

Design of Functional Coating on Cellulose Nanocrystals for Advanced Applications

by

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Examining Committee Membership

The following served on the Examining Committee for this thesis. The decision of the Examining Committee is by majority vote.

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by the examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis is based upon a combination of published works. Various chapters are adapted from the following list of publications, with specific reference to the published work provided within the chapter.

Chapter 1 and 2 are partially adapted from: **Lee, Y.**, Zhang, H., Yu, H. Y., & Tam, K. C. (2022). Electroconductive cellulose nanocrystals—Synthesis, properties and applications: A review. Carbohydrate Polymers, 289, 119419. DOI: <https://doi.org/10.1016/j.carbpol.2022.119419>

The paper was co-authored by myself, my supervisor, Dr. Michael Tam, co-op student Haoyu Zhang, and Dr. Yu. I made the outline of the paper and wrote the manuscript. Haoyu Zhang wrote a conductive polymer part of the manuscript. Dr. Yu contributed to the discussion on the conductive polymer coating and sensor application. All authors reviewed the manuscript.

Chapter 3: **Lee, Y.**, Nasser, R., & Tam, K. C. (2020). Interfacial Control of the Synthesis of Cellulose Nanocrystal Gold Nanoshells. Langmuir, 36(38), 11215-11224. DOI: <https://doi.org/10.1021/acs.langmuir.0c01283>

The paper was co-authored by myself, my supervisor, Dr. Michael Tam, and Dr. Nasser. Dr. Nasser and I equally contributed to this research. In this work, I designed and performed the experiments, collected and analyzed the experimental results, and wrote the manuscript. Dr. Nasser contributed to the design of the experiments, discussion on the results, and wrote the manuscript. All authors reviewed the manuscript.

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The paper was co-authored by myself, my supervisor, Dr. Michael Tam, Hyunwoo Choi, Haoyu Zhang, Dr. Wu, Dabin Lee, Dr. Wong, Dr. Tang, Dr. Park, and Dr. Yu. I contributed to the design of the experiment protocols, synthesis of materials, collection and analysis of the experimental data, and writing the manuscript. Haoyu Zhang and Dr. Yu contributed to the design of conductive cellulose nanocrystals and the collecting the characterization results. The contribution of Dr. Wu and Dr. Tang is on the 3D printing related experiments and discussion. Hyunwoo Choi, Dabin Lee, Dr. Wong, and Dr. Park helped with the characterization of the composite materials and discussion on the experimental results. All authors reviewed the manuscript.

Chapter 5 consists of a manuscript that was co-authored by myself, my supervisor, Dr. Michael Tam, Dabin Lee, Lian Han, James Cheon, Weinan Zhao, Jiaxin Xu, Dr. Juhyun Park, and Dr. William A. Anderson. I contributed to the design and synthesis of the materials, conducted antimicrobial testing and characterization, as well as writing the manuscript. Dabin Lee and Weinan Zhao, and Dr. Park assisted with some characterization of the materials. Lian Han and Jiaxin Xu contributed to the discussion on the yeast and antibacterial tests. Dr. Anderson provided his laboratory and equipment for the antibacterial test.

Abstract

As a result of the increasing demand for high-performance, sustainable consumer products, renewable materials with benign characteristics are receiving considerable attention. Among many renewable materials, cellulose nanocrystal (CNC) is recognized as a promising candidate for the development of functional nanomaterials for various applications. CNC possesses many attractive characteristics, and it can be easily modified to produce the desired functionalities for a specific application. The modification of CNC can be achieved via chemical or physical pathways by utilizing the abundant surface hydroxyl groups and strong surface charge. The most straightforward CNC modification method is to generate the required functional coating rather than using other complicated chemical modification methods. Therefore, this thesis focuses on designing various functional coatings on the CNC surface and explores its potential applications.

In the initial part of the research, gold nanoshell coated CNC was successfully fabricated using two different approaches, namely a seed-mediated *ex-situ* method and an *in-situ* one-pot syntheses. Especially, a novel *in-situ* one-pot synthesis approach successfully simplified the CNC gold nanoshell synthesis by precisely controlling the electrostatic interaction between the chemical species and result in uniform gold shell coating on CNC. In the following study, Poly(3,4-ethylenedioxythiophene) (PEDOT) conductive polymer coated CNC was synthesized and employed to fabricate a highly stretchable, sensitive, and self-healing strain sensor for human motion detection. Compared to the pure PEDOT sensor (gauge

factor = 9.35), CNC/PEDOT sensor demonstrated higher sensitivity ($GF = 21.25$) due to the CNC template, lowering the electrical percolation onset of the composite and improving PEDOT dispersity within the hydrophilic PVA matrix. Also, glycerol plasticizer enable the sensor to have skin-like modulus and the prepared sensor effectively monitor a range of human motions, such as complex joint bending motions and subtle muscle motions. A rapid and effective antibacterial system based on inexpensive and sustainable Cu_2O nanoparticle-coated CNC was developed. CNC template allows stable and small size Cu_2O nanoparticle synthesis and CNC/PEI/ Cu_2O demonstrated higher antimicrobial performance than CNC/PEI/Cu, which is attributed to the high toxicity of the Cu^+ ion. It was then successfully coated onto fabrics using a simple spray coating method, and the prepared antibacterial fabrics rapidly eliminated the bacteria in less than 3 min for *E. coli* and 10 min for *S. aureus* while it maintained the breathability and filtration properties of the original fabrics.

In conclusion, this doctoral thesis describes the development of functional coating on CNC, providing novel properties and synergistic effects with pristine CNC. It demonstrated the limitless potential of CNC by expanding its conventional research and application fields.

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Dedication

I would like to dedicate this thesis to my beloved family.

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List of Abbreviations

Abbreviation	Meaning
4-AP	4-aminophenol
4-NP	4-nitrophenol
AGU	Anhydroglucose unit
APS	Ammonium persulfate
ATP	Adenosine triphosphate
AuNPs	Gold nanoparticles
BC	Bacterial cellulose
CNC	Cellulose nanocrystal
CNF	Cellulose nanocrystal
CNT	Carbon nanotube
CTAB	Hexadecyltrimethylammonium bromide
DIW	Direct ink writing
DLS	Dynamic light scattering
DNA	Deoxyribonucleic acid
ECAs	Electrically conductive adhesives
<i>E.coli</i>	<i>Escherichia coli</i>
EDOT	3,4-Ethylenedioxythiophene
EDS	Energy-dispersive X-ray spectroscopy
EN	Epoxy natural rubber
FTIR	Fourier transform infrared
Gly	Glycerol
GO	Graphene oxide
IR	Infrared
LBL	Layer-by-layer
LSPR	Localized surface plasmon resonance
MCC	Microcrystalline cellulose
MDR	Multidrug resistance
MIC	Minimum inhibitory concentration
NCC	Cellulose nanocrystal
NR	Natural rubber
PAA	Poly(acrylic acid)
PANI	Polyaniline

