benaissa, and B. Jaber. 2011. Preparation of ZnO nanoparticles without any annealing and ripening treatment. *Journal of Material Sciences and Engineering* 1:985–90.
- Cushen, M., J. Kerry, M. Morris, M. Cruz-Romero, and E. Cummins. 2014. Evaluation and simulation of silver and copper nanoparticle migration from polyethylene nanocomposites to food and an associated exposure assessment. *Journal of Agricultural and Food Chemistry* 62 (6):1403–11.
- Das, S., and V. C. Srivastava. 2017. Synthesis and characterization of ZnO/CuO nanocomposite by electrochemical method. *Materials Science in Semiconductor Processing* 57:173–7.
- Delgado, K., R. Quijada, R. Palma, and H. Palza. 2011. Polypropylene with embedded copper metal or copper oxide nanoparticles as a novel plastic antimicrobial agent. *Letters in Applied Microbiology* 53 (1):50–4.
- Dhar, P., S. M. Bhasney, A. Kumar, and V. Katiyar. 2016. Acid functionalized cellulose nanocrystals and its effect on mechanical, thermal, crystallization and surfaces properties of poly (lactic acid) bionanocomposites films: A comprehensive study. *Polymer* 101: 75–92.
- Dhar, P., S. S. Gaur, N. Soundararajan, A. Gupta, S. M. Bhasney, M. Milli, A. Kumar, and V. Katiyar. 2017. Reactive extrusion of polylactic acid/cellulose nanocrystal films for food packaging applications: Influence of filler type on thermomechanical, rheological, and barrier properties. *Industrial & Engineering Chemistry Research* 56 (16): 4718–35.
- Díez-Pascual, A. M., and A. L. Díez-Vicente. 2014. ZnO-reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate) bionanocomposites with antimicrobial function for food packaging. *ACS Applied Materials & Interfaces* 6(12):9822–34.
- Dogan, H., and N. D. Hilmioglu. 2009. Dissolution of cellulose with NMMO by microwave heating. *Carbohydrate Polymers* 75 (1):90–4.
- Dong, H., J. F. Snyder, D. T. Tran, and J. L. Leadore. 2013. Hydrogel, aerogel and film of cellulose nanofibrils functionalized with silver nanoparticles. *Carbohydrate Polymers* 95 (2):760–7.
- Drogat, N., R. Granet, V. Sol, A. Memmi, N. Saad, C. Klein Koerkamp, P. Bressollier, and P. Krausz. 2011. Antimicrobial silver nanoparticles generated on cellulose nanocrystals. *Journal of Nanoparticle Research* 13 (4):1557–62.
- Dufresne, A. 2008. Cellulose-based composites and nanocomposites. In: *Monomers, polymers and composites from renewable resources*. Oxford: Elsevier, UK; p. 401–418.
- Dufresne, A., J.-Y. Cavaillé, and M. R. Vignon. 1997. Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *Journal of Applied Polymer Science* 64 (6):1185–94.
- Eichhorn, S. J., A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, et al. 2010. Review: Current international research into cellulose nanofibres and nanocomposites. *Journal of Materials Science* 45 (1):1–33.
- El-Trass, A., H. Elshamy, I. El-Mehasseb, and M. El-Kemary. 2012. CuO nanoparticles: Synthesis, characterization, optical properties and interaction with amino acids. *Applied Surface Science* 258 (7): 2997–3001.
- Elayaraja, S., K. Zagorsek, F. Li, and J. Xiang. 2017. In situ synthesis of silver nanoparticles into TEMPO-mediated oxidized bacterial cellulose and their antivibriocidal activity against shrimp pathogens. *Carbohydrate Polymers* 166:329–37.
- Elazzouzi-Hafraoui, S., Y. Nishiyama, L. Heux, F. Dubreuil, C. Rochas, and J. Putaux. 2008. The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose the shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacromolecules* 9 (1):57–65.
- Etefagh, R., E. Azhir, and N. Shahtahmasebi. 2013. Synthesis of CuO nanoparticles and fabrication of nanostructural layer biosensors for detecting *Aspergillus niger* fungi. *Scientia Iranica* 20:1055–8.
- Evans, B. R., H. M. O'Neill, V. P. Malyvanh, I. Lee, and J. Woodward. 2003. Palladium-bacterial cellulose membranes for fuel cells. *Biosensors and Bioelectronics* 18 (7):917–23.
- Farhoudian, S., M. Yadollahi, and H. Namazi. 2016. Facile synthesis of antibacterial chitosan/CuO bio-nanocomposite hydrogel beads. *International Journal of Biological Macromolecules* 82:837–43.
- Fernández-Bolaños, J., B. Felizón, A. Heredia, R. Rodríguez, R. Guillén, and A. Jiménez. 2001. Steam-explosion of olive stones: Hemicellulose solubilization and enhancement of enzymatic hydrolysis of cellulose. *Bioresource Technology* 79 (1):53–61.

- Fernández, A., P. Picouet, and E. Lloret. 2010. Cellulose-silver nanoparticle hybrid materials to control spoilage-related microflora in absorbent pads located in trays of fresh-cut melon. *International Journal of Food Microbiology* 142 (1–2):222–8.
- Ferrer, A., L. Pal, and M. Hubbe. 2017. Nanocellulose in packaging: Advances in barrier layer technologies. *Industrial Crops and Products* 95:574–82.
- Festucci-Buselli, R. A., W. C. Otoni, and C. P. Joshi. 2007. Structure, organization, and functions of cellulose synthase complexes in higher plants. *Brazilian Journal of Plant Physiology* 19 (1):1–13.
- Fink, H. P., P. Weigel, H. J. Purz, and J. Ganster. 2001. Structure formation of regenerated cellulose materials from NMMO-solutions. *Progress in Polymer Science* 26 (9):1473–524.
- Fortunati, E., I. Armentano, Q. Zhou, A. Iannoni, E. Saino, L. Visai, L. A. Berglund, and J. M. Kenny. 2012. Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohydrate Polymers* 87 (2):1596–605.
- Fortunati, E., I. Armentano, Q. Zhou, D. Puglia, A. Terenzi, L. A. Berglund, and J. M. Kenny. 2012. Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose. *Polymer Degradation and Stability* 97 (10):2027–36.
- Fortunati, E., F. Luzi, D. Puglia, A. Terenzi, M. Vercellino, L. Visai, C. Santulli, L. Torre, and J. M. Kenny. 2013. Ternary PVA nanocomposites containing cellulose nanocrystals from different sources and silver particles: Part II. *Carbohydrate Polymers* 97 (2):837–48.
- Fortunati, E., M. Peltzer, I. Armentano, A. Jiménez, and J. M. Kenny. 2013. Combined effects of cellulose nanocrystals and silver nanoparticles on the barrier and migration properties of PLA nano-biocomposites. *Journal of Food Engineering* 118 (1):117–24.
- Fortunati, E., M. Peltzer, I. Armentano, L. Torre, A. Jiménez, and J. M. Kenny. 2012. Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydrate Polymers* 90 (2):948–56.
- Fortunati, E., S. Rinaldi, M. Peltzer, N. Bloise, L. Visai, I. Armentano, A. Jiménez, L. Latterini, and J. M. Kenny. 2014. Nano-biocomposite films with modified cellulose nanocrystals and synthesized silver nanoparticles. *Carbohydrate Polymers* 101:1122–33.
- Fras, L., L. S. Johansson, P. Stenius, J. Laine, K. Stana-Kleinschek, and V. Ribitsch. 2005. Analysis of the oxidation of cellulose fibers by titration and XPS. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 260 (1–3):101–8.
- Fu, F., J. Gu, X. Xu, Q. Xiong, Y. Zhang, X. Liu, and J. Zhou. 2017. Interfacial assembly of ZnO-cellulose nanocomposite films via a solution process: A one-step biomimetic approach and excellent photocatalytic properties. *Cellulose* 24 (1):147–62.
