

Cellulose Nanocrystals: A Brief Review on Properties and General Applications

Open Access

Siti Aisyah Razali¹, Nor Azwadi Che Sidik^{2,*}, Hasan Koten⁴

¹ Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

² Malaysia – Japan International Institute of Technology (MJIT), Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia

³ Faculty of Engineering and Natural Sciences, Dumlupınar D100 Karayolu No:98, 34720 Kadıköy/İstanbul, Turkey

ARTICLE INFO

ABSTRACT

Article history:

Received 23 May 2019

Received in revised form 25 August 2019

Accepted 2 September 2019

Available online 6 November 2019

Cellulose is one of the most widespread natural polymers developed in the ecosystem and have been used in many applications and industrial products since ancient time. Although wood and plant fibers are the main sources of cellulose, other sources can also be found, including algae, fungal bacteria and even some marine animals (such as tunicates). Cellulosic materials are converted into cellulose nanocrystals (CNCs) using mechanical or chemical techniques. Cellulose nanocrystals (CNCs) with high hydrophilicity have emerged as a promising sustainable material for various applications due to increased demand for environmentally friendly, biodegradable and biocompatible goods. The performance of nanocellulose in different applications has been documented by a large number of studies to date. Herein we review existing literature and present an overview of the brief introduction and summarize of recent application nanocellulose such as energy and electronic sectors, wastewater treatment, biomedical, drilling, food and packaging, vehicle, and concrete with a special emphasize on heat transfer application.

Keywords:

Cellulose nanocrystals; heat transfer; nanocellulose

Copyright © 2019 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Growth in the development and innovation of more sustainable and more efficient material has taken place over the last few decades. Therefore, to satisfy this increasing trend, renewable and sustainable resources need to be exploited. Over a century ago, cellulose was used as an energy source, for building materials and clothing in the form of wood and plant fibers. However, these fibers can undergo further mechanical and chemical treatments to produce a more efficient class of nanocellulose materials. Nanocellulose can be divided into three main subcategories; cellulose nanocrystals, nanofibrillated cellulose, and bacterial nanocellulose (Table 1). In the present review, the focus will be on the cellulose nanocrystals.

* Corresponding author.

E-mail address: azwadi@utm.my (Nor Azwadi Che Sidik)

Table 1
 Family of nanocellulose materials [8]

Type of nano-cellulose	Selected references and synonyms	Typical sources	Formation and average size
microfibrillated cellulose (MFC)	microfibrillated cellulose, nanofibrils and microfibrils, nanofibrillated cellulose	wood, sugar beet, potato tuber, hemp, flax	delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment diameter: 5–60 nm length: several micrometers
nanocrystalline cellulose (NCC)	cellulose nanocrystals, crystallites, whiskers, rodlike cellulose microcrystals bacterial	wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel, tunicin, cellulose from algae and bacteria	acid hydrolysis of cellulose from many sources diameter: 5–70 nm length: 100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria)
bacterial nano-cellulose (BNC)	bacterial cellulose, microbial cellulose, biocellulose	low-molecular-weight sugars and alcohols	bacterial synthesis diameter: 20–100 nm; different types of nanofiber networks

Nickerson and Habrle first reported cellulose nanocrystals (CNCs) in 1947[1], but a series of articles released by Derek Gray and colleagues in the 1990s concentrated on the physicochemical characteristics of CNCs [2],[3] prompted the widespread interest in their use. CNCs, also known as nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW), are the rod-like nanocrystal configuration extracted from wood fiber through acid hydrolysis. The acid destroys the amorphous part of cellulose microfibrils and yield rod-like cellulose nanocrystals with a diameter of a few nanometers and a length varying from tens to hundreds of nanometers [4],[5] as demonstrated in Fig. 1. Cellulose nanocrystal stands the wide range of properties such as gigantic surface area, excellent stability, captivating mechanical (higher specific strength as well as modulus), and also astonishing optical properties.

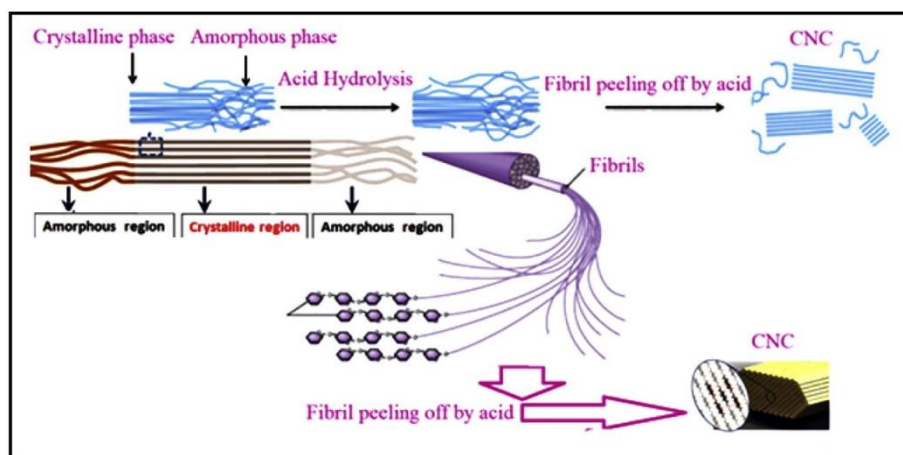


Fig. 1. Extraction of cellulose nanocrystal (CNC) [6]

Cellulose nanocrystals have received a significant amount of attention in different areas such as energy and electronic sectors, wastewater treatment, biomedical, heat transfer, drilling, food and packaging, concrete etc. A brief review is primarily devoted to highlighting recent work by various researchers on applications of cellulose nanocrystals in various fields and also exploring the perspectives of the application of cellulose nanocrystals on heat transfer technology.