PD	Polydopamine
PDADMAC	Poly(diallyldimethylammonium chloride)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEI	Polyethylenimine
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic acid)
PPE	Personal protective equipment
PPy	Polypyrrole
PR	Polyrhodanine
PSS	Poly(4-styrenesulfonic acid)
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
REEs	Rare Earth Elements
RNA	Ribonucleic acid
ROS	Reactive oxygen species
<i>S.cerevisiae</i>	<i>Saccharomyces cerevisiae</i>
<i>S.aureus</i>	<i>Staphylococcus aureus</i>
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
THPC	Tetrakis(hydroxymethyl)phosphonium chloride
TSC	Trisodium citrate
UV	Ultraviolet
Vis	Visible
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction

1.1 Research background and motivation*

The increasing demand for materials to meet an expanding range of consumer goods has resulted in environmental contamination and the depletion of limited and scarce resources. To circumvent this problem, a new class of environmentally benign processes and materials derived from renewable resources is being explored to replace traditional materials.¹⁻³ One of the recent efforts to address sustainability is to utilize biomass-derived resources, such as cellulose, starch, chitin/chitosan, alginate, pectin, and gum that are considered renewable and eco-friendly materials. These natural biopolymers have enormous potential to be applied to many applications in the field of biomedical engineering, wastewater treatment, energy harvesting, electronics, and personal care, due to their abundant reservoir, unique structural features, nontoxicity, and chemical accessibility for modification.

Among many sustainable natural materials, cellulose is one of the most abundant bio-renewable materials found on the earth.^{4, 5} Also, the innovations in nanotechnology have contributed to the production of nano-structured cellulose to take the full advantage of this abundant renewable biopolymer. Particularly, cellulose nanocrystal (CNC) obtained through mechanical/chemical treatment of cellulose pulp possessed extraordinary properties, compared to bulk cellulose and other common materials, such as carbon nanotube or stainless steel. This

*This chapter is partially adapted from “Lee, Y., Zhang, H., Yu, H. Y., & Tam, K. C. (2022). Electroconductive cellulose nanocrystals—Synthesis, properties and applications: A review. *Carbohydrate Polymers*, 289, 119419” with permission from Elsevier.

novel class of sustainable nanomaterial is a rapidly growing discipline due to its many attractive features, such as outstanding mechanical strength, excellent dispersion stability in water, high aspect ratio, large surface area, and abundant surface functional groups, as shown in Figure 1.1. Furthermore, it is worthwhile to note that CNC is a commercially available product that guarantees consistent properties as well as stable material supply in Canada and across the globe.

There have been extensive research efforts on developing greener and more efficient production of CNC. The properties of CNC also have been widely and thoroughly investigated for a better understanding of its nature, leading to effective utilization. The recent study trend is mainly focused on the functionalization/modification of CNC. Pristine CNC is a sufficiently attractive nanomaterial in composite applications as a nanofiller by improving barrier properties or enhancing mechanical performance. In recent years, the application fields of CNC have been extended to functional properties by modifying the surface of CNC. The CNC modification aims to endow novel functionalities, thereby imparting the desirable characteristics to CNC for specific applications. For instance, the intrinsic insulating property of CNC can be modified to be conductive, while naturally benign CNC can act as an antimicrobial agent to kill microorganisms.

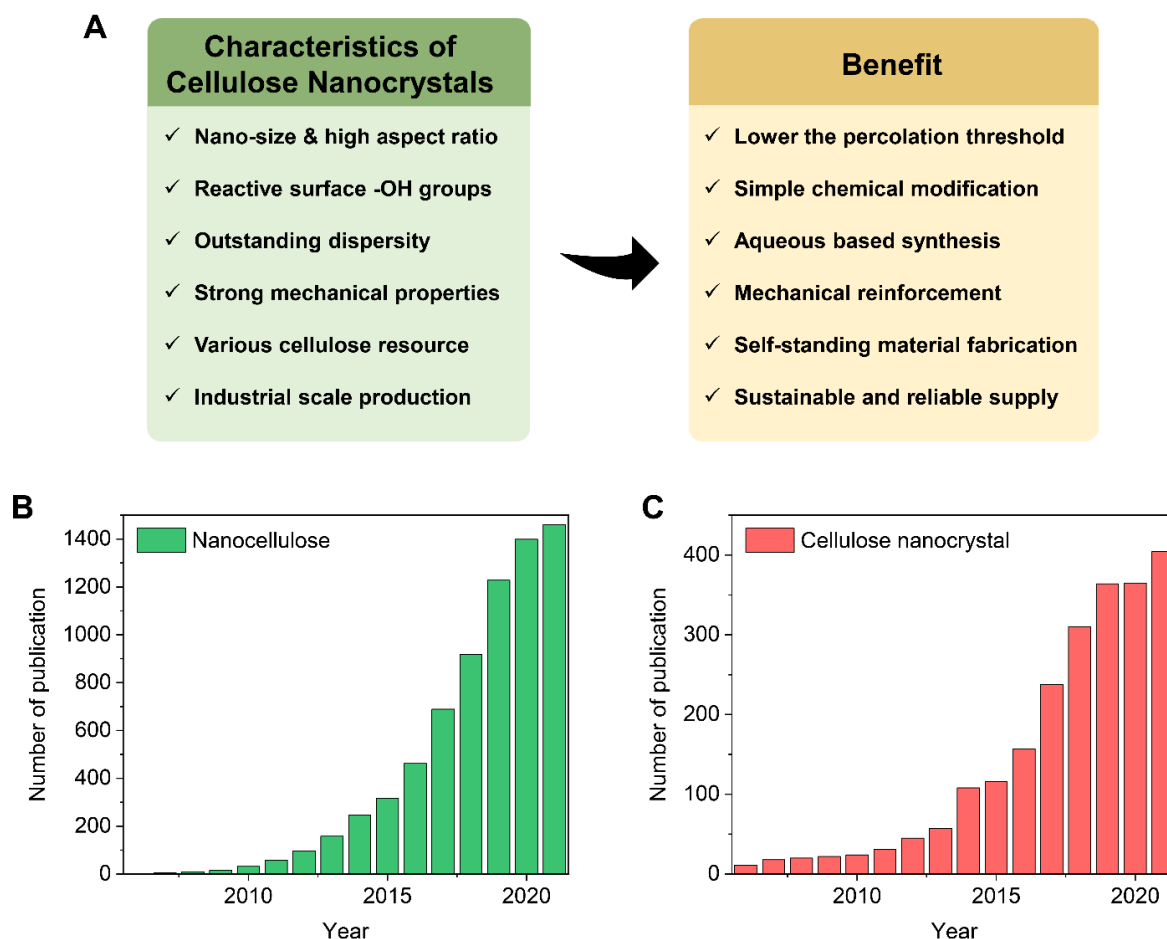


Figure 1.1 (A) Summary of the properties of CNC and its benefit for various advanced and sustainable applications. (B) Illustration of the number of papers published each year using the search terms ‘nanocellulose’ and ‘cellulose nanocrystal’ according to the Web of Science © 2022 Clarivate.