- Fu, F., Y. Guo, Y. Wang, Q. Tan, J. Zhou, and L. Zhang. 2014. Structure and properties of the regenerated cellulose membranes prepared from cellulose carbamate in NaOH/ZnO aqueous solution. *Cellulose* 21 (4):2819–30.
- Fukuzumi, H., T. Saito, and A. Isogai. 2013. Influence of TEMPO-oxidized cellulose nanofibril length on film properties. *Carbohydrate Polymers* 93 (1):172–7.
- Fukuzumi, H., T. Saito, T. Iwata, Y. Kumamoto, and A. Isogai. 2009. Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules* 10 (1):162–5.
- Fukuzumi, H., T. Saito, Y. Okita, and A. Isogai. 2010. Thermal stabilization of TEMPO-oxidized cellulose. *Polymer Degradation and Stability* 95 (9):1502–8.
- García-Barrasa, J., J. López-de-Luzuriaga, and M. Monge. 2011. Silver nanoparticles: synthesis through chemical methods in solution and biomedical applications. *Central European Journal of Chemistry* 9:7–19.
- García, A., A. Gandini, J. Labidi, N. Belgacem, and J. Bras. 2016. Industrial and crop wastes: a new source for nanocellulose biorefinery. *Ind Crops Prod* 93:26–38.
- Gebald, C., J. A. Wurzbacher, P. Tingaut, T. Zimmermann, and A. Steinfeld. 2011. Amine-based nanofibrillated cellulose as adsorbent for CO₂ capture from air. *Environmental Science & Technology* 45 (20):9101–8.
- Goh, K. Y., Y. C. Ching, C. H. Chuah, L. C. Abdullah, and N. S. Liou. 2016. Individualization of microfibrillated celluloses from oil palm empty fruit bunch: Comparative studies between acid hydrolysis and ammonium persulfate oxidation. *Cellulose* 23 (1):379–90.
- Habibi, Y. 2014. Key advances in the chemical modification of nanocelluloses. *Macromolecules* 45 (20):9220.
- Habibi, Y., H. Chanzy, and M. R. Vignon. 2006. TEMPO-mediated surface oxidation of cellulose whiskers. *Cellulose* 13 (6):679–87.
- Habibi, Y., L. A. Lucia, and O. J. Rojas. 2010. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews* 110(6):3479–500.
- Hamou, K. Ben, H. Kaddami, A. Dufresne, S. Boufi, A. Magnin, and F. Erchiqui. 2018. Impact of TEMPO-oxidation strength on the properties of cellulose nanofibril reinforced polyvinyl acetate nanocomposites. *Carbohydrate Polymers* 181:1061–70.
- Hannon, J. C., J. Kerry, M. Cruz-Romero, M. Morris, and E. Cummins. 2015. Advances and challenges for the use of engineered nanoparticles in food contact materials. *Trends in Food Science and Technology* 43 (1):43–62.
- Hassan, E. A., and M. L. Hassan. 2016. Rice straw nanofibrillated cellulose films with antimicrobial properties via supramolecular route. *Industrial Crops and Products* 93:142–51.
- Hiasa, S., S. Iwamoto, T. Endo, and Y. Edashige. 2014. Isolation of cellulose nanofibrils from mandarin (*Citrus unshiu*) peel waste. *Industrial Crops and Products* 62:280–5.
- Hiraoki, R., Y. Ono, T. Saito, and A. Isogai. 2015. Molecular mass and molecular-mass distribution of TEMPO-oxidized celluloses and TEMPO-oxidized cellulose nanofibrils. *Biomacromolecules* 16(2):675–81.
- Hoeng, F., A. Denneulin, C. Neuman, and J. Bras. 2015. Charge density modification of carboxylated cellulose nanocrystals for stable silver nanoparticles suspension preparation. *Journal of Nanoparticle Research* 17:244–58.
- Hu, S., and YLo Hsieh. 2015. Synthesis of surface-bound silver nanoparticles on cellulose fibers using lignin as multi-functional agent. *Carbohydrate Polymers* 131:134–41.
- Ifuku, S., M. Tsuji, M. Morimoto, H. Saimoto, and H. Yano. 2009. Synthesis of silver nanoparticles templated by TEMPO-mediated oxidized bacterial cellulose nanofibers. *Biomacromolecules* 10 (9):2714–7.
- Imam, S. H., G. M. Glenn, and E. E. Chiellini. 2012. Utilization of bio-based polymers in: food packaging: Assessment of materials, production and commercialization. In: *Emerging food packaging technologies: Principles and practice*. Cambridge: Woodhead Publishing Company, UK; p. 435–468.
- Ingle, A. P., N. Duran, and M. Rai. 2014. Bioactivity, mechanism of action, and cytotoxicity of copper-based nanoparticles: A review. *Applied Microbiology and Biotechnology* 98 (3):1001–9.
- Isogai, A., and R. H. Atalla. 1998. Dissolution of cellulose in aqueous NaOH solutions. *Cellulose* 5 (4):309–19.
- Isogai, A., S. Saito, and H. Fukuzumi. 2011. TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3 (1):71–85.
- Iwatake, A., M. Nogi, and H. Yano. 2008. Cellulose nanofiber-reinforced polylactic acid. *Composites Science and Technology* 68 (9):2103–6.
- Jaramillo-Páez, C., J. A. Navío, M. C. Hidalgo, and M. Macías. 2017. High UV-photocatalytic activity of ZnO and Ag/ZnO synthesized by a facile method. *Catalysis Today* 284:121–8.
- Jawaid, M., S. Boufi, and IKHPS. Abdu. 2017. *Cellulose-Reinforced nanofibre composites: Production, properties and applications*. Chennai, India: Mathew Deans.
- Jiang, F., and Y. L. Hsieh. 2014. Synthesis of cellulose nanofibril bound silver nanoprism for surface-enhanced raman scattering. *Biomacromolecules* 15:3680–16.
- Jiang, F., and YLo Hsieh. 2013. Chemically and mechanically isolated nanocellulose and their self-assembled structures. *Carbohydrate Polymers* 95 (1):32–40.

- Jiang, Z., Y. Fang, J. Xiang, Y. Ma, A. Lu, H. Kang, Y. Huang, H. Guo, A. Liu, and L. Zhang. 2014. Intermolecular interactions and 3D structure in cellulose-NaOH-urea aqueous system. *The Journal of Physical Chemistry. B* 118 (34):10250–7.
- Jorfi, M., and E. J. Foster. 2015. Recent advances in nanocellulose for biomedical applications. *Journal of Applied Polymer Science* 132: 41719–38.
- Kaboorani, A., B. Riedl, and P. Blanchet. 2013. Ultrasonication technique: a method for dispersing nanoclay in wood adhesives. *Journal of Nanomaterials* 2013:1–9.
- Karande, V. S., A. K. Bharimalla, G. B. Hadge, S. T. Mhaske, and N. Vigneshwaran. 2011. Nanofibrillation of cotton fibers by disc refiner and its characterization. *Fibers and Polymers* 12 (3):399–404.
- Kaushik, M., and A. Moores. 2016. Review: Nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis. *Green Chemistry* 18:622–37.
- Khalil, A. M., M. L. Hassan, and A. A. Ward. 2017. Novel nanofibrillated cellulose/polyvinylpyrrolidone/silver nanoparticles films with electrical conductivity properties. *Carbohydrate Polymers* 157: 503–11.
- Khalil, H. P. S. A., Y. Y. Tye, C. P. Leh, C. K. Saurabh, F. Arif, H. M. Fizree, A. Mohamed, and A. B. Suriani. 2018. Cellulose reinforced biodegradable polymer composite film for packaging applications. In: *Bionanocomposites for packaging applications*. Cham, Switzerland: Springer; p. 49–69.