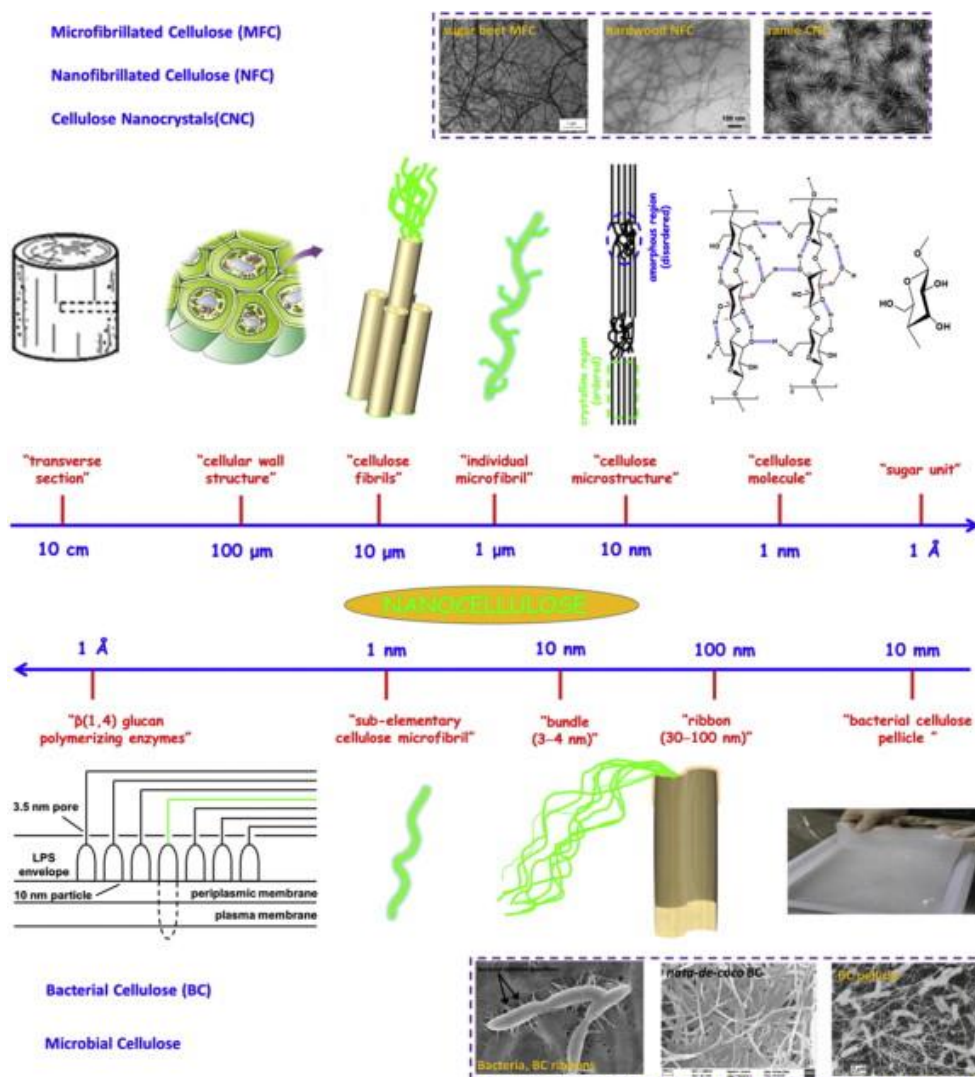


Fig. 2. Hierarchical structure of cellulose: top image: plant cellulose; bottom image: bacterial cellulose [7]

2. Heat transfer application

Numerous research results have shown that nanofluids have outstanding thermophysical properties and are an interesting candidate for applications of heat transfer. Such nanofluids usually contain metal oxide particles like TiO_2 and SiO_2 , but these metal oxides can lead to significant pollution issues. Therefore, a study focuses on introducing the potential of using a plant-based material such as CNC to develop an enhanced and environmentally friendly material for heat transfer applications. Ramachandran *et al.*, [9] measured the thermal conductivity and viscosity of nanocellulose with the weight concentration of 40/60% (EG-water) volume ratio. Experiments were conducted in the temperature range from 30 °C to 70 °C and in the volume concentration range from

0.1% to 1.3%. Results indicated that the thermal conductivity increases with the increase of mixture temperature and volume of the nanofluid. The enhancement ratio was 1.104 times at 1.3%. Meanwhile, they also found that the viscosity decreases exponentially with temperature and increases as the volume fraction increases. The enhancement ratio was 4.16 times at 1.3%. The author also proposed a new correlation to predict the thermal properties of CNC.

The same author [10] carried out combined experimental-statistical approach for effective thermal conductivity and relative viscosity determination in (EG-water) mixture. CNC were prepared by two different ways, (1) Nanoparticles dispersed in ethylene glycol and water in the ratio of 40: 60, and (2) Nanoparticles dispersed in ethylene glycol and water in the ratio of 50: 50 by weight. The maximum effective thermal conductivity was 1.127 which is recorded at volume concentration 0.9%, temperature of 70 °C and BR of 0.5. Observations showed that effective thermal conductivity depends on the particle volumetric concentration and the temperature. The maximum relative viscosity recorded was 4.521 at volume concentration of 0.9%, 70 °C and BR 0.5. Relative viscosity had proportional relation with volume concentration and temperature.

Another work by same author [11] experimentally studied the density and specific heat capacity for CNC nanoparticles suspended in 40: 60 (by weight) EG and water mixture. Experiments were performed using nanofluids with particle volume percentage from 0.1% to 0.9% and temperatures 30°C to 90 °C. The value of density was found to be highest at a temperature of 30°C and volume concentration of 0.9%. Their result also recorded maximum specific heat capacity is 3972J/kg.°C at a temperature of 90°C and volume concentration of 0.1%. The author also proposed empirical model for relative specific density and relative specific heat capacity.

Meanwhile, a number of studies on CNC in heat transfer application were carried out by some researchers. Samyilingam *et al.*, [12] investigated the thermophysical properties of cellulose nanocrystal (CNC) – ethylene glycol (EG) + Water (W) based nanofluid and the capable to improve the thermal transport and machining performance. Their results prove that the nanofluid capable of reducing the heat generated by the cutting tool which leads for improved tool life. Also, CNC based nanofluid evidently proved to be superior heat transfer fluid compared to MWF to be used in machining operation in conjunction with MQL technique.

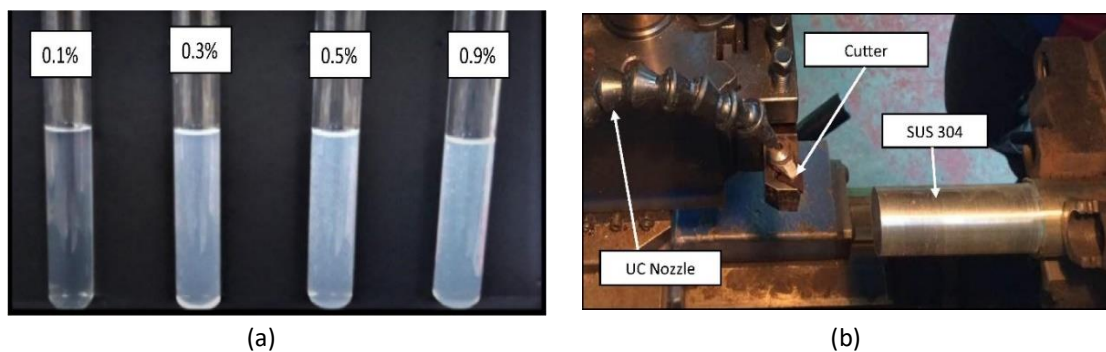


Fig. 3. (a) Sedimentation observation, (b) Lathe machining setup [12]

In another study, Kadirgama *et al.*, [13] conducted a research to evaluate ethylene glycol/nanocellulose-based nanofluid in terms of its thermo-physical properties and its effectiveness in machining performances which is temperature distribution in cutting tool and compare its effectiveness with MWF. They found out that ethylene glycol/nanocellulose-based nanofluid coolant better than the conventional machining coolant which is MWF in MQL cooling system due to a lower

percentage of Aluminum of 7.14 wt% cutting tool and more carbon 45.06 wt% with less continuous chips formed.

Furthermore, Anamalai *et al.*, [14] extended this work to investigate the optimized machining parameters (cutting speed, feed rate and depth of cut) for machining using CNC-based nanofluid. By comparing between CNC and MWF using MQL coolant system it was found that the selected nanofluid concentration (0.5%) shown to have a superior thermal conductivity (0.449 W m⁻¹ K⁻¹) than conventional MWF (0.267 W m⁻¹ K⁻¹) at 30 °C. The obtained heat transfer at cutting tool using MWF was 1130 J, while CNC-based nanofluid was 863 J.