The surface modification of CNC is easily conducted by either chemical or physical methods benefitting from its large surface hydroxyl groups. Reactive surface hydroxyl groups of CNC can be replaced with other active chemical moieties, or they can also form hydrogen bonds with other organic molecules or polymers. Furthermore, most commercial CNC possesses a strong surface charge due to the sulfate ester groups that prevents aggregation and

yields a stable dispersion. This allows the CNC to be utilized as a nano-template for facile layer-by-layer (LBL) assembly, leading to the formation of functional coatings.

CNC coated with functional materials is particularly promising because of its new characteristics and synergistic effect between the functional coating and the CNC. The conductive CNC coated with a conductive polymer is an example. The high aspect ratio of CNC with conductive properties can lower the electrical percolation threshold, and it renders the higher electrical conductivity with a reduced amount of conductive materials. Additionally, when we consider the enormous specific surface area of CNC, it can easily carry an immense amount of functional materials. In this regard, the motivation of this research is to design the CNC with various functional coatings as innovative nanomaterials for a wide range of advanced applications.

1.2 Research objectives

Based on the discussion above, this thesis focuses on developing functional coating on CNC to impart novel functions to the sustainable CNC templates. More importantly, introducing new functions would synergize the unique properties of CNC, leading to a promising versatile nanomaterial with tremendous potential for real-world applications. Considering its practical use, the convenient and facile modification methods should be explored rather than complicated and time-consuming chemical modification.

The specific hypothesis and objectives of this study include:

Hypothesis:

- i) Simple physical adsorption and/or hydrogen bonding facilitate the formation of desired coating layers (interlayer coating and further functional coating) instead of complex methods.
- ii) Precise control of electrostatic interaction between CNCs, chemical substances, and metal precursors can facilitate innovative and facile metal coating synthesis.
- iii) CNC template can enhance the dispersity of conductive polymer in water and hydrophilic polymer matrix.
- iv) High aspect ratio of CNC with conductive polymer coating can lower the electrical percolation threshold.
- v) CNC template can immobilize the metal ions and metal nanoparticles, resulting in stable and smaller size metal nanoparticles.

Objectives:

- i) Interfacial control of gold nano-structure coated CNC.
- ii) Preparation of conductive polymer coated CNC for the fabrication of sensitive, stretchable, and sustainable conductive nanocomposite.
- iii) Synthesis of copper and cuprous oxide coated CNC for the fabrication of antimicrobial fabrics

1.3 Thesis outline

This thesis comprises 6 chapters. Chapter 1 covers the overview of the research background and motivation, follows by a discussion on research objectives and an outline of the thesis. Chapter 2 provides a literature review on CNC, the core material in this research, from the general aspects and modification strategies to applications. This chapter also introduces a comprehensive review of metal nanomaterials, approaches to conductive CNC preparation, and antimicrobial systems. The results of the study are described in Chapter 3, 4, and 5 based on the manuscript format. Chapter 3 explores the synthesis of gold nanoparticle and/or gold nanoshell coated CNC (CNC-PDADMAC-AuNP and CNC-PDADMAC-gold nanoshell) and compares the two different synthesis strategies. Chapter 4 presents the synthesis and performance of conductive polymer coated CNC (CNC/PVP/PEDOT) as a conductive nanofiller in strain sensor fabrication. Chapter 5 describes the synthesis of copper and copper oxide nanoparticle coated CNC (CNC/PEI/Cu and CNC/PEI/Cu₂O) and their antimicrobial performance, as well as the fabrication of durable antibacterial fabrics. Chapter 6 summarizes the key conclusions and major contributions in this thesis, followed by recommendations for future research.

Chapter 2

Literature Review

2.1 Cellulose nanocrystal

Cellulose nanocrystal (CNC) is the primary material being studied in this research; therefore, the first part of the literature review will cover the fundamental characteristics of CNC and preparation methods. Then the surface modification of CNC will be discussed since it is the essential research topic for the development of functional CNC, and the research on the utilization of CNC for various applications will be introduced.

2.1.1 General aspects of CNC[†]

Cellulose-based materials have been used for thousands of years in numerous fields, from fuel to textiles and clothing to building materials. Unlike petroleum resources, which have limited reserve, approximately 1.5×10^{12} tons of cellulose is produced by plants per year via photosynthesis.^{6, 7} With the recent development in nanotechnology, cellulose derived nanomaterials have gained increasing attention from research communities seeking to find alternative materials that will replace conventional systems derived from non-sustainable petroleum-based sources.

[†] This chapter is partially adapted from “Lee, Y., Zhang, H., Yu, H. Y., & Tam, K. C. (2022). Electroconductive cellulose nanocrystals—Synthesis, properties and applications: A review. *Carbohydrate Polymers*, 289, 119419” with permission from Elsevier.

Nanocelluloses are obtained from a wide range of cellulose sources, such as wood, plant, tunicate, algae, and bacteria. The nanocellulose derived from cellulose fibers can be categorized based on the treatment conditions, origins, and dimensions. The three main types of nanocellulose are cellulose nanofiber (CNF), cellulose nanocrystal (CNC or NCC), and bacterial cellulose (BC).^{8,9} All these three forms of nanocellulose have been actively explored for many applications, and recently CNC have attracted increasing attention since it is currently being manufactured on an industrial scale, making it the most practical nanocellulose that can be applied to various applications.

In the production of CNC, purification and pre-treatment of cellulosic materials are required to isolate the cellulose nanomaterials from the cellulosic sources, such as the removal of hemicellulose and lignin.¹⁰ This step is accomplished by a pulping process in which wood is disassembled chemically and/or mechanically into individual fibers, and the resultant fibers are further treated with high pressure homogenization and purified to be disintegrated into microfibrils.¹¹ These microfibrils consist of mixture of amorphous and crystalline cellulose chain domain as shown in Figure 2.1. After the purification, the nanocellulose can be extracted from the pretreated cellulosic materials through mechanical treatment,^{12, 13} acid hydrolysis,¹⁴ and enzymatic hydrolysis^{12, 15} or the combination of these processes. An acid-induced de-structuring process with hydrochloric, hydrobromic, or sulfuric acids, is commonly used for the isolation of CNC.^{16, 17} During the acid hydrolysis, acid molecules selectively permeate into the amorphous (disordered) cellulose fiber domains and break the glycoside bonds yielding the CNC and sugar molecules (Figure 2.1). As a result, CNC is extracted from the relatively

resistant crystalline (ordered) regions of cellulose. The most frequent extraction method is via sulfuric acid, where the sulfuric acid introduces the half-ester sulfate groups via the reaction with hydroxyl groups on the cellulose surface and CNC with excellent aqueous stability is produced.^{1, 18}