- Khan, A., T. Huq, R. A. Khan, B. Riedl, and M. Lacroix. 2014. Nanocellulose-based composites and bioactive agents for food packaging. *Critical Reviews in Food Science and Nutrition* 54 (2):163–74.
- Khandanlou, R., G. C. Ngoh, W. T. Chong, S. Bayat, and E. Saki. 2016. Fabrication of silver nanoparticles supported on rice straw: In vitro antibacterial activity and its heterogeneous catalysis in the degradation of 4-nitrophenol. *Bioresources* 11:3691–708.
- Khatri, V., K. Halász, L. V. Trandafilović, S. Dimitrijević-Branković, P. Mohanty, V. Djoković, and L. Csóka. 2014. ZnO-modified cellulose fiber sheets for antibody immobilization. *Carbohydrate Polymers* 109:139–47.
- Kim, J.-H., B. S. Shim, H. S. Kim, Y.-J. Lee, S.-K. Min, D. Jang, Z. Abas, and J. Kim. 2015. Review of nanocellulose for sustainable future materials. *International Journal of Precision Engineering and Manufacturing-Green Technology* 2 (2):197–213.
- Kim, T. S., R. Cha, and M. S. Gong. 2017. Investigation of the antimicrobial and wound healing properties of silver nanoparticle-loaded cotton prepared using silver carbamate. *Textile Research Journal* 12:1–11.
- Kim, U. J., and S. Kuga. 2001. Ion-exchange chromatography by dicarboxyl cellulose gel. *Journal of Chromatography. A* 919 (1):29–37.
- Klemm, D., B. Heublein, H. P. P. Fink, and A. Bohn. 2005. Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie (International ed. In English)* 44 (22):3358–93.
- Koga, H., T. Saito, T. Kitaoka, M. Nogi, K. Suganuma, and A. Isogai. 2013. Transparent, conductive, and printable composites consisting of TEMPO-oxidized nanocellulose and carbon nanotube. *Biomacromolecules* 14(4):1160–5.
- Krumm, C., J. Pfäendner, and P. J. Dauenhauer. 2016. Millisecond pulsed films unify the mechanisms of cellulose fragmentation. *Chemistry of Materials* 28 (9):3108–14.
- Lee, B.-H., H.-J. Kim, and W.-R. Yu. 2009. Fabrication of long and discontinuous natural fiber reinforced polypropylene biocomposites and their mechanical properties. *Fibers and Polymers* 10 (1):83–90.
- Lefatshe, K., C. M. Muiva, and L. P. Kebaabetswe. 2017. Extraction of nanocellulose and in-situ casting of ZnO/cellulose nanocomposite with enhanced photocatalytic and antibacterial activity. *Carbohydrate Polymers* 164:301–8.
- Leung, A. C. W., S. Hrapovic, E. Lam, Y. Liu, K. B. Male, K. A. Mahmoud, and J. H. T. Luong. 2011. Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small* 7 (3):302–5.
- Li, F., E. Mascheroni, and L. Piergiorganni. 2015. The potential of nanocellulose in the packaging field: A review. *Packaging Technology and Science* 28 (6):475–508.
- Li, J., X. Wei, Q. Wang, J. Chen, G. Chang, L. Kong, J. Su, and Y. Liu. 2012. Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization. *Carbohydrate Polymers* 90 (4):1609–13.
- Li, R., M. He, T. Li, and L. Zhang. 2015. Preparation and properties of cellulose/silver nanocomposite fibers. *Carbohydrate Polymers* 115: 269–75.
- Li, S. M., N. Jia, M. G. Ma, Z. Zhang, Q. H. Liu, and R. C. Sun. 2011. Cellulose-silver nanocomposites: Microwave-assisted synthesis, characterization, their thermal stability, and antimicrobial property. *Carbohydrate Polymers* 86 (2):441–7.
- Li, W. R., X. B. Xie, Q. S. Shi, H. Y. Zeng, Y. S. Ou-Yang, and Y. Ben Chen. 2010. Antibacterial activity and mechanism of silver nanoparticles on *Escherichia coli*. *Applied Microbiology and Biotechnology* 85 (4):1115–22.
- Li, X., Y. Xing, Y. Jiang, Y. Ding, and W. Li. 2009. Antimicrobial activities of ZnO powder-coated PVC film to inactivate food pathogens. *International Journal of Food Science & Technology* 44 (11):2161–8.
- Li, X., X. Zhang, L. Li, L. Huang, W. Zhang, J. Ye, and J. Hong. 2016. Preparation of nano-ZnO/regenerated cellulose composite particles via co-gelation and low-temperature hydrothermal synthesis. *Materials Letters*. 175:122–5.
- Li, Y., H. Zhu, M. Xu, Z. Zhuang, M. Xu, and H. Dai. 2014. High yield preparation method of thermally stable cellulose nanofibers. *BioResources* 9:1986–97.
- Lima, M. M. D. S., and R. Borsali. 2004. Rodlike cellulose microcrystals: Structure, properties, and applications. *Macromolecular Rapid Communications* 25(7):771–87.
- Lin, D., H. Wu, R. Zhang, and W. Pan. 2009. Enhanced photocatalysis of electrospun Ag-ZnO heterostructured nanofibers. *Chemistry of Materials* 21(15):3479–84.
- Lin, N., C. Bruzzese, and A. Dufresne. 2012. TEMPO-oxidized nanocellulose participating as crosslinking aid for alginate-based sponges. *ACS Applied Materials & Interfaces* 4(9):4948–59.
- Lin, N., and A. Dufresne. 2014. Nanocellulose in biomedicine: Current status and future prospect. *Eur Polym J* 59:302–25.
- Lin, N., J. Huang, P. R. Chang, J. Feng, and J. Yu. 2011. Surface acetylation of cellulose nanocrystal and its reinforcing function in poly(lactic acid). *Carbohydrate Polymers* 83(4):1834–42.
- Liou, P., F. X. Navigiziki, F. Kong, A. Mustapha, and M. Lin. 2017. Cellulose nanofibers coated with silver nanoparticles as a SERS platform for detection of pesticides in apples. *Carbohydrate Polymers* 157:643–50.
- Liu, D., Y. Dong, and G. Sui. 2016. Isolation of cellulose nanowhiskers and their Nanocomposites. In: *Nano-size polymers preparation, properties, applications*. Switzerland: Springer International Publishing; p. 155–177.
- Liu, H., J. Song, S. Shang, Z. Song, and D. Wang. 2012. Cellulose nanocrystal/silver nanoparticle composites as bifunctional nanofillers within waterborne polyurethane. *ACS Applied Materials & Interfaces* 4 (5):2413–9.
- Liu, H., D. Wang, Z. Song, and N. Á. A. Á. 2011. Preparation of silver nanoparticles on cellulose nanocrystals and the application in electrochemical detection of DNA hybridization. *Cellulose* 18 (1):67–74.
- Liu, R., Y. Huang, A. Xiao, and H. Liu. 2010. Preparation and photocatalytic property of mesoporous ZnO/SnO₂ composite nanofibers. *Journal of Alloys and Compounds* 503 (1):103–10.
- Liu, Y., L. He, A. Mustapha, H. Li, Z. Q. Hu, and M. Lin. 2009. Antibacterial activities of zinc oxide nanoparticles against *Escherichia coli* O157:H7. *Journal of Applied Microbiology* 107 (4): 1193–201.
- Liu, Y., H. Wang, G. Yu, Q. Yu, B. Li, and X. Mu. 2014. A novel approach for the preparation of nanocrystalline cellulose by using phosphotungstic acid. *Carbohydrate Polymers* 110:415–22.
- Liu, Z., H. Wang, C. Liu, Y. Jiang, G. Yu, X. Mu, and X. Wang. 2012. Magnetic cellulose-chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions. *Chemical Communications (Cambridge, England)* 48 (59):7350–2.