Awang *et al.*, [15-16] proposed a Cellulose Nanocrystals (CNC) as green additives for improving tribological properties of lubricants in engine oil. It emerged nano lubricant of CNC particles at 0.1 wt% concentration was the most suitable concentration for improving properties of SAE 40 engine oil. In addition, best results were obtained for nano lubricants with 0.1 wt% of CNC nanoparticles for the reduction of COF. Meanwhile, for the wear rate value, the reduction was observed maximum, up to 69% when the concentration of 0.1% CNC. Also, it shows that the addition of CNC nanoparticles exhibited improved wear behavior compared to the base oil SAE 40.

Benedict *et al.*, [17-18] numerically and experimentally investigated convection heat transfer coefficients of CNC and Al₂O₃/CNC nanofluids for different base mixture at concentration of 0.1%, 0.5%, and 0.9% and working temperature of 30, 50, 70°C in 40:60(EG:W) base mixture fluid with volume concentration of 0.1%, 0.5%, 0.9% and 1.3% in radiator coolant. Their result revealed addition of CNC provides a better heat transfer efficiency compared to usage of distilled water as radiator coolant.

Naiman *et al.*, [19-20] studied the performance characteristics and effectiveness of the radiator with addition of nanoparticles (CNC). It was found that 0.5% of volume concentration nanofluid of ratio 60:40 (EG:W) displays a better rate of heat transfer compared to distilled water. Also, thermal conductivity test showed cellulose nanofluids have better thermal conductivity compared to Ethylene Glycol and the highest thermal conductivity possessed by 0.5% cellulose nanofluids was 0.519 W/m.°C .

Table 2
 The variant of CNC study in heat transfer applications

Author	Study	Base fluid/oil	concentration
Ramachandran <i>et al.</i> , [9]	<ul style="list-style-type: none"> •experimental • thermal conductivity •viscosity 	(EG-water) 40/60% volume	•0.1,0.5,0.9,1.3
Ramachandran <i>et al.</i> , [10]	<ul style="list-style-type: none"> •experimental-statistical approach(theoretical) • effective thermal conductivity •relative viscosity 	(EG-water) •50:50 (BR = 0.5) •60:40 (BR = 0.6)	•0.1,0.5,0.9
Ramachandran <i>et al.</i> , [11]	<ul style="list-style-type: none"> •experimental-statistical approach(theoretical) • density • specific heat capacity 	(EG-water) 40/60% volume	•0.1,0.5,0.9
Samyilingam <i>et al.</i> , [12]	<ul style="list-style-type: none"> •experimental • thermal conductivity •viscosity •Cutting tool and chip thermal analysis 	(EG-water) 40/60% volume	•0.1,0.3,0.5,0.7,0.9,1.1,1.3,.5

Kadirgama <i>et al.</i> , [13]	<ul style="list-style-type: none"> •experimental • thermal conductivity •viscosity •Thermal analysis at cutting tool •Thermal distribution of chip •Surface roughness 	(EG-water) 40/60% volume	•0.1,0.5,0.9,1.3
Anamalai <i>et al.</i> , [14]	<ul style="list-style-type: none"> •experimental • thermal conductivity •viscosity •Cutting tool thermal behavior •Analysis of thermal distribution at the chip formation •Multi-objective optimization 	(EG-water) 40/60% volume	•0.1,0.5,0.9,1.3
Awang <i>et al.</i> , [15]	<ul style="list-style-type: none"> •experimental •Tribological properties •Worn morphology •Kinematic viscosity •Viscosity index VI 	engine oil SAE 40	•0.1,0.3,0.5,0.7,0.9
Awang <i>et al.</i> , [16]	<ul style="list-style-type: none"> •experimental •Kinematic viscosity •Viscosity index VI 	engine oil SAE 40	•0.1,0.3,0.5,0.7,0.9
Benedict <i>et al.</i> , [17]	<ul style="list-style-type: none"> •experimental •simulation 1 dimensional 	(EG-water) 40/60% volume	0.5
Benedict <i>et al.</i> , [18]	<ul style="list-style-type: none"> •experimental • thermal conductivity •viscosity • density • specific heat capacity 	(EG-water) 40/60% volume	•0.1,0.5,0.9,1.3
Naiman <i>et al.</i> , [19]	<ul style="list-style-type: none"> •experimental •simulation 1 dimensional • thermal conductivity •viscosity 	(EG-water) 40/60% volume	•0.1,0.5,0.9,1.3
Naiman <i>et al.</i> , [20]	<ul style="list-style-type: none"> •experimental •simulation 1 dimensional 	(EG-water) 60/40% volume	•0.1,0.5,0.9

3. Biomedical engineering

3.1 Drug Engineering

Due to their biocompatibility, biodegradability and stimulus sensitivity, nanocelluloses and their derivatives are ideal candidates for controlled drug delivery systems. Nanocellulose's unique physicochemical, rheological and barrier properties help make sure that air / water and oil / water interfaces are stabilized. Their large area-to-volume ratios also give an opportunity for positive molecular interactions with drugs that are poorly soluble. Wan et al produced a novel green technology of preparing CNC/gelatin hydrogels utilizing gamma which potentially suitable for drug-delivery applications [21]. Three hydrogels were tested namely, gelatin hydrogel (100% gelatin), hydrogel A (cellulose/gelatin), and hydrogel B (CNCs/gelatin) to examine the efficiency of drug release, and they were found that CNC/gelatin hydrogel get 20% of riboflavin loading, which indicated the higher drug-loading efficiency. In addition, the CNC/gelatin hydrogel being a better drug carrier because it was more rigid and exhibited a higher storage modulus and more rigid pores than the gelatin hydrogel.

Magnetic nanocellulose alginate hydrogel beads were prepared by Supramaniam et al which act as a carrier for ibuprofen delivery application [22]. They modified the CNCs using co-precipitation method with iron oxide nanoparticles after extracted from rice husk waste via acid hydrolysis. Then, they combined alginate hydrogels beads with Magnetic cellulose nanocrystals. They obtained that the encapsulation efficiencies of the beads with 3 wt% m-CNCs relative to alginate increase and reaches an optimum level of 38%. Meanwhile, the drug loading started to drop to 3.1% and 1.3% when the amount of m-CNCs was increased to 6% and 10%.

Orasugh and co-authors [23] researched the influence of cellulose nanocrystals (CNC) on the in-situ gelation behavior of Poloxamer 407 (PM) and in vitro release of pilocarpine hydrochloride from the nanocomposites formulations. They found that the addition of nanocellulose to 16.6% (wt/v) poloxamer sol-gel led to an increase in the strength of the gel to a higher percentage. The interaction between H₂O and poloxamer 407 molecules have been reduced by the hydrophilic CNC which reducing the temperature of gel formation and the gelation energy. They also obtained that compared with the pure PM gel, the reinforcing nature of CNC via H-bonding in the in-situ nanocomposite gel has also led to the gel strength increased along with the sustained release of loaded drugs.