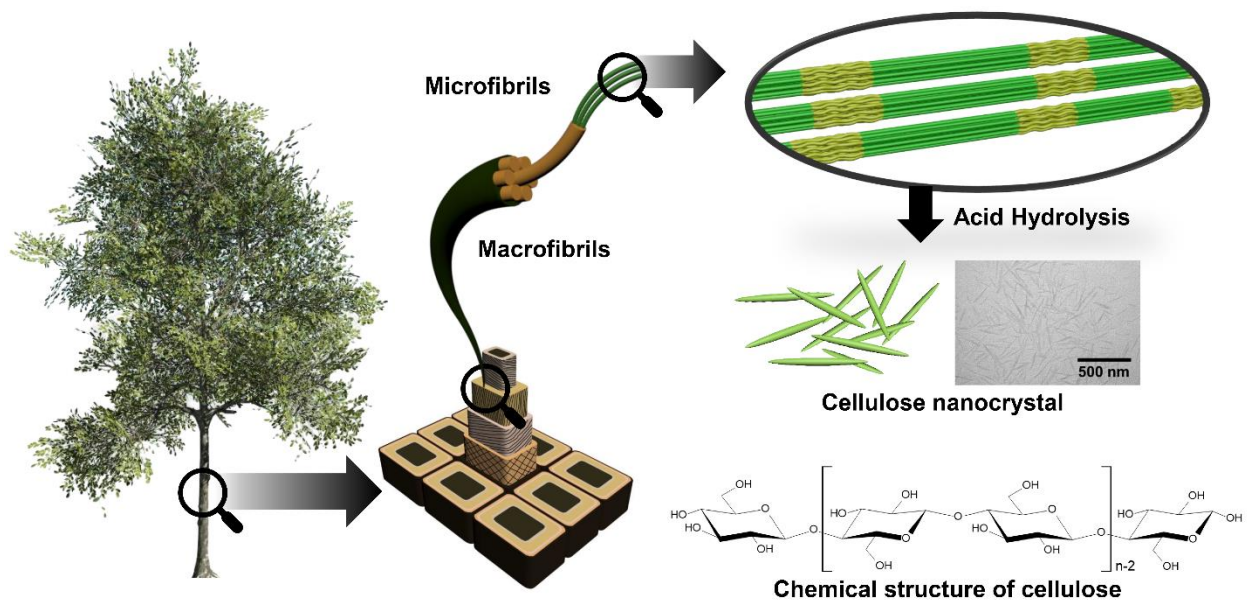


Figure 2.1 Schematic describing the hierarchical structure of wood from the tree to the cell walls, fibrils and CNC, and cellulose molecular structure.

CNC has a needle-shaped structure with a high aspect ratio (length/width) of about 10-70.¹⁹ The geometrical dimension of CNC depends on the starting cellulosic material and processing conditions as shown in Figure 2.2. They range from 100 to 500 nm in length and 10 to 50 nm in diameter.^{20, 21} CNC possesses many attractive characteristics, such as large specific surface area (250–500 m²/g), superior mechanical strength (tensile strength of 7500 MPa and Young's modulus of 100–140 GPa), abundant hydroxyl groups for functionalization,

excellent colloidal stability, biodegradability, and biocompatibility.^{4, 5, 7, 22} Additionally, at high concentrations, CNC can self-assemble into a chiral-nematic crystalline phase.²³ Because of this, CNC has received a tremendous amount of interest, both in industry and academia. Recently, the mass-production of CNC has become a reality, and it is now a catalyst for the development of CNC enabled products and processes for a wide range of industrial applications.²¹ CNC has found extensive application in biomedical engineering,²⁴⁻²⁸ wastewater treatment,^{29, 30} Pickering emulsifiers,³¹⁻³³ packaging films,^{34, 35} electronics, and energy storage devices.^{36, 37}

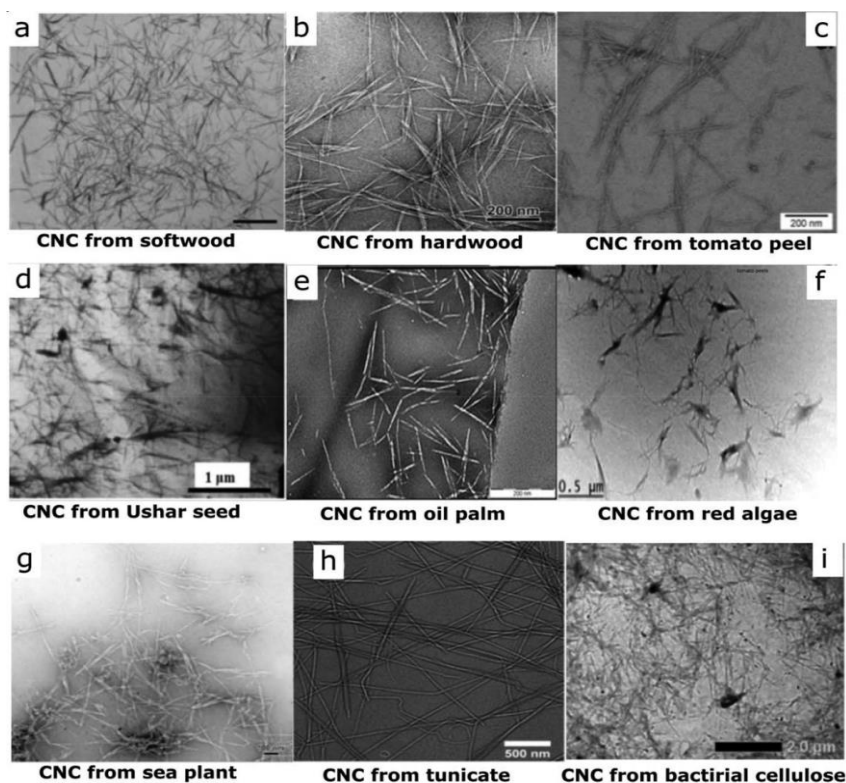


Figure 2.2 Transmission electron microscope (TEM) images of cellulose nanocrystals derived from different cellulosic sources. Adapted with permission from ref 21. Copyright 2017 Royal Society of Chemistry.²¹

2.1.2 Surface modification of CNC

The surface modification of CNC is essential to extend their use to a wide range of advanced engineering applications. Surface modification strategies are used to: (i) prevent self-aggregation and improve dispersion stability in polar solvents or hydrophilic polymeric matrices; (ii) enhance the compatibility with non-polar solvents or hydrophobic polymer matrices; (iii) introduce desired chemical functionality on CNC surface for various advanced application. Before we discuss the chemical modification of CNC, it is important to identify the underlying structure of cellulose. Cellulose is a homopolysaccharide consisting of an anhydroglucose unit (AGU) linked by β 1-4 glycosidic bonds, as shown in Figure 2.3. Each AGU of the cellulose chain has three hydroxyl groups of 2-OH, 3-OH, and 6-OH, and the reactivities of these hydroxyl groups are different. While the 6-OH possesses much higher reactivity than others, since it is linked to the alkyl group on the edge of the anhydrous glucose unit, the reactivity of 2-OH and 3-OH are quite low because both hydroxyl groups are directly attached to the alkyl groups on the glucose ring and are subjected to steric effect.³⁸