- Lokanathan, A. R., K. M. A. Uddin, O. J. Rojas, and J. Laine. 2014. Cellulose nanocrystal-mediated synthesis of silver nanoparticles:

- Role of sulfate groups in nucleation phenomena. *Biomacromolecules* 15 (1):373–9.
- Lu, P., and Y. L. Hsieh. 2012. Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohydrate Polymers* 87 (1): 564–73.
- Luo, X., and L. Zhang. 2009. High effective adsorption of organic dyes on magnetic cellulose beads entrapping activated carbon. *Journal of Hazardous Materials* 171 (1–3):340–7.
- Luzi, F., E. Fortunati, A. Jiménez, D. Puglia, A. Chiralt, and L. Torre. 2017. PLA nanocomposites reinforced with cellulose nanocrystals from *Posidonia oceanica* and ZnO nanoparticles for packaging application. *Journal of Renewable Materials* 5 (2):103–15.
- Ma, M. G., S. J. Qing, S. M. Li, J. F. Zhu, L. H. Fu, and R. C. Sun. 2013. Microwave synthesis of cellulose/CuO nanocomposites in ionic liquid and its thermal transformation to CuO. *Carbohydrate Polymers* 91 (1):162–8.
- Ma, P., L. Jiang, M. Yu, W. Dong, and M. Chen. 2016. Green antibacterial nanocomposites from poly(lactide)/poly(butylene adipate-co-terephthalate)/nanocrystal cellulose-silver nanohybrids. *ACS Sustainable Chemistry & Engineering* 4 (12):6417–26.
- Madhup, M. K., N. K. Shah, and P. M. Wadhvani. 2015. Investigation of surface morphology, anti-corrosive and abrasion resistance properties of nickel oxide epoxy nanocomposite (NiO-ENC) coating on mild steel substrate. *Progress in Organic Coatings* 80:1–10.
- Mahapatra, O., M. Bhagat, C. Gopalakrishnan, and K. D. Arunachalam. 2008. Ultrafine dispersed CuO nanoparticles and their antibacterial activity. *Journal of Experimental Nanoscience* 3 (3):185–93.
- Mahmoud, K. A., K. B. Male, S. Hrapovic, and J. H. T. Luong. 2009. Cellulose nanocrystal/gold nanoparticle composite as a matrix for enzyme immobilization. *ACS Applied Materials & Interfaces* 1 (7): 1383–6.
- Maia, T. H. S., N. M. Larocca, C. A. G. Beatrice, A. J. de Menezes, G. de Freitas Siqueira, L. A. Pessan, A. Dufresne, M. P. Franca, and A. de Almeida Lucas. 2017. Polyethylene cellulose nanofibrils nanocomposites. *Carbohydrate Polymers* 173:50–6.
- Maleki, A., and M. Kamalzare. 2014. Fe₃O₄@cellulose composite nanocatalyst: Preparation, characterization and application in the synthesis of benzodiazepines. *Catalysis Communications* 53:67–71.
- Maleki, A., Z. Hajizadeh, and R. Firouzi-Haji. 2018. Eco-friendly functionalization of magnetic halloysite nanotube with SO₃H for synthesis of dihydropyrimidinones. *Microporous and Mesoporous Materials* 259:46–53.
- Maleki, A., R. Firouzi-Haji, and Z. Hajizadeh. 2018. Magnetic guanidylated chitosan nanobiocomposite: A green catalyst for the synthesis of 1,4-dihydropyridines. *International Journal of Biological Macromolecules* 116:320–6.
- Maleki, A., H. Movahed, and P. Ravaghi. 2017. Magnetic cellulose/Ag as a novel eco-friendly nanobiocomposite to catalyze synthesis of chromene-linked nicotinonitriles. *Carbohydrate Polymers* 156: 259–67.
- Maleki, A., P. Zand, and Z. Mohseni. 2016. Fe₃O₄@PEG-SO₃H rod-like morphology along with the spherical nanoparticles: Novel green nanocomposite design, preparation, characterization and catalytic application. *RSC Advances* 6 (112):110928–34.
- Maleki, A., P. Zand, Z. Mohseni, and R. Firouzi-Haji. 2018. Green composite nanostructure (Fe₃O₄@PEG-SO₃H): Preparation, characterization and catalytic performance in the efficient synthesis of -amino carbonyl compounds at room temperature. *Nano-Structures & Nano-Objects* 16:31–7.
- Martínez-Sanz, M., A. Lopez-Rubio, and J. M. Lagaron. 2011. Optimization of the nanofabrication by acid hydrolysis of bacterial cellulose nanowhiskers. *Carbohydrate Polymers* 85 (1):228–36.
- Martins, N. C. T., C. S. R. Freire, C. P. Neto, A. J. D. Silvestre, J. Causio, G. Baldi, P. Sadocco, and T. Trindade. 2013. Antibacterial paper based on composite coatings of nanofibrillated cellulose and ZnO. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 417:111–9.
- Maruthupandy, M., Y. Zuo, J. S. Chen, J. M. Song, H. L. Niu, C. J. Mao, S.-Y. Zhang, and Y. H. Shen. 2017. Synthesis of metal oxide nanoparticles (CuO and ZnO NPs) via biological template and their optical sensor applications synthesis of metal oxide nanoparticles (CuO and ZnO NPs) via biological template and their optical sensor applications. *Applied Surface Science* 397:167–74.
- Mary, G., S. K. Bajpai, and N. Chand. 2009. Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. *Journal of Applied Polymer Science* 113 (2):757–66.
- Mascheroni, E., R. Rampazzo, M. A. Ortenzi, G. Piva, S. Bonetti, and L. Piergiovanni. 2016. Comparison of cellulose nanocrystals obtained by sulfuric acid hydrolysis and ammonium persulfate, to be used as coating on flexible food-packaging materials. *Cellulose* 23 (1): 779–93.
- Medronho, B., and B. Lindman. 2015. Brief overview on cellulose dissolution/regeneration interactions and mechanisms. *Advances in Colloid and Interface Science* 222:502–8.
- Mohammadi, M., S. Sabbaghi, H. Sadeghi, M. M. Zerafat, and R. Pooladi. 2014. Preparation and characterization of TiO₂/ZnO/CuO nanocomposite and application for phenol removal from wastewaters. *Desalination and Water Treatment* 57:1–11.
- Mondal, B., B. Basumatari, J. Das, C. Roychaudhury, H. Saha, and N. Mukherjee. 2014. ZnO-SnO₂ based composite type gas sensor for selective hydrogen sensing. *Sensors and Actuators B* 194:389–96.
- Moon, R. J., A. Martini, J. Nairn, J. Simonsen, and J. Youngblood. 2011. Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chemical Society Reviews* 40 (7):3941–94.
- Moriana, R., F. Vilaplana, and M. Ek. 2016. Cellulose nanocrystals from forest residues as reinforcing agents for composites: A study from macro- to nano-dimensions. *Carbohydrate Polymers* 139: 139–49.
- Mukherjee, T., M. Czaka, N. Kao, R. K. Gupta, H. J. Choi, and S. Bhattacharya. 2014. Dispersion study of nanofibrillated cellulose based poly(butylene adipate-co-terephthalate) composites. *Carbohydrate Polymers* 102:537–42.
- Müller, B., M. Gebert-Germ, and A. Russler. 2012. Viscount HT - the future of high-performance viscose filaments and their textile applications. *Lenzinger Berichte - Technische Informationsbibliothek* 90: 64–71.
- Murzin, S. P., and A. N. Kryuchkov. 2017. Formation of ZnO/CuO heterostructure caused by laser-induced vibration action. *Procedia Engineering* 176:546–51.