Jayaramudu *et al.*, [24] investigated swelling behavior of cellulose nanocrystal (CNC)-based polyacrylamide hydrogels produced via free-radical polymerization. They reported that the PAC hydrogels showed excellent swelling behaviors in terms of pH, temperature, and temperature with pH. The PAC3 hydrogel exhibited a 6 times higher swelling ratio than the initial condition when the pH with temperature increasing. They also found that the swelling ratio gradually increased with time at room temperature, and the CNC content affected the swelling ratio.

3.2 Tissue Engineering

CNCs have been commonly used in tissue engineering for the past few years due to their highly hydrated three-dimensional porous structure which mimics biological tissue, as well as the excellent mechanical properties by integrating CNCs. Their usage has been researched in certain applications, such as bone tissue regeneration, vascular grafts, injectable tissue scaffolds, and improving bone implant adhesion. For instance, Zheng *et al.*, [25] explored the possible mechanisms and therapeutic efficacy of NT-loaded PLGA/CNC nanofiber membranes in full-thickness skin wounds in spontaneously diabetic mice. They reported that PLGA/CNC/NT resulted in the sustained release of NT, which had powerful anti-inflammatory activities by inhibiting IL-1b and IL-6. PLGA/CNC/NT nanofiber membranes successfully accelerated collagen deposition and re-epithelialization of diabetic wounds. Hence, PLGA/CNC/NT nanofiber membranes for sustained delivery of NT may effectively promote tissue regeneration for the treatment of DFUs.

Shaheen *et al.*, [26] fabricated the chitosan/alginate/hydroxyapatite/nanocrystalline cellulose scaffolds via freeze-drying method. They evaluated effect of impregnation of CNC in the 3D network scaffold composed of chitosan/alginate/hydroxyapatite (SC-HA) composite on the properties respecting to bone tissue engineering application. Their results revealed that all prepared scaffolds containing CNC exhibited a worthy enhancement in their properties such as swelling, porosity and compression strength. Moreover, the scaffold with 1.0% CNC showed the highest improvement in the forementioned properties.

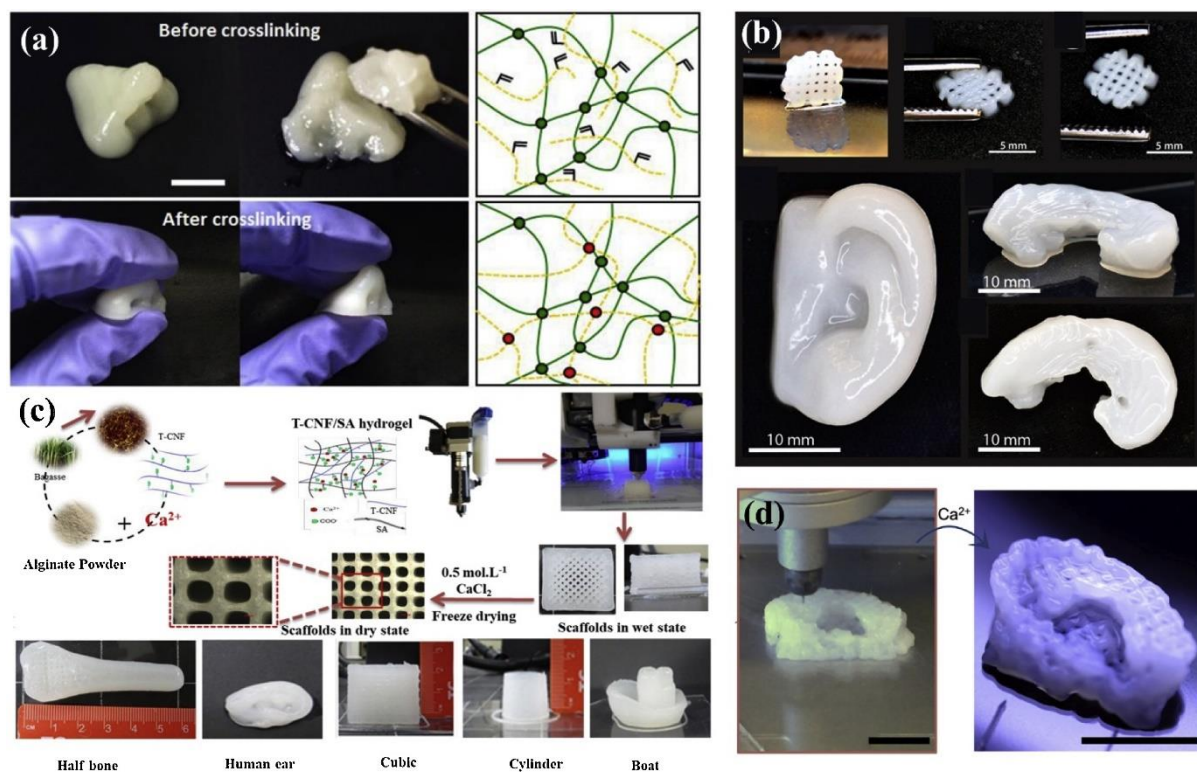


Fig. 4. (a) 3D printed human nose structure before and after chemical crosslinking of GelMA. (b) 3D printed small grids and human ear with Ink8020. (c) Fabrication process for 3D printing scaffolds from T-CNF/SA hydrogels and scaffolds printed in different forms and designs from the optimum hydrogel formulation. (d) Image of a 3D printed human ear with human nasal chondrocytes (hCN)-laden auricular constructs and open inner structure formed by Ca²⁺ ionic cross-linking [27]

Osorio *et al.*, [28] showed that HA/CNC based scaffold, cross-linked with either sulfate half-ester groups (S-CNCs) or phosphate half-ester groups (P-CNCs), have potential as bone tissue scaffolds through preliminary *in vitro* protein adhesion studies and simulated body fluid (SBF) testing. They found that S-CNC and P-CNC aerogels exhibited ideal scaffold characteristics, including macropores in the range of 10–950 μm to allow cell migration, unique mesopore morphology, and a large specific surface area to promote cell adhesion and proliferation. In addition, SBF testing showed that aerogels were capable of growing HA after a CaCl₂ pre-treatment, showing potential for osteoconduction *in vivo*.

Another work evaluated the thermo-mechanical properties and cell proliferation of cellulose nanocrystals (CNC), poly (butylene adipate-co-terephthalate) (PBAT), poly(ϵ -caprolactone) (PCL) films and their bionanocomposites with 2 wt% of CNC obtained by casting technique. They reported that the addition of CNCs in the PBAT and PCL matrices induced higher storage moduli due to the reinforcement effects of CNCs. Cell proliferation assay of pure CNC indicated CNC contributes to osteoblasts proliferation. The nature of the polymeric matrix or the presence of CNC among the films practically does not affect the cell proliferation [29].