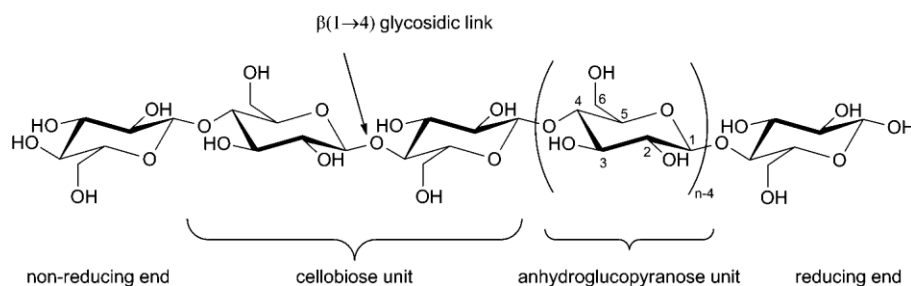


Figure 2.3 Representation of a cellulose chain showing the anhydroglucose unit in the chair conformation along with atom numbering, the glycosidic link, and both reducing and non-reducing ends of the polymer. Adapted with permission from ref 39. Copyright 2014 Royal Society of Chemistry.³⁹

The approaches to modifying the surface of CNC can be classified into three main categories. The first method is functionalization during CNC isolation. The representative case of this method is CNC with sulfate ester groups from sulfuric acid hydrolysis, which impart dispersion stability in water. Furthermore, the hydrochloric acid, acetic acid hydrolysis produces CNC with hydroxyl, and acetyl groups, respectively, as well as hydrochloric acid treatment with citric acid that introduces high contents of carboxylic acid on the CNC surface.^{10, 40} This strategy is relatively simple and requires less time and cost compared to other methods for imparting the desired surface functional groups on the CNC surface. However, it is challenging to control the degree of surface modification while producing CNC with high yield and quality, and there is a limit on resulting chemical groups because the CNC extraction condition is generally rather harsh.

Secondly, the chemical modifications of CNC via the formation of covalent bonds after their extraction have been extensively reported, as shown in Figure 2.4. These modification methods rely on surface functionality, such as hydroxyl groups, which can react with a myriad of functional (macro) molecules using various chemistries. 2,2,6,6-Tetramethylpyperidine-1-oxy radical (TEMPO) mediated oxidation to make carboxylic acid groups functionalized CNC is a widely used method.⁴¹ During the oxidation process, the hydroxymethyl groups (6-OH) on cellulose are selectively converted to carboxylic groups.^{7, 41} The carboxyl groups impart negative surface charges to the CNC that enhances their stability and also allows the possibility for further surface modification. Furthermore, this approach is available for not only substitution of surface functional groups with small molecules but also polymer grafting using

the ‘graft to’ or ‘graft from’ method.⁴² The ‘grafting to’ method uses the chemical reaction to form covalent bonds between desired polymers and the reactive surface functional groups on the CNC. This method is straightforward and widely used to graft various polymers to the CNC surface, although the steric hindrance of polymer could yield a low grafting density. On the contrary, the ‘grafting from’ method, called surface-initiated polymerization, results in relatively higher grafting density since it requires the immobilization of initiators on the CNC surface followed by growth of polymers.^{43, 44}

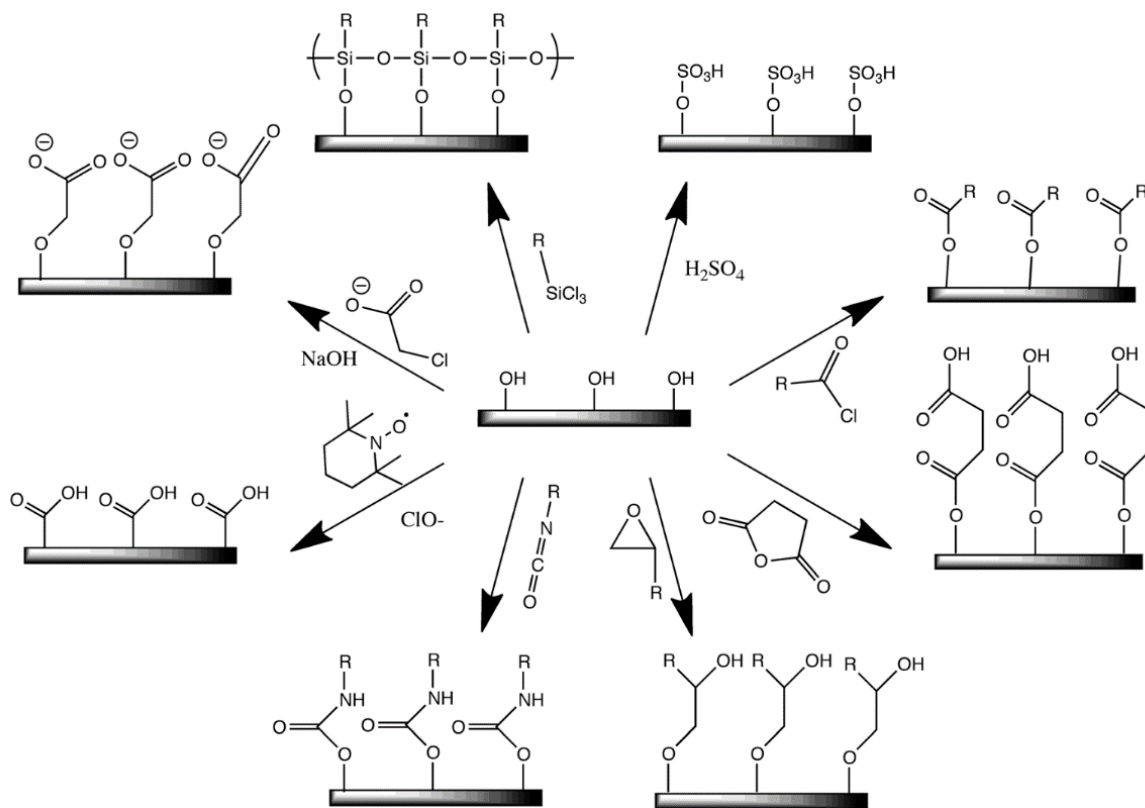


Figure 2.4. Common modification chemistries of CNC surfaces. Adapted with permission from ref 10. Copyright 2011 Royal Society of Chemistry.¹⁰

The third approach is a noncovalent surface chemical modification, which is the most convenient way to obtain the required characteristics through the adsorption of surfactants, oppositely charged entities, or polyelectrolytes. This method is based on relatively weak physical inter-molecule forces, namely, hydrogen bond, electrostatic interaction, or van der Waals forces (Figure 2.5).^{10, 42} This modification strategy is mainly applied to improve the compatibility of CNC with matrices, including polymers, and obtain stable dispersion of CNC in non-polar solvents.⁴⁵ Furthermore, it is worth mentioning that the polymer coating using this noncovalent method can effectively screen the heterogeneous surface of CNC leading to the formation of the uniform secondary functional coating.^{46, 47}