- Nabeela, K., R. T. Thomas, J. B. Nair, K. K. Maiti, K. G. K. Warriar, and S. Pillai. 2016. TEMPO-oxidized nanocellulose fiber-directed stable aqueous suspension of plasmonic flower-like silver nanoconstructs for ultra-trace detection of analytes. *ACS Applied Materials & Interfaces* 8 (43):29242–51.
- Naika, H. R., K. Lingaraju, K. Manjunath, D. Kumar, G. Nagaraju, D. Suresh, and H. Nagabhushana. 2015. Green synthesis of CuO nanoparticles using gloriosa superba L. extract and their antibacterial activity. *Integrative Medicine Research* 9 (1):7–12.
- Nascimento, JHOdo, R. F. Luz, F. M. F. Galvão, J. D. D. Melo, F. R. Oliveira, R. Lachumananandasivam, and A. Zille. 2015. Extraction and characterization of cellulosic nanowhisker obtained from discarded cotton fibers. *Materials Today: Proceedings* 2 (1):1–7.
- Nechyporchuk, O., M. N. Belgacem, and J. Bras. 2016. Production of cellulose nanofibrils: a review of recent advances. *Industrial Crops and Products* 93:2–25.
- Nirmala, M., M. G. Nair, K. Rekha, A. Anukaliani, S. K. Samdarshi, and R. G. Nair. 2010. Photocatalytic activity of ZnO nanopowders synthesized by DC thermal plasma. *Applied Sciences* 2:161–6.
- Nishiyama, Y., P. Langan, and H. Chanzy. 2002. Crystal structure and hydrogen-bonding system in cellulose I_{beta} from synchrotron X-ray and neutron fiber diffraction. *Journal of the American Chemical Society* 124 (31):9074–82.
- Nishiyama, Y., J. Sugiyama, H. Chanzy, and P. Langan. 2003. Crystal structure and hydrogen bonding system in cellulose I_x from synchrotron x-ray and neutron fiber diffraction. *Journal of the American Chemical Society* 125 (47):14300–6.
- Nogi, M., S. Iwamoto, A. N. Nakagaito, and H. Yano. 2009. Optically transparent nanofiber paper. *Advanced Materials* 21 (16):1595–8.

- Noguchi, Y., I. Homma, and Y. Matsubara. 2017. Complete nanofibrillation of cellulose prepared by phosphorylation. *Cellulose* 24:1–10.
- Nooy, A. E. J., A. C. Besemer, and H. van Bekkum. 1995. Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans. *Carbohydrate Research* 269 (1):89–98.
- O'Sullivan, A. C. 1997. Cellulose: the structure slowly unravels. *Cellulose* 4:173–207.
- Oun, A. A., and J. W. Rhim. 2017a. Carrageenan-based hydrogels and films: Effect of ZnO and CuO nanoparticles on the physical, mechanical, and antimicrobial properties. *Food Hydrocolloids* 67:45–53.
- Oun, A. A., and J. W. Rhim. 2017b. Characterization of carboxymethyl cellulose-based nanocomposite films reinforced with oxidized nanocellulose isolated using ammonium persulfate method. *Carbohydrate Polymers* 174:484–92.
- Oun, A. A., and J. W. Rhim. 2015a. Effect of post-treatments and concentration of cotton linter cellulose nanocrystals on the properties of agar-based nanocomposite films. *Carbohydrate Polymers* 134:20–9.
- Oun, A. A., and J. W. Rhim. 2015b. Preparation and characterization of sodium carboxymethyl cellulose/cotton linter cellulose nanofibril composite films. *Carbohydrate Polymers* 127:101–9.
- Oun, A. A., and J. W. Rhim. 2016a. Characterization of nanocelluloses isolated from ushar (*Calotropis procera*) seed fiber: Effect of isolation method. *Materials Letters* 168:146–50.
- Oun, A. A., and J. W. Rhim. 2016b. Isolation of cellulose nanocrystals from grain straws and their use for the preparation of carboxymethyl cellulose-based nanocomposite films. *Carbohydrate Polymers* 150:187–200.
- Oun, A. A., and J. W. Rhim. 2017c. Effect of oxidized chitin nanocrystals isolated by ammonium persulfate method on the properties of carboxymethyl cellulose-based films. *Carbohydrate Polymers* 175: 712–20.
- Phanthong, P., P. Reubroycharoen, X. Hao, G. Xu, A. Abudula, and G. Guan. 2018. Nanocellulose: Extraction and application. *Carbon Resources Conversion* 1 (1):32–43.
- Peltzer, M., A. Pei, Q. Zhou, L. Berglund, and A. Jiménez. 2014. Surface modification of cellulose nanocrystals by grafting with poly(lactic acid). *Polymer International* 63 (6):1056–62.
- Peng, B. L., N. Dhar, H. L. Liu, and K. C. Tam. 2011. Chemistry and applications of nanocrystalline cellulose and its derivatives: a nanotechnology perspective. *The Canadian Journal of Chemical Engineering* 89 (5):1191–206.
- Perelshtein, I., Y. Ruderman, N. Perkash, J. Beddow, G. Singh, M. Vinatoru, E. Joyce, T. J. Mason, M. Blanes, K. Mollá, and A. Gedanken. 2013. The sonochemical coating of cotton withstands 65 washing cycles at hospital washing standards and retains its antibacterial properties. *Cellulose* 20 (3):1215–21.
- Petkova, P., A. Francesko, M. M. Fernandes, E. Mendoza, I. Perelshtein, A. Gedanken, and T. Tzanov. 2014. Sonochemical coating of textiles with hybrid ZnO/chitosan antimicrobial nanoparticles. *ACS Applied Materials & Interfaces* 6 (2):1164–72.
- Pickering, K. L., M. G. A. Efendy, and T. M. Le. 2016. A review of recent developments in natural fiber composites and their mechanical performance. *Composites Part A: Applied Science and Manufacturing* 83:98–112.
- Pinkert, A., K. N. Marsh, S. Pang, and M. P. Staiger. 2009. Ionic liquids and their interaction with cellulose. *Chemical Reviews* 109(12): 6712–28.
- Pinto, R. J. B., M. C. Neves, C. P. Neto, and T. Trindade. 2012. Composites of cellulose and metal nanoparticles. In: *Nanocomposites - New trends and developments*, p. 73–96. London, UK: INTECH.
- Puangsin, B., S. Fujisawa, R. Kuramae, T. Saito, and A. Isogai. 2013. TEMPO-mediated oxidation of hemp bast holocellulose to prepare cellulose nanofibrils dispersed in water. *Journal of Polymers and the Environment* 21 (2):555–63.
- Puangsin, B., Q. Yang, T. Saito, and A. Isogai. 2013. Comparative characterization of TEMPO-oxidized cellulose nanofibril films prepared from non-wood resources. *International Journal of Biological Macromolecules* 59:208–13.
- Qi, H., J. Cai, L. Zhang, and S. Kuga. 2009. Properties of films composed of cellulose nanowhiskers and a cellulose matrix regenerated from alkali/urea solution. *Biomacromolecules* 10 (6):1597–602.
- Qi, H., E. Mäder, and J. Liu. 2013. Electrically conductive aerogels composed of cellulose and carbon nanotubes. *Journal of Materials Chemistry A* 1 (34):9714.
- Qin, X., A. Lu, and L. Zhang. 2013. Gelation behavior of cellulose in NaOH/urea aqueous system via cross-linking. *Cellulose* 20 (4): 1669–77.
- Qu, P., Y. Gao, G. F. Wu, and L. P. Zhang. 2010. Nanocomposites of poly(lactic acid) reinforced with cellulose nanofibrils. *BioResources* 5: 1811–23.
- Ramani, M., S. Ponnusamy, C. Muthamizhchelvan, and E. Marsili. 2014. Amino acid-mediated synthesis of zinc oxide nanostructures and evaluation of their facet-dependent antimicrobial activity. *Colloids Surf B Biointerf* 117:233–9.