4. Wastewater treatment

Water can be contaminated by industrial waste that often contains large quantities of heavy metals such as lead, copper, mercury, chromium and zinc when disposed incorrectly. Owing to their high tendency for bioaccumulation, these heavy metals are highly toxic and could damage the brain

cells, the cardiovascular, central nervous, endocrine, and digestive systems of humans, animals, also harm a plant. Therefore, CNC which have demonstrated excellent adsorption capacity are used to eliminate heavy metals from wastewater. Liu et al grafted CNC with polyacrylamide and poly (N, N-dimethylacrylamide) via “macro-RAFT assisted” strategy for the flocculation of kaolin suspension. It was found that flocculants with highest carboxylic content appear best flocculation performance. Other than that, flocculants with settling time as 2 min also showed efficient flocculation. The author also suggested polymer modified cellulose nanocrystals as flocculants might have higher flocculation performance, but needs further verification [30].

Meanwhile, an adsorption of methylene blue (MB) by self-assembled nanocrystalline cellulose (NCC) flakes was investigated by Tan *et al.*, [31]. Their result showed that self-assembled NCC flakes have the highest maximum adsorption capacity (188.87 mg/g) compared to other more toxic nanomaterials. In addition, their work is greener because it only need water to self-assemble the NCC flakes compared to self-assembled carbon nanotubes, which require additional chemicals.

In other study, Rani and his team [32] produced Banana fiber Cellulose Nano Crystals grafted with butyl acrylate for the removal of toxic heavy metal lead (II) from aqueous solution. Their results revealed that the removal of Pb (II) increased with the increase in the contact time and reached a maximum at 360 min. Also, the removal efficiency increased with the increase of adsorbent dosage, contact time and the decrease of initial metal concentration.

5. Energy and Electronic Sector

5.1 Supercapacitors

Abidin *et al.*, [33] have compared hybrid nanocomposites of PEDOT doped with three different carbon materials (MWCNT, GO, and NCC), were successfully prepared using a facile potentiostatic method. They reported an incorporation of PEDOT with GO shows the highest specific capacitance (120.13 F/g) and excellent stability retention (87.99%) due to the higher mechanical strength and larger surface area provided by GO.

Lyu *et al.*, [34] developed an aerogel based on wood pulp fibre (WPF) and cellulose nanocrystals (CNC), for use as a porous substrate for LbL assembly of nanostructural polyaniline (PANI) and graphene oxide (GO) or carboxylic multi-walled carbon nanotubes (CMCNT). Their results reveal that assembled symmetric supercapacitors also have very high real specific capacitances (1.95 and 1.49 F cm⁻²) and good energy density (168.64 and 113.57 mW h cm⁻²). Moreover, the aerogel electrodes also showed stable cycling performance, good rate capability, and flexibility.

Kulandaivalu and Sulaiman [35] have designed bilayer composite (PPy/rGO and MWCNT/rGO/NCC) film prepared by in-situ polymerization through a vacuum filtration method followed by a chemical reduction in the presence of hydrazine vapor. The r-PGMGN showed mesopores with high surface area (106.02 m² g⁻¹) by combining the pseudocapacitance of PPy and electrical double layer capacitance of carbon materials in an LBL assembly. They also exhibited a high specific capacitance of 882.2 F g⁻¹ at 10 mV s⁻¹ with an extraordinary specific energy 44.6 Wh kg⁻¹.

5.2 Sensors

Hiratani *et al.*, [36] reported that centimeter-scale mono-domain hydrogels with high loadings sulfate half-ester-functionalized CNCs with a nematic organization can be fabricated using mechanical shearing indicating the potential for novel types of optics and sensors with a wide variety of possible stimuli-responsive optical properties. Their results showed higher concentration makes the sheared CNC hydrogel (SH4) shrink with a drastic change in the volume ratio ($\Delta V/V_0 \approx 0.55$). Also,

the change in the swelling ratio for SH4 is very sensitive to [NaCl], responding even at $\approx 10^{-3}$ M which is much lower concentration in comparison with that for the 1D photonic hydrogel composed of ionic block-copolymer ($>10^{-2}$ M).

Zhang *et al.*, [37] synthesized a novel dual-emitting fluorescent phosphor from cellulose nanocrystal (CNC)- assisted carbon dots (CDs)-grafted SrAl_2O_4 , Eu^{2+} , Dy^{3+} (SAO) through a facile core-shell process for temperature sensing. Their results reveal relatively good cycling performance, which illustrates the reusable characteristics of the sensing films for temperature monitoring between 243 and 383 K. Additionally, strong linear behavior was obtained for such sensitive sensors.

Daniyal *et al.*, [38] has been developed an optical sensor for Cu^{2+} by combining the SPR with nanocrystalline cellulose modified by hexadecyltrimethylammonium bromide and graphene oxide composite (CTA-NCC/GO) thin film. It was found that the SPR sensor in Cu^{2+} sensing was enhanced in the presence of CTA-NCC/GO when compared with bare gold thin film. Also, CTA-NCC/GO-SPR sensor can detect Cu^{2+} as low as 0.01 ppm until 0.5 ppm. Moreover, CTA-NCC/GO thin film has high binding affinity constant towards Cu^{2+} , i.e. $4.075 \times 10^3 \text{ M}^{-1}$.

6. Other applications

6.1 Drilling

Li *et al.*, [39-40] demonstrated the effectiveness of cellulose nanoparticles (CNPs), including microfibrillated cellulose (MFC) and cellulose nanocrystals (CNCs) in enhancing the rheological and filtration performances of bentonite (BT) water-based drilling fluids (WDFs). MFC and CNCs were added to increase the rheological properties of BT-WDFs, including the viscosity, shear stress, and yield point, demonstrating the development in the cuttings transport capacity. Also, CNCs yielded better rheological and filtration performances than MFC in BT-WDFs application.

Song *et al.*, [41-42] investigated effects of CNP dimension and concentration on the rheological and filtration properties of the fluids. They found that due to the excellent shear thinning properties of water suspensions of CNPs, fluids with CNPs showed similar non-Newtonian fluid behavior to the control fluid. In addition, the viscosity, yield point, and gel strength of the fluids increased with an increasing concentration of CNPs.

6.2 Food Sector

Hutton-Prager *et al.*, [43] investigated improvements in thermal barrier performance and hydrophobicity of Nano- TiO_2 , nanoclay, and cellulose nanocrystals (CNC) which introduced into calcium carbonate coatings common in paper/paperboard applications. From their result, it was found coated samples with CNC showed excellent thermal barrier performance; reduced thermal conductivity; and improvement in hydrophobicity. Also, an additional 28.3°C temperature difference, or 2.5 times improvement, across the coated substrate and a 22% reduction in k when 2% CNC added to the base formulation.

Oliveira *et al.*, [44] produced aerogels by obtaining cellulose nanocrystals from valorization of rice and oat husks for food packaging applications. Their results revealed that water absorption capacity of aerogels of cellulose nanocrystals ranged from 264.2% to 402.8% and the aerogel of oat cellulose nanocrystals had the highest water absorption.

6.3 Oil-Pickering emulsion

Ojala *et al.*, [45] studied preparation and properties of marine diesel oil-in-water (o/w) emulsion stabilized by bifunctionalized cellulose nanocrystals (But-CNCs). It was found that bifunctionalized CNCs reduced the oil-droplet size in emulsions and acted as a stabilizer. Meanwhile, increasing the salt (NaCl) concentration in the emulsions increased the oil-droplet size, but at the highest concentration (5% [wt]) the droplet sizes were still over 50% smaller than with the reference sample in the absence of electrolytes.