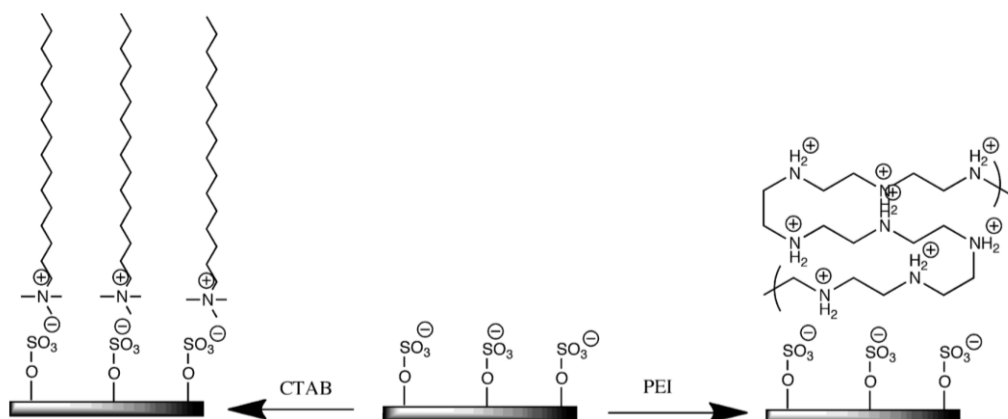


Figure 2.5. Electrostatic adsorption to (sulfonated) cellulose nanoparticle examples. Adapted with permission from ref 10. Copyright 2011 Royal Society of Chemistry.¹⁰

Besides the purposes discussed above, the modification of CNC is crucial to improve its thermal stability. Degradation of cellulose at a high temperature is a critical issue for large-scale nanocomposite manufacturing because common polymeric matrices for nanocomposite

are often processed at temperatures exceeding 200 °C. CNC obtained from typical sulfuric acid hydrolysis has limited thermal stability due to the sulfate groups on their surface and the decomposition of sulfate groups catalyzes and initiates the degradation of CNC at high temperatures.⁴⁸ Therefore, the strategy to improve the thermal stability of CNC has been considered for many years. The desulphation is one way to remove or control the number of surface sulfate groups on CNC, thereby enhancing its thermal stability. Another simple strategy was through the simple surfactant absorption on CNC by protecting the sulfate half ester groups.⁴⁵ The quaternary ammonium salts modified CNC shows increased degradation temperature compared to pristine CNC, and it is stably processed by melting process at high temperature.

2.1.3 Applications of CNC

2.1.3.1 CNC reinforced nanocomposites

CNC has been extensively studied as a nanofiller to reinforce a range of polymer matrices to improve its mechanical properties as well as barrier properties.^{19, 49-51} The outstanding mechanical properties of CNC result from the strong intermolecular and intramolecular hydrogen bonding networks among the cellulose chains within CNC. Therefore, the addition of cheap and sustainable CNC to polymer matrices can efficiently enhance the mechanical properties. The key step to benefit from the excellent mechanical properties of CNC is to homogeneously mix the CNC with the matrices. If the polymer matrices are hydrophilic, the pristine CNC could be successfully dispersed into the system.

However, when the matrices have poor miscibility with pristine CNC, typically in the case of a hydrophobic matrix, the modification of CNC or other methods (solvent exchange) should be considered. Peng *et al.* reported improved mechanical properties of epoxy nanocomposite by reinforcing with modified CNC.⁵² The surface modification of CNC with acetyl, hexanoyl, and dodecanoyl carboxylic acids, increased the compatibility of the CNC with the epoxy matrix. The Young's modulus and ultimate tensile strength of both CNC-acetyl (CNC-a) and CNC-hexanoyl (CNC-h) applied composites increased with increasing the modified CNC content, which was ascribed to the enhanced dispersion. (Figure 2.6)

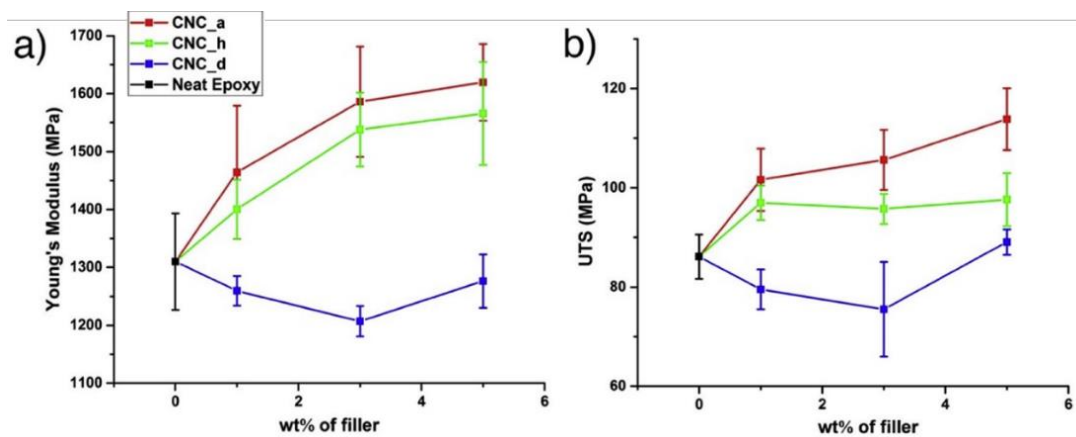


Figure 2.6 Tensile properties of different types of grafted CNC/epoxy nanocomposites: a) Young's modulus, b) Ultimate tensile strength. Adapted with permission from ref 52. Copyright 2017 Elsevier.⁵²

The use of CNC in packaging applications has also attracted much attention. The barrier properties of nanocomposite depend on the tortuosity path affected by geometry and dispersion of filler. Therefore, CNC can be an ideal nanofiller to effectively increase the tortuosity path due to its small size, high aspect ratio, and low permeability. Fortunati *et al.*

demonstrated that the water and oxygen barrier property of poly(lactic acid) (PLA) film can be significantly enhanced by the addition of surfactant modified CNC as well as pristine CNC due to the high dispersity of CNC fillers within the PLA matrix.⁵³