- Ramezanzadeh, B., and M. M. Attar. 2013. Evaluation of the effects of surface treatments on the cathodic delamination and anticorrosion performance of an epoxy-nanocomposite on steel substrate. *Journal of Coatings Technology and Research* 10 (1):47–55.
- Ramyadevi, J., K. Jeyasubramanian, A. Marikani, G. Rajakumar, and A. A. Rahuman. 2012. Synthesis and antimicrobial activity of copper nanoparticles. *Materials Letters* 71:114–6.
- Rånby, B. G., A. Banderet, and L. G. Sillén. 1949. Aqueous colloidal solutions of cellulose micelles. *Acta Chemica Scandinavica* 3:649–50.
- Raus, V., A. Šturcová, J. Dybal, M. Šlouf, T. Vacková, P. Šálek, L. Kobera, and P. Vlček. 2012. Activation of cellulose by 1,4-dioxane for dissolution in N,N-dimethylacetamide/LiCl. *Cellulose* 19(6): 1893–906.
- Reiniati, I., A. N. Hrymak, and A. Margaritis. 2016. Recent developments in the production and applications of bacterial cellulose fibers and nanocrystals. *Critical Reviews in Biotechnology* 8551:1–15.
- Rhim, J. W., L. F. Wang, Y. Lee, and S. I. Hong. 2014. Preparation and characterization of bio-nanocomposite films of agar and silver nanoparticles: Laser ablation method. *Carbohydrate Polymers* 103:456–65.
- Roberson, M., V. Rangari, S. Jeelani, T. Samuel, and C. Yates. 2014. Synthesis and characterization of silver, zinc oxide and hybrid silver/zinc oxide nanoparticles for antimicrobial applications. *Nano LIFE* 04 (01):1440003–11.
- Rodríguez-Castellanos, W., J. F. Flores-Ruiz, F. Martínez-Bustos, F. Chiñas-Castillo, and F. J. Espinoza-Beltrán. 2015. Nanomechanical properties and thermal stability of recycled cellulose reinforced starch-gelatin polymer composite. *Journal of Applied Polymer Science* 132:35–41.
- Sacui, I. A., R. C. Nieuwendaal, D. J. Burnett, S. J. Stranick, M. Jorfi, C. Weder, E. J. Foster, R. T. Olsson, and J. W. Gilman. 2014. Comparison of the properties of cellulose nanocrystals and cellulose nanofibrils isolated from bacteria, tunicate, and wood processed using acid, enzymatic, mechanical, and oxidative methods. *ACS Applied Materials & Interfaces* 6 (9):6127–38.
- Sadeghifar, H., I. Filpponen, S. P. Clarke, D. F. Brougham, and D. S. Argyropoulos. 2011. Production of cellulose nanocrystals using hydrobromic acid and click reactions on their surface. *Journal of Materials Science* 46 (22):7344–55.
- Saini, S., C. Y. Falco, M. N. Belgacem, and J. Bras. 2016. Surface cationized cellulose nanofibrils for the production of contact active antimicrobial surfaces. *Carbohydrate Polymers* 135:239–47.
- Saito, T., S. Kimura, Y. Nishiyama, and A. Isogai. 2007. Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8 (8):2485–91.
- Saito, T., R. Kuramae, J. Wohlert, L. A. Berglund, and A. Isogai. 2013. An ultrastrong nanofibrillar biomaterial: the strength of single cellulose nanofibrils revealed via sonication-induced fragmentation. *Biomacromolecules* 14 (1):248–53.
- Saito, T., Y. Nishiyama, J. L. Putaux, M. Vignon, and A. Isogai. 2006. Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* 7 (6):1687–91.
- Saito, T., I. Shibata, A. Isogai, N. Suguri, and N. Sumikawa. 2005. Distribution of carboxylate groups introduced into cotton linters by

- the TEMPO-mediated oxidation. *Carbohydrate Polymers* 61 (4): 414–9.
- Salem, W., D. R. Leitner, F. G. Zingl, G. Schratter, R. Prassl, W. Goessler, J. Reidl, and S. Schild. 2015. Antibacterial activity of silver and zinc nanoparticles against *Vibrio cholerae* and enterotoxigenic *Escherichia coli*. *International Journal of Medical Microbiology* : *Ijmm* 305 (1):85–95.
- Saoud, K., R. Alsoubaihi, N. Bensalah, T. Bora, M. Bertino, and J. Dutta. 2015. Synthesis of supported silver nano-spheres on zinc oxide nanorods for visible light photocatalytic applications. *Materials Research Bulletin*. 63:134–40.
- Saxena, I. M., and R. M. Brown. 2005. Cellulose biosynthesis: Current views and evolving concepts. *Annals of Botany* 96 (1):9–21.
- Shah, K. J., and T. Imae. 2016. Selective gas capture ability of gas-adsorbent-incorporated cellulose nanofiber films. *Biomacromolecules* 17 (5):1653–61.
- Shak, K. P. Y., Y. L. Pang, and S. K. Mah. 2018. Nanocellulose: Recent advances and its prospects in environmental remediation. *Beilstein Journal of Nanotechnology* 9:2479–98.
- Shankar, S., A. A. Oun, and J. W. Rhim. 2018. Preparation of antimicrobial hybrid nano-materials using regenerated cellulose and metallic nanoparticles. *International Journal of Biological Macromolecules* 107 (Pt A):17–27.
- Shankar, S., and J. W. Rhim. 2015. Amino acid mediated synthesis of silver nanoparticles and preparation of antimicrobial agar/silver nanoparticles composite films. *Carbohydrate Polymers* 130:353–63.
- Shankar, S., and J. W. Rhim. 2017. Facile approach for large-scale production of metal and metal oxide nanoparticles and preparation of antibacterial cotton pads. *Carbohydrate Polymers* 163:137–45.
- Shankar, S., and J. W. Rhim. 2016a. Preparation of nanocellulose from micro-crystalline cellulose: the effect on the performance and properties of agar-based composite films. *Carbohydrate Polymers* 135: 18–26.
- Shankar, S., and J. W. Rhim. 2016b. Tocopherol-mediated synthesis of silver nanoparticles and preparation of antimicrobial PBAT/silver nanoparticles composite films. *Lebensmittel-Wissenschaft & Technologie* 72:149–56.
- Shankar, S., L. F. Wang, and J. W. Rhim. 2017. Preparation and properties of carbohydrate-based composite films incorporated with CuO nanoparticles. *Carbohydrate Polymers* 169:264–71.
- Shao, W., S. Wang, J. Wu, M. Huang, H. Liu, and H. Min. 2016. Synthesis and antimicrobial activity of copper nanoparticle loaded regenerated bacterial cellulose membranes. *RSC Advances* 6 (70): 65879–84.
- Schenzel, K., S. Fischer, and E. Brendler. 2005. New method for determining the degree of cellulose I crystallinity by means of FT raman spectroscopy. *Cellulose* 12 (3):223–31.
- Shi, X., T. A. Nguyen, Z. Suo, Y. Liu, and R. Avci. 2009. Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating. *Surface and Coatings Technology* 204 (3):237–45.
- Shi, Z., J. Tang, L. Chen, C. Yan, S. Tanvir, W. A. Anderson, R. M. Berry, and K. C. Tam. 2015. Enhanced colloidal stability and antibacterial performance of silver nanoparticles/cellulose nanocrystal hybrids. *Journal of Materials Chemistry B* 3 (4):603–11.
- Singla, R., S. Soni, P. M. Kulurkar, A. Kumari, M. S. V. Patial, Y. S. Padwad, and S. K. Yadav. 2017. In situ functionalized nanobiocomposites dressings of bamboo cellulose nanocrystals and silver nanoparticles for accelerated wound healing. *Carbohydrate Polymers* 155: 152–62.