Pandey *et al.*, [46] reported an oil-in-water emulsions stabilized by cellulose nanocrystals (CNCs) with two different degrees of surface charge and aggregation state. Their result showed that emulsions stabilized by a-CNCs had faster adsorption kinetics due to the lower electrostatic barrier between the particles and the oil/water interface which resulted in a smaller droplet size, a lower interfacial coverage owing to the higher aspect ratio of aggregated a-CNCs, a multilayer of CNCs at the interface, and a smaller amount of non-adsorbed CNCs in the continuous phase.

6.4 Concrete

Barnat-Hunek *et al.*, [47] studied the impact of ACNF and CCNC on the physical properties, durability and microstructure of concrete. They found that in CCNC1 mixture, the compressive strength increased by 37.9%, while in ACNF1 mixture, it improved by 23.3%. This is due to different structure of both nanocelluloses: ACNF is longer and has lower crystallinity degree than CCNC. Meanwhile, the density improved, change pore structure and interface characteristics, concrete 's strength improved, the freezing-thawing resistance and hydrophobic properties by using nanocellulose.

Table 3

The application of CNC with the specific and product features

Application field	Specific field	Product features	References
Heat transfer	thermophysical properties measurement	CNC + water-EG	[9]
	thermophysical properties measurement	CNC + water-EG	[10]
	thermophysical properties measurement	CNC + water-EG	[11]
	Machining performance study	CNC + water-EG	[12]
	Machining performance study	CNC + water-EG	[13]
	Machining performance study	CNC + water-EG	[14]
	lubricating additive in engine oil	CNC + engine oil SAE 40	[15], [16]
	Car radiator coolant	CNC + water-EG	[17] , [18]
	Car radiator coolant	CNC + water-EG	[19], [20]

Biomedical	Drug delivery	CNC+ gelatin hydrogels + gamma radiation	[21]
	Ibuprofen delivery	CNC + magnetic NP + alginate hydrogel beads	[22]
	Drug delivery	CNC +Poloxamer 407 (PM)	[23]
	Drug delivery	CNC +PAC hydrogels	[24]
	Tissue/wound	CNC+PLGA+ NT	[25]
	bone tissue	CNC+Chitosan+alginate+SC-HA	[26]
	bone tissue	P-CNCs /S-CNCs+HA	[28]
	tissue	CNC+ PBAT+ PCL	[29]
Wastewater treatment	flocculants	CNC + polyacrylamide CNC +poly(N,N-dimethylacrylamide)	[30]
	adsorbents	NCC flakes	[31]
	adsorbents	CNC + butyl acrylate	[32]
Energy & Electronic sector	supercapacitors	MWCNT, GO, and NCC	[33]
	supercapacitors	(CNC) (PANI) (CMCNT)	[34]
	supercapacitors	(PPy/rGO and MWCNT/rGO/NCC)	[35]
	sensors	CNC hydrogel (SH4)	[36]
	temperature sensing	(CNC)- assisted carbon dots (CDs)-grafted SrAl ₂ O ₄ , Eu ²⁺ , Dy ³⁺ (SAO)	[37]
	optical sensor	CTA-NCC/GO-SPR	[38]
drilling	drilling	bentonite (BT) water-based drilling fluids (WDFs)	[39], [40]
	drilling	CNPs, BT, and other additives including sodium hydroxide, lignite, polyanionic cellulose (PAC), and Rev dust were	[41], [42]
Food	Food packaging	Nano-TiO ₂ , nanoclay, and cellulose nanocrystals (CNC)	[43]
	Food packaging	CNC + poly (vinyl alcohol) (PVA)	[44]
Oil-Pickering emulsion	marine diesel oil-in-water (o/w) emulsion	bifunctionalized cellulose nanocrystals (But-CNCs)	[45]
	oil-in-water emulsions stabilized	CNC + HCl, CNC + NaOH	[46]
concrete	properties & durability of concrete with admixture cellulose nanocrystals (CCNC)	concrete with carrot cellulose nanocrystals (CCNC)	[47]

7. Conclusion

Cellulose is the most ancient and important natural polymer on earth. It is proved to be an excellent replacement for oil, coal, natural gas, and other natural resources and the growing concern over white pollution produced by plastic. Nanocellulose is defined as the products or extracts from native cellulose (found in plants, bacteria and animals,) composed of the nanoscaled structure material. The present article comprehensively reviews the current state of research and future development of cellulose nanocrystals in the application through the discussion of selected paper. Undoubtedly, cellulose nanocrystals have tremendous potential for greater involvement in industry and modern society.

CNCs have drawn industry and academic community attention because of their interesting characteristics such as low cost, extraction from renewable sources, low toxicity, high mechanical properties. The high thermal conductivity nanofluid have the ability of acting as a thermal transporter by carrying most of the heat produced and thus prolong the tool failure and helps to produce fine surface finish on the workpiece for heat transfer sector. Furthermore, their biocompatibility enables their usage as tissue scaffolds for bone regeneration and when loaded with bioactive molecules, the sustained release of drugs after grafting could improve the medical treatments. Meanwhile, the potential to destabilized by contaminants makes them efficient flocculants and give strength to membranes for filtration applications in wastewater treatment. In addition, the large surface area improves charge storage for supercapacitors, while the porous structures make them ideal for use as separators in batteries. There are also possibilities for the use of CNCs in cosmetics and engineered food formulations due to the promising characteristics of CNCs and their low toxicity, both of which can enhances the health and well-being of civilization.

Finally, various CNC-based commercial products, inventions and patents illustrate the scientific and technological outcome from this multipurpose nanomaterial. Reported literature on cellulose nanocrystals have provide the route to remarkable advancement with the aptitude of even greater advances foresaw to come in the future.

References

- [1] Nickerson, R. F., and J. A. Habrle. "Cellulose intercrystalline structure." *Industrial & Engineering Chemistry* 39, no. 11 (1947): 1507-1512.
- [2] Dong, Xue Min, Tsunehisa Kimura, Jean-François Revol, and Derek G. Gray. "Effects of ionic strength on the isotropic–chiral nematic phase transition of suspensions of cellulose crystallites." *Langmuir* 12, no. 8 (1996): 2076-2082.
- [3] Hanley, Shaune J., Julie Giasson, Jean-François Revol, and Derek G. Gray. "Atomic force microscopy of cellulose microfibrils: comparison with transmission electron microscopy." *Polymer* 33, no. 21 (1992): 4639-4642.
- [4] Miao, Chuanwei, and Wadood Y. Hamad. "Cellulose reinforced polymer composites and nanocomposites: a critical review." *Cellulose* 20, no. 5 (2013): 2221-2262.
- [5] Bitinis, Natacha, Elena Fortunati, Raquel Verdejo, Julien Bras, Jose Maria Kenny, Luigi Torre, and Miguel Angel López-Manchado. "Poly (lactic acid)/natural rubber/cellulose nanocrystal bionanocomposites. Part II: Properties evaluation." *Carbohydrate polymers* 96, no. 2 (2013): 621-627.
- [6] Mishra, Raghvendra Kumar, Arjun Sabu, and Santosh K. Tiwari. "Materials chemistry and the futurist eco-friendly applications of nanocellulose: Status and prospect." *Journal of Saudi Chemical Society* 22, no. 8 (2018): 949-978.
- [7] Lin, Ning, and Alain Dufresne. "Nanocellulose in biomedicine: Current status and future prospect." *European Polymer Journal* 59 (2014): 302-325.
- [8] Klemm, Dieter, Friederike Kramer, Sebastian Moritz, Tom Lindström, Mikael Ankerfors, Derek Gray, and Annie Dorris. "Nanocelluloses: a new family of nature-based materials." *Angewandte Chemie International Edition* 50, no. 24 (2011): 5438-5466.
- [9] Ramachandran, Kaaliarasan, A. M. Hussein, K. Kadirgama, D. Ramasamy, W. H. Azmi, F. Tarlochan, and G. Kadirgama. "Thermophysical properties measurement of nano cellulose in ethylene glycol/water." *Applied Thermal Engineering* 123 (2017): 1158-1165.