2.1.3.2 CNC Pickering emulsifier

Another important application of CNC is Pickering emulsifier. Pickering emulsion is an emulsion that is stabilized by solid particles instead of traditional surfactants. Considering the growing concerns about toxicity of traditional surfactants and interest in sustainability, Pickering emulsion has gained increasing attention. One very promising system that could be an efficient Pickering emulsifier is CNC, a cheap, sustainable, and biomass-based particle suitable for various industrial fields, from enhanced oil recovery to pharmaceutical and food. The early studies of CNC stabilized Pickering emulsion were reported by Capron *et al.*^{32, 54, 55} Their research showed that CNC derived from hydrochloric acid hydrolysis could effectively stabilize 4 μm monodispersed hexadecane/water interface droplets for several months.⁵⁴ In a further study, they controlled the amphiphilic properties of CNC to better understand the stabilization mechanism and found that the control of the interface was governed by electrostatic interaction regardless of the cellulose source.³² CNC with a high surface charge density were not able to efficiently stabilize at the emulsion droplet because of strong repulsive forces between CNC. The effect of aspect ratio of CNC was also investigated in terms of interfacial coverage.⁵⁵ Although there was no noticeable difference in the size of emulsion droplets stabilized by CNC with aspect ratios ranging from 13 to 160, the CNC with a low

aspect ratio resulted in a dense interfacial coverage while the high aspect ratio led to partially covered droplets. (Figure 2.7)

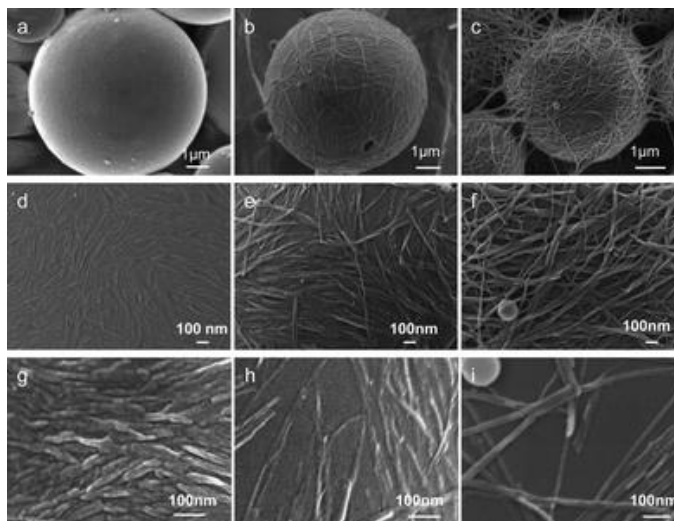


Figure 2.7 SEM images of polymerized styrene–water emulsions stabilized by cotton CNC (a, d and g), bacterial CNC (b, e and h), and Cladophora CNC (c, f and i) at two different nanocrystal concentrations: 5 g L⁻¹ (d–f), and 1 g L⁻¹ (g and h). Adapted with permission from ref 55. Copyright 2013 Royal Society of Chemistry.⁵⁵

The modification of CNC has expanded the role of a sustainable CNC emulsifier to smart hybrid materials. Sarkar and coworkers prepared the pH and ion-responsive Pickering emulsions to design targeted delivery vehicles.⁵⁶ Octenyl succinic anhydride-modified CNC possessed emulsifying capacity due to the increased hydrophobicity, which was partially wetted by both oil and water phases and capable of stabilizing O/W emulsions for up to 4 weeks. The prepared Pickering emulsions were sensitive, and flocculated to larger droplets at pH < 4.0 or ionic strength ≥ 20mM NaCl due to the reduction in electrostatic repulsive forces between the droplets. More complicated multi-stimuli responsive Pickering emulsion was

demonstrated using temperature-, photo-, and pH-responsive CNC-grafted polymers by Tajmoradi *et al.*⁵⁷ The prepared CNC-grafted copolymers, consisting of light-sensitive poly(o-nitrobenzyl acrylate) (PNBA) block and pH- and temperature-sensitive Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) block, exhibited switchable stabilization effect for oil-in water suspension upon different stimuli. It was also used as well a multi-stimuli-responsive surfactant for stabilization of Pickering polymerization media.

2.1.3.3 CNC adsorbent for water treatment

CNC have also been used as adsorbents for pollutants such as heavy metal ions, synthetic organic dyes, pesticides, and pharmaceuticals compounds in wastewater treatment. The adsorption method is a promising water treatment technique that relies on various materials for purifying water. While the production of traditional adsorbents such as active carbon often involves high costs, a large amount of energy consumption, and greenhouse gas emissions, there is growing interest in low cost and more sustainable CNC-based adsorbents that possess excellent adsorption capacity due to their large specific surface area, hydrophilicity, biodegradability. In the early study of CNC for water treatment, pristine CNC and TEMPO-oxidized CNC showed very promising adsorption performance for methylene blue (MB), a common water-soluble cationic dye.⁵⁸ The adsorption capacity of pristine CNC was 118 mg dye/g CNC, and it significantly increased to 769 mg dye/g CNC after TEMPO oxidation, which is comparable to activated carbon due to its vast surface area and charge density. Polyethylenimine (PEI) cross-linked cellulose nanocrystal (CNC) was further developed for the separation and recovery of Rare Earth Elements (REEs) from an aqueous solution.⁵⁹ The

PEI acted as a cross-linker to form the sustainable adsorbents with CNC, and it also introduced metal-chelating groups. The prepared PEI-CNC materials showed rapid and high adsorption capacities of 0.611, 0.670, and 0.719 mmol g⁻¹ toward La(III), Eu(III), and Er(III), respectively. The adsorbents also exhibited preferential adsorption for Er(III) in comparison with La(III) and Eu(III) in a ternary REE solution. Gao *et al.* demonstrated that the incorporation of CNC into graphene oxide membranes rendered synergistic effects for efficient antibiotic removal at high nutrient recovery.⁶⁰ The hybrid membrane displayed improved water permeability compared to pure Graphene oxide (GO) membrane due to the hydrophilic nature of CNC, leading to improved antibiotics removal rates toward levofloxacin (Levo), and norfloxacin (Nor), while enabling a higher passage of desirable nutrients.

2.1.3.4 Energy and electronics sector ‡

Over the last few decades, efficient energy storage devices have attracted considerable attention, driven by the rapid and growing energy consumption and demand. Also, with the increasing concern over resource depletion and interest in sustainable development, increasing attention has been devoted to CNC as a renewable material in the development of high-performance, cheap, and sustainable advanced energy devices. Liew *et al.* demonstrated that the incorporation of carboxylated CNC as a dopant anion into the Polypyrrole (PPy) structure improved the stability and specific capacitance of pure PPy.⁶¹ As shown in Figure 2.8A the

‡ This chapter is partially adapted from “Lee, Y., Zhang, H., Yu, H. Y., & Tam, K. C. (2022). Electroconductive cellulose nanocrystals—Synthesis, properties and applications: A review. *Carbohydrate Polymers*, 289, 119419” with permission from Elsevier.