- Siqueira, G., J. Bras, and A. Dufresne. 2010. Cellulosic bionanocomposites: a review of preparation, properties and applications. *Polymers* 2 (4):728–65.
- Siró, I., D. Plackett, M. Hedenqvist, M. Ankerfors, and T. Lindström. 2011. Highly transparent films from carboxymethylated microfibrillated cellulose: The effect of multiple homogenization steps on key properties. *Journal of Applied Polymer Science* 119 (5):2652–60.
- Soni, B., E. B. Hassan, M. W. Schilling, and B. Mahmoud. 2016. Transparent bionanocomposite films based on chitosan and TEMPO-oxidized cellulose nanofibers with enhanced mechanical and barrier properties. *Carbohydrate Polymers* 151:779–89.
- Sun, X. F., F. Xu, R. C. Sun, P. Fowler, and M. S. Baird. 2005. Characteristics of degraded cellulose obtained from steam-exploded wheat straw. *Carbohydrate Research* 340 (1):97–106.
- Sun, X., Q. Wu, S. Ren, and T. Lei. 2015. Comparison of highly transparent all-cellulose nanopaper prepared using sulfuric acid and TEMPO-mediated oxidation methods. *Cellulose* 22 (2):1123–33.
- Szabo, O. E., and E. Csizsar. 2017. Some factors affecting efficiency of the ultrasound-aided enzymatic hydrolysis of cotton cellulose. *Carbohydrate Polymers* 156:357–63.
- Talebian, N., S. M. Amininezhad, and M. Doudi. 2013. Controllable synthesis of ZnO nanoparticles and their morphology-dependent antibacterial and optical properties. *Journal of Photochemistry and Photobiology. B, Biology* 120:66–73.
- Taniguchi, T., and K. Okamura. 1998. New films produced from microfibrillated natural fibers. *Polymer International* 47 (3):291–4.
- Tankhiwale, R., and S. K. Bajpai. 2012. Preparation characterization and antibacterial applications of ZnO-nanoparticles coated polyethylene films for food packaging. *Colloids and Surfaces B: Biointerfaces* 90:16–20.
- Taufik, A., and R. Saleh. 2017. Synthesis of iron(II,III) oxide/zinc oxide/copper(II) oxide (Fe₃O₄/ZnO/CuO) nanocomposites and their photosonocatalytic property for organic dye removal. *Journal of Colloid and Interface Science* 491:27–36.
- Thatoi, P., R. G. Kerry, S. Gouda, G. Das, K. Pramanik, H. Thatoi, and J. K. Patra. 2016. Photo-mediated green synthesis of silver and zinc oxide nanoparticles using aqueous extracts of two mangrove plant species, *heritiera fomes* and *sonneratia apetala* and investigation of their biomedical applications. *Journal of Photochemistry and Photobiology. B, Biology* 163:311–8.
- Tian, J., J. Xu, F. Zhu, T. Lu, C. Su, and G. Ouyang. 2013. Application of nanomaterials in sample preparation. *Journal of Chromatography. A* 1300:2–16.
- Trandafilovic, L. V., R. K. Whiffen, S. Dimitrijevic-Brankovic, M. Stojiljkovic, A. S. Luyt, and V. Djokovic. 2014. ZnO/Ag hybrid nanocubes in alginate biopolymer: Synthesis and properties. *Chemical Engineering Journal* 253:341–9.
- Turbak, A. F., F. W. Snyder, and K. R. Sandberg. 1983. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. In: *Proceedings of the ninth cellulose conference*. New York: Applied Polymer Symposia. Vol. 37, p. 815–827.
- Uddin, K. M. A., L. R. Arcot, A. Liljestrom, X. Chen, O. J. Rojas, and J. Laine. 2014. Silver nanoparticle synthesis mediated by carboxylated cellulose nanocrystals. *Green Materials* 2 (4):183–92.
- Uetani, K., T. Okada, and H. T. Oyama. 2015. Crystallite size effect on thermal conductive properties of nonwoven nanocellulose sheets. *Biomacromolecules* 16 (7):2220–7.
- Uetani, K., and H. Yano. 2011. Nanofibrillation of wood pulp using a high-speed blender. *Biomacromolecules* 12 (2):348–53.
- Ul-Islam, M., W. A. Khattak, M. W. Ullah, S. Khan, and J. K. Park. 2014. Synthesis of regenerated bacterial cellulose-zinc oxide nanocomposite films for biomedical applications. *Cellulose* 21 (1):433–47.
- Ummartyotin, S., and H. Manuspiya. 2015. A critical review on cellulose: from fundamental to an approach on sensor technology. *Renewable & Sustainable Energy Reviews* 41:402–12.
- Usha, R., E. Prabu, M. Palaniswamy, C. K. Venil, and R. Rajendran. 2010. Synthesis of metal oxide nano particles by streptomyces Sp for development of antimicrobial textiles. *Global Journal Of Biotechnology & Biochemistry* 5:153–60.
- Usman, M. S., N. A. Ibrahim, K. Shamel, N. Zainuddin, and W. M. Z. W. Yunus. 2012. Copper nanoparticles mediated by chitosan: Synthesis and characterization via chemical methods. *Molecules (Basel, Switzerland)* 17 (12):14928–36.
- Vainio, U., K. Pirkkalainen, K. Kisko, G. Goerigk, N. E. Kotelnikova, and R. Serimaa. 2007. Copper and copper oxide nanoparticles in a cellulose support studied using anomalous small-angle X-ray scattering. *The European Physical Journal D* 42 (1):93–101.
- Varaprasad, K., M. Pariguana, G. M. Raghavendra, T. Jayaramudu, and E. R. Sadiku. 2017. Development of biodegradable metaloxide/polymer nanocomposite films based on poly-ε-caprolactone and terephthalic acid. *Materials Science and Engineering: C* 70:85–93.

- Varaprasad, K., G. M. Raghavendra, T. Jayaramudu, and J. Seo. 2016. Nano zinc oxide-sodium alginate antibacterial cellulose fibres. *Carbohydrate Polymers* 135:349–55.
- Wang, M. S., F. Jiang, Y. L. Hsieh, and N. Nitin. 2014. Cellulose nanofibrils improve dispersibility and stability of silver nanoparticles and induce production of bacterial extracellular polysaccharides. *Journal of Materials Chemistry B* 2 (37):6226–35.
- Wang, Q., J. Cai, L. Zhan, M. Xu, H. Cheng, C. C. Han, S. Kuga, J. Xiao, and R. Xiao. 2013. A bioplastic with high strength constructed from a cellulose hydrogel by changing the aggregated structure. *Journal of Materials Chemistry A* 1 (22):6678–86.
- Wang, S., A. Lu, and L. Zhang. 2016. Recent advances in regenerated cellulose materials. *Progress in Polymer Science* 53:169–206.
- Wei, L., J. Lu, H. Xu, A. Patel, Z. S. Chen, and G. Chen. 2015. Silver nanoparticles: synthesis, properties, and therapeutic applications. *Drug Discovery Today* 20 (5):595–601.
- Weishaupt, R., G. Siqueira, M. Schubert, P. Tingaut, K. Maniura-Weber, T. Zimmermann, L. Thöny-Meyer, G. Faccio, and J. Ihssen. 2015. TEMPO-oxidized nanofibrillated cellulose as a high density carrier for bioactive molecules. *Molecules. Biomacromolecules* 16 (11):3640–50.
- Wiley, B., Y. Sun, B. Mayers, and Y. Xia. 2005. Shape-controlled synthesis of metal nanostructures: the case of silver. *Chemistry (Weinheim an Der Bergstrasse, Germany)* 11 (2):454–63.
- Wu, C. N., T. Saito, S. Fujisawa, H. Fukuzumi, and A. Isogai. 2012. Ultrastrong and high gas-barrier nanocellulose/clay-layered composites. *Biomacromolecules* 13 (6):1927–32.