- [10] Ramachandran, K., K. Kadirgama, D. Ramasamy, W. H. Azmi, and F. Tarlochan. "Investigation on effective thermal conductivity and relative viscosity of cellulose nanocrystal as a nanofluidic thermal transport through a combined experimental–Statistical approach by using Response Surface Methodology." *Applied Thermal Engineering* 122 (2017): 473-483.
- [11] Ramachandran, Kaaliarasan, Kumaran Kadirgama, Devarajan Ramasamy, Mahendran Samykan, Lingenthiran Samyalingam, Faris Tarlochan, and Gholamhassan Najafi. "Evaluation of Specific Heat Capacity and Density for Cellulose Nanocrystal-based Nanofluid." *J. Adv. Res. Fluid Mech. Therm. Sci.* 51, no. 2 (2018): 169-186.
- [12] Samyalingam, L., K. Anamalai, K. Kadirgama, M. Samykan, D. Ramasamy, M. M. Noor, G. Najafi, M. M. Rahman, Hong Wei Xian, and Nor Azwadi Che Sidik. "Thermal analysis of cellulose nanocrystal-ethylene glycol nanofluid coolant." *International Journal of Heat and Mass Transfer* 127 (2018): 173-181.
- [13] Kadirgama, K., K. Anamalai, K. Ramachandran, D. Ramasamy, M. Samykan, A. Kottasamy, and M. M. Rahman. "Thermal analysis of SUS 304 stainless steel using ethylene glycol/nanocellulose-based nanofluid coolant." *The International Journal of Advanced Manufacturing Technology* 97, no. 5-8 (2018): 2061-2076.
- [14] Anamalai, K., L. Samyalingam, K. Kadirgama, M. Samykan, G. Najafi, D. Ramasamy, and M. M. Rahman. "Multi-objective optimization on the machining parameters for bio-inspired nanocoolant." *Journal of Thermal Analysis and Calorimetry* 135, no. 2 (2019): 1533-1544.
- [15] Awang, N. W., D. Ramasamy, K. Kadirgama, G. Najafi, and Nor Azwadi Che Sidik. "Study on friction and wear of Cellulose Nanocrystal (CNC) nanoparticle as lubricating additive in engine oil." *International Journal of Heat and Mass Transfer* 131 (2019): 1196-1204.
- [16] Awang, N. W., D. Ramasamy, K. Kadirgama, M. Samykan, G. Najafi, and Nor Azwadi Che Sidik. "An experimental study on characterization and properties of nano lubricant containing Cellulose Nanocrystal (CNC)." *International Journal of Heat and Mass Transfer* 130 (2019): 1163-1169.
- [17] Benedict, F., K. Kadirgama, D. Ramasamy, M. M. Noor, M. Samykan, M. M. Rahman, Z. Ghazali, and B. Sagmesh. "Nanocellulose as heat transfer liquid in heat exchanger." In *AIP Conference Proceedings*, vol. 2059, no. 1, p. 020044. AIP Publishing, 2019.
- [18] Benedict, F., K. Kadirgama, D. Ramasamy, M. M. Noor, M. Asok Raj Kumar, M. M. Rahman, Z. Ghazali, and B. Sagmesh. "Thermal management of vehicle radiator by nanocellulose with one-dimensional analysis." In *AIP Conference Proceedings*, vol. 2059, no. 1, p. 020043. AIP Publishing, 2019.
- [19] Ibrahim, Ihsan Naiman, Norazlianie Sazali, Devarajan Ramasamy, Ahmad Shahir Jamaludin, Mohd Syafiq Sharip, and Haziqatulhanis Ibrahim. "Effect of Impregnate Nanocellulose With Ethylene Glycol for Car Radiator Application." *J. Adv. Res. Fluid Mech. Therm. Sci.*, 58, no. 1 (2019): 43–50.
- [20] Naiman, I., D. Ramasamy, and K. Kadirgama. "Experimental and one dimensional investigation on nanocellulose and aluminium oxide hybrid nanofluid as a new coolant for radiator." In *IOP Conference Series: Materials Science and Engineering*, vol. 469, no. 1, p. 012096. IOP Publishing, 2019.
- [21] Wan Ishak, Wan, Ishak Ahmad, Suria Ramli, and Mohd Mohd Amin. "Gamma Irradiation-Assisted Synthesis of Cellulose Nanocrystal-Reinforced Gelatin Hydrogels." *Nanomaterials* 8, no. 10 (2018): 749.
- [22] Supramaniam, Jagadeesen, Rohana Adnan, Noor Haida Mohd Kaus, and Rani Bushra. "Magnetic nanocellulose alginate hydrogel beads as potential drug delivery system." *International journal of biological macromolecules* 118 (2018): 640-648.
- [23] Orasugh, Jonathan Tersur, Gunjan Sarkar, Nayan Ranjan Saha, Beauty Das, Amartya Bhattacharyya, Sreyasi Das, Roshnara Mishra et al. "Effect of cellulose nanocrystals on the performance of drug loaded in situ gelling thermo-responsive ophthalmic formulations." *International journal of biological macromolecules* 124 (2019): 235-245.
- [24] Li, Peng, Nam Hoon Kim, and Joong Hee Lee. "Swelling behavior of polyacrylamide/laponite clay nanocomposite hydrogels: pH-sensitive property." *Composites Part B: Engineering* 40, no. 4 (2009): 275-283.
- [25] Zheng, Zhifang, Yishu Liu, Wenhua Huang, Yunfei Mo, Yong Lan, Rui Guo, and Biao Cheng. "Neurotensin-loaded PLGA/CNC composite nanofiber membranes accelerate diabetic wound healing." *Artificial cells, nanomedicine, and biotechnology* 46, no. sup2 (2018): 493-501.
- [26] Shaheen, Th I., A. S. Montaser, and Suming Li. "Effect of cellulose nanocrystals on scaffolds comprising chitosan, alginate and hydroxyapatite for bone tissue engineering." *International journal of biological macromolecules* 121 (2019): 814-821.
- [27] Du, Haishun, Wei Liu, Miaomiao Zhang, Chuanling Si, Xinyu Zhang, and Bin Li. "Cellulose nanocrystals and cellulose nanofibrils based hydrogels for biomedical applications." *Carbohydrate polymers* (2019).
- [28] Osorio, Daniel A., Bryan EJ Lee, Jacek M. Kwiecien, Xiaoyue Wang, Iflah Shahid, Ariana L. Hurley, Emily D. Cranston, and Kathryn Grandfield. "Cross-linked cellulose nanocrystal aerogels as viable bone tissue scaffolds." *Acta biomaterialia* 87 (2019): 152-165.
- [29] Branciforti, Marcia Cristina, Caroline Faria Bellani, Carolina Lipparelli Morelli, Alice Ferrand, Nadia Benkirane-Jessel, and Rosario Elida Suman Bretas. "Poly (Butylene Adipate-Co-Terephthalate) and Poly (ϵ -Caprolactone) and Their