electrochemically deposited PPy/CNC nanocomposite on a working glassy carbon disk electrode displayed highly porous structure consisting of CNC coated with a thin film of PPy. This advanced structure demonstrated a high capacitance of 256 F g^{-1} according to electrochemical impedance spectroscopy measurements (measured at 0.0 V and 0.012 Hz). The electrochemical stability test also demonstrated that the renewable and inexpensive PPy/CNC nanocomposite is more durable than the cellulose/Carbon nanotube (cellulose/CNT) composite. Yang and Shi reported the development of flexible, lightweight, and highly porous hybrid aerogels for flexible energy storage devices using 3D cellulose aerogel structure with capacitive nanoparticles, namely PPy nanofiber, PPy coated CNT, and MnO_2 nanoparticle (Figure 2.8B).⁶² The area-normalized specific capacitance from the prepared device was $2.14 - 3.32 \text{ mF cm}^{-2}$ at a scan rate of 2 mV s^{-1} , and capacitance retention was between 61.66 – 92.28 % after 2000 cycles. The high mass ratio of active material to the total aerogel mass leads to the outstanding capacitance retention even at high charge-discharge rates. Pang *et al.* described a sulfur electrode using a dual doped porous carbon for lithium-sulfur batteries (Figure 2.8C).⁶³ The nitrogen–sulfur-doped nanoporous carbon was prepared from the carbonization of polyrhodanine coated CNC, which provided a tunable hierarchical pore structure with a high surface area and strong polysulfide chemisorption. The XPS confirmed the effective binding of both Li^+ and S_n^{2-} to the N, S dual-doped carbon compared to single doped or non-doped carbons. Also, the resulting sulfur electrodes exhibited a high discharge capacity of 1370 mA h g^{-1} at C/20 rate and a very low capacity fading of 0.052% per cycle over 1100 cycles.

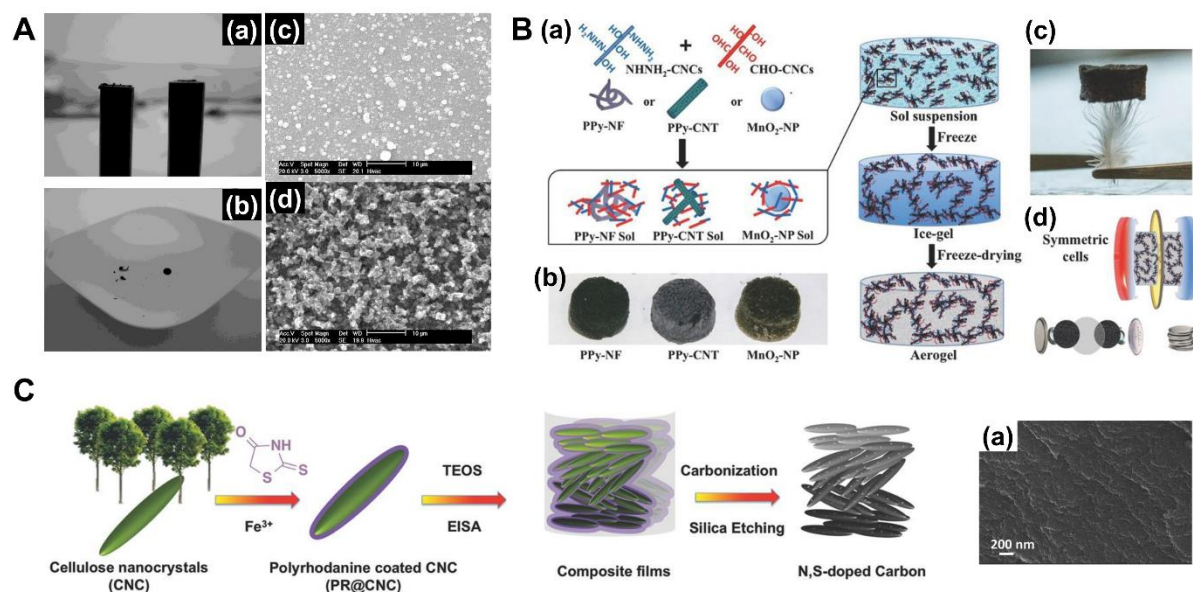


Figure 2.8 Conductive CNC for energy storage devices. (A) Photographs of (a) a (PPy)Cl film (left) and a PPy/CNC film (right) on an electrode surface, and (b) films after removal from the electrode surface; (c) the SEM image of (PPy)Cl, and (d) a PPy/CNC nanocomposite. Reproduced with permission from ref 61. Copyright 2010 American Chemical Society.⁶¹ (B) CNC and capacitive nanoparticles aerogel; (a) the schematic illustration of aerogels preparation; also (b) the photograph of the fabricated hybrid aerogels and (c) a hybrid aerogel resting on top of a feather. (d) Schematic representation of the fabrication of symmetric supercapacitor cells in CR2032-type coin-cell cases. Reproduced with permission from ref 62. Copyright 2015 WILEY-VCH.⁶² (C) Schematic representation of the synthesis of nitrogen/sulfur-doped CNC (NSC) and (a) the SEM image of NSC. Reproduced with permission from ref 63. Copyright 2015 WILEY-VCH.⁶³

CNC have been applied to sensors as template materials for functional coatings to enhance the detection of chemicals or mechanical deformation. The large specific surface area and high aspect ratio of CNC allow sensors to have a large active surface area and control of the percolation threshold leading to highly sensitive devices. Fan *et al.* fabricated a sensitive amperometric sensor based on nanocomposites of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with CNC for the detection of dopamine (Figure 2.9A).⁶⁴ *In-situ* polymerization of

PEDOT onto CNC nanorods was conducted by both oxidative chemical and electrochemical polymerization. They successfully prepared PEDOT/CNC nanocomposite from both processes, which displayed large surface area and outstanding conductivity compared to only polymerized PEDOT. When comparing the synthesis methods, the electrochemical polymerized PEDOT/CNC showed lower electrochemical impedance as well as superior electrochemical catalytic activity compared to its chemically polymerized counterpart. The prepared amperometric sensor, composed of electrodeposited PEDOT/CNC, exhibited a very fast catalytic response and sensitive detection of dopamine with a distinct linear response across an extensive concentration range of 0.2 to 62.0 mM. Recently, by taking advantage of the high aspect ratio of CNC as a conductive nanofiller, strain sensors were developed where they could achieve precision sensitivity over subtle changes. Wang *et al.* incorporated CNC into CNT/natural rubber (CNT/NR) composite to lower the electrical percolation threshold of the strain sensor (Figure 2.9B).⁶⁵ Amphiphilic CNC allowed the hydrophobic CNT to be homogeneously dispersed in aqueous solutions that enhanced the construction of an integrated 3D conductive network structure. The fabricated CNT/CNC/NR nanocomposites exhibited a significantly lower percolation threshold of 1.6 vol%, which is 4-fold lower than that of the CNT/NR composites. Also, due to the presence of the CNC scaffold, it possessed a high mechanical rigidity, reversible resistivity, and sensitivity over a broad range of tensile strain (0–100%), making it suitable for applications in stretchable skin sensors and wearable electronic devices. Liu *et al.* developed a strain sensor composed of 1-dimensional Ag nanohybrid using CNC via a simple, efficient, and green strategy (Figure 2.9C).⁶⁶