- Xiong, R., C. Lu, W. Zhang, Z. Zhou, and X. Zhang. 2013. Facile synthesis of tunable silver nanostructures for antibacterial application using cellulose nanocrystals. *Carbohydrate Polymers* 95 (1):214–9.
- Xu, L., Y. Zhou, Z. Wu, G. Zheng, J. He, and Y. Zhou. 2017. Improved photocatalytic activity of nanocrystalline ZnO by coupling with CuO. *Journal of Physical Chemistry Solids*. 106:29–36.
- Xu, X., F. Liu, L. Jiang, J. Y. Zhu, D. Haagenson, and D. P. Wiesenborn. 2013. Cellulose nanocrystals vs. cellulose nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Applied Materials & Interfaces* 5 (8): 2999–3009.
- Xu, X., Y. Q. Yang, Y. Y. Xing, J. F. Yang, and S. F. Wang. 2013. Properties of novel polyvinyl alcohol/cellulose nanocrystals/silver nanoparticles blend membranes. *Carbohydrate Polymers* 98 (2): 1573–7.
- Yan, J., A. M. Abdelgawad, M. E. El-Naggar, and O. J. Rojas. 2016. Antibacterial activity of silver nanoparticles synthesized in-situ by solution spraying onto cellulose. *Carbohydrate Polymers* 147:500–8.
- Yang, H., C. Liu, D. Yang, H. Zhang, and Z. Xi. 2009. Comparative study of cytotoxicity, oxidative stress and genotoxicity induced by four typical nanomaterials: the role of particle size, shape and composition. *Journal of Applied Toxicology: Jat* 29 (1):69–78.
- Yang, Q., H. Fukuzumi, T. Saito, A. Isogai, and L. Zhang. 2011. Transparent cellulose films with high gas barrier properties fabricated from aqueous alkali/urea solutions. *Biomacromolecules* 12(7): 2766–71.
- Yang, R. T., H. Y. Yu, M. L. Song, Y. W. Zhou, and J. M. Yao. 2016. Flower-like zinc oxide nanorod clusters grown on spherical cellulose nanocrystals via simple chemical precipitation method. *Cellulose* 23(3):1871–84.
- Yang, Y. J., J. M. Shin, T. H. Kang, S. Kimura, M. Wada, and U. J. Kim. 2014. Cellulose dissolution in aqueous lithium bromide solutions. *Cellulose* 21(3):1175–81.
- Yao, K., Y. Y. Dong, J. Bian, M. G. Ma, and J. F. Li. 2015. Understanding the mechanism of ultrasound on the synthesis of cellulose/Cu(OH)₂/CuO hybrids. *Ultrasonics Sonochemistry* 24:27–35.
- Yin, X., W. Que, D. Fei, F. Shen, and Q. Guo. 2012. Ag nanoparticle/ZnO nanorods nanocomposites derived by a seed-mediated method and their photocatalytic properties. *Journal of Alloys and Compounds* 524:13–21.
- Yoksan, R., and S. Chirachanchai. 2010. Silver nanoparticle-loaded chitosan-starch based films: Fabrication and evaluation of tensile, barrier and antimicrobial properties. *Materials Science and Engineering: C* 30 (6):891–7.
- Yoon, M., J. E. Lee, Y. J. Jang, J. W. Lim, A. Rani, and D. H. Kim. 2015. Comprehensive study on the controlled plasmon-enhanced photocatalytic activity of hybrid Au/ZnO systems mediated by thermoresponsive polymer linkers. *ACS Applied Materials & Interfaces* 7 (38):21073–81.
- Yu, H. Y., H. Zhang, M.-L. Song, Y. Zhou, J. Yao, and Q. Q. Ni. 2017. From celluloses nanospheres, nanorod to nanofibers: Various aspect ratios induced different nucleation/reinforcing effect on polylactic acid for robust-barrier food packaging. *ACS Applied Materials & Interfaces* 9 (50):43920–38.
- Yu, H., Z. Qin, B. Liang, N. Liu, Z. Zhou, and L. Chen. 2013. Facile extraction of thermally stable cellulose nanocrystals with a high yield of 93% through hydrochloric acid hydrolysis under hydrothermal conditions. *Journal of Materials Chemistry A* 1 (12):3938–44.
- Yu, H., B. Sun, D. Zhang, G. Chen, X. Yang, and J. Yao. 2014. Reinforcement of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with cellulose nanocrystal/silver nanohybrids as bifunctional nanofillers. *Journal of Materials Chemistry B* 2 (48): 8479–89.
- Yu, H. Y., G. Y. Chen, Y. B. Wang, and J. M. Yao. 2015. A facile one-pot route for preparing cellulose nanocrystal/zinc oxide nanohybrids with high antibacterial and photocatalytic activity. *Cellulose* 22 (1): 261–73.
- Yu, H. Y., Z. Y. Qin, B. Sun, C. F. Yan, and J. M. Yao. 2014. One-pot green fabrication and antibacterial activity of thermally stable corn-like CNC/Ag nanocomposites. *Journal of Nanoparticle Research* 16: 2202–14.
- Yu, H. Y., X. Y. Yang, F. F. Lu, G. Y. Chen, and J. M. Yao. 2016. Fabrication of multifunctional cellulose nanocrystals/poly(lactic acid) nanocomposites with silver nanoparticles by spraying method. *Carbohydrate Polymers* 140:209–19.
- Zhang, H., H. Y. Yu, C. Wang, and J. Yao. 2017. Effect of silver contents in cellulose nanocrystal/silver nanohybrids on PHBV crystallization and property improvements. *Carbohydrate Polymers* 173: 7–16.
- Zhang, K., P. Sun, H. Liu, S. Shang, J. Song, and D. Wang. 2016. Extraction and comparison of carboxylated cellulose nanocrystals from bleached sugarcane bagasse pulp using two different oxidation methods. *Carbohydrate Polymers* 138:237–43.
- Zhang, L., H. Ge, M. Xu, J. Cao, and Y. Dai. 2017. Physicochemical properties, antioxidant and antibacterial activities of dialdehyde microcrystalline cellulose. *Cellulose* 24:1–12.
- Zhang, X. F., Z. G. Liu, W. Shen, and S. Gurunathan. 2016. Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches. *International Journal of Molecular Sciences* 17 (9):1534–68.
- Zhao, X., L. Zhang, and D. Liu. 2012. Biomass recalcitrance. Part II: Fundamentals of different pre-treatments to increase the enzymatic digestibility of lignocellulose. *Biofuels, Bioprod Bioref* 6 (5):561–79.
- Zhou, C., L. Xu, J. Song, R. Xing, S. Xu, D. Liu, and H. Song. 2014. Ultrasensitive non-enzymatic glucose sensor based on three-dimensional network of ZnO-CuO hierarchical nanocomposites by electrospinning. *Scientific Reports* 4:7382–91.
- Zhou, J., C. Chang, R. Zhang, and L. Zhang. 2007. Hydrogels prepared from unsubstituted cellulose in NaOH/urea aqueous solution. *Macromolecular Bioscience* 7(6):804–9.
- Zhou, Z., C. Lu, X. Wu, and X. Zhang. 2013. Cellulose nanocrystals as novel support for CuO nanoparticles catalysts: facile synthesis and their application to 4-nitrophenol reduction. *RSC Advances* 3(48): 26066–73.
- Zimmermann, T., E. Pöhler, and T. Geiger. 2004. Cellulose fibrils for polymer reinforcement. *Advanced Engineering Materials* 6 (9): 754–61.
- Zarei, S., M. Niad, and H. Raanaei. 2018. The removal of mercury ion pollution by using Fe₃O₄-nanocellulose: Synthesis, characterizations and DFT studies. *Journal of Hazardous Materials* 344(15):258–73.