- Bionanocomposites with Cellulose Nanocrystals: Thermo-Mechanical Properties and Cell Viability Study." (2019).
- [30] Liu, Ting, Enyong Ding, and Feng Xue. "Polyacrylamide and poly (N, N-dimethylacrylamide) grafted cellulose nanocrystals as efficient flocculants for kaolin suspension." *International journal of biological macromolecules* 103 (2017): 1107-1112.
- [31] Tan, Kok Bing, Alavy Kifait Reza, Ahmad Zuhairi Abdullah, Bahman Amini Horri, and Babak Salamatinia. "Development of self-assembled nanocrystalline cellulose as a promising practical adsorbent for methylene blue removal." *Carbohydrate polymers* 199 (2018): 92-101.
- [32] Rani, K., T. Gomathi, K. Vijayalakshmi, M. Saranya, and P. N. Sudha. "Banana fiber Cellulose Nano Crystals grafted with butyl acrylate for heavy metal lead (II) removal." *International journal of biological macromolecules* 131 (2019): 461-472.
- [33] Abidin, Syed Zainol, Shariffah Nur Jannah, Nur Hawa Nabilah Azman, Shalini Kulandaivalu, and Yusran Sulaiman. "Poly (3, 4-ethylenedioxythiophene) doped with carbon materials for high-performance supercapacitor: a comparison study." *Journal of Nanomaterials* 2017 (2017).
- [34] Lyu, Shaoyi, Yanping Chen, Shenjie Han, Limin Guo, Zhilin Chen, Yun Lu, Yuan Chen, Na Yang, and Siqun Wang. "Layer-by-layer assembled polyaniline/carbon nanomaterial-coated cellulosic aerogel electrodes for high-capacitance supercapacitor applications." *RSC advances* 8, no. 24 (2018): 13191-13199.
- [35] Kulandaivalu, Shalini, and Yusran Sulaiman. "Designing an advanced electrode of mixed carbon materials layered on polypyrrole/reduced graphene oxide for high specific energy supercapacitor." *Journal of Power Sources* 419 (2019): 181-191.
- [36] Hiratani, Takayuki, Osamu Kose, Wadood Y. Hamad, and Mark J. MacLachlan. "Stable and sensitive stimuli-responsive anisotropic hydrogels for sensing ionic strength and pressure." *Materials Horizons* 5, no. 6 (2018): 1076-1081.
- [37] Zhang, Longfei, Shaoyi Lyu, Qijun Zhang, Yuntao Wu, Chuck Melcher, Stephen C. Chmely, Zhilin Chen, and Siqun Wang. "Dual-emitting film with cellulose nanocrystal-assisted carbon dots grafted SrAl₂O₄, Eu²⁺, Dy³⁺ phosphors for temperature sensing." *Carbohydrate polymers* 206 (2019): 767-777.
- [38] Daniyal, Wan Mohd Ebtisyam Mustaqim Mohd, Yap Wing Fen, Jaafar Abdullah, Silvan Saleviter, and Nur Alia Sheh Omar. "Preparation and characterization of hexadecyltrimethylammonium bromide modified nanocrystalline cellulose/graphene oxide composite thin film and its potential in sensing copper ion using surface plasmon resonance technique." *Optik* 173 (2018): 71-77.
- [39] Li, Mei-Chun, Qinglin Wu, Kunlin Song, Yan Qing, and Yiqiang Wu. "Cellulose nanoparticles as modifiers for rheology and fluid loss in bentonite water-based fluids." *ACS applied materials & interfaces* 7, no. 8 (2015): 5006-5016.
- [40] Li, Mei-Chun, Qinglin Wu, Kunlin Song, Corneils F. De Hoop, Sunyoung Lee, Yan Qing, and Yiqiang Wu. "Cellulose nanocrystals and polyanionic cellulose as additives in bentonite water-based drilling fluids: Rheological modeling and filtration mechanisms." *Industrial & Engineering Chemistry Research* 55, no. 1 (2015): 133-143.
- [41] Song, Kunlin, Qinglin Wu, Meichun Li, Suxia Ren, Lili Dong, Xiuqiang Zhang, Tingzhou Lei, and Yoichi Kojima. "Water-based bentonite drilling fluids modified by novel biopolymer for minimizing fluid loss and formation damage." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 507 (2016): 58-66.
- [42] Song, Kunlin, Qinglin Wu, Mei-Chun Li, Andrew K. Wojtanowicz, Lili Dong, Xiuqiang Zhang, Suxia Ren, and Tingzhou Lei. "Performance of low solid bentonite drilling fluids modified by cellulose nanoparticles." *Journal of Natural Gas Science and Engineering* 34 (2016): 1403-1411.
- [43] Hutton-Prager, Brenda, Mohammed Mustafees Khan, Clinton Gentry, Charlie Brandon Knight, and Anas Khalaf Anas Al-Abri. "Thermal barrier enhancement of calcium carbonate coatings with nanoparticle additives, and their effect on hydrophobicity." *Cellulose* 26, no. 8 (2019): 4865-4880.
- [44] de Oliveira, Jean Paulo, Graziella Pinheiro Bruni, Shanise Lisie Mello el Halal, Fabiano Cleber Bertoldi, Alvaro Renato Guerra Dias, and Elessandra da Rosa Zavareze. "Cellulose nanocrystals from rice and oat husks and their application in aerogels for food packaging." *International journal of biological macromolecules* 124 (2019): 175-184.
- [45] Ojala, Jonna, Juho Antti Sirviö, and Henriikki Liimatainen. "Nanoparticle emulsifiers based on bifunctionalized cellulose nanocrystals as marine diesel oil-water emulsion stabilizers." *Chemical Engineering Journal* 288 (2016): 312-320.
- [46] Pandey, Aseem, Maziar Derakhshandeh, Stephanie A. Kedzior, Brandy Pilapil, Neta Shomrat, Tamar Segal-Peretz, Steven L. Bryant, and Milana Trifkovic. "Role of interparticle interactions on microstructural and rheological properties of cellulose nanocrystal stabilized emulsions." *Journal of colloid and interface science* 532 (2018): 808-818.
- [47] Barnat-Hunek, Danuta, Monika Szymańska-Chargot, Monika Jarosz-Hadam, and Grzegorz Łągód. "Effect of cellulose nanofibrils and nanocrystals on physical properties of concrete." *Construction and Building Materials* 223 (2019): 1-11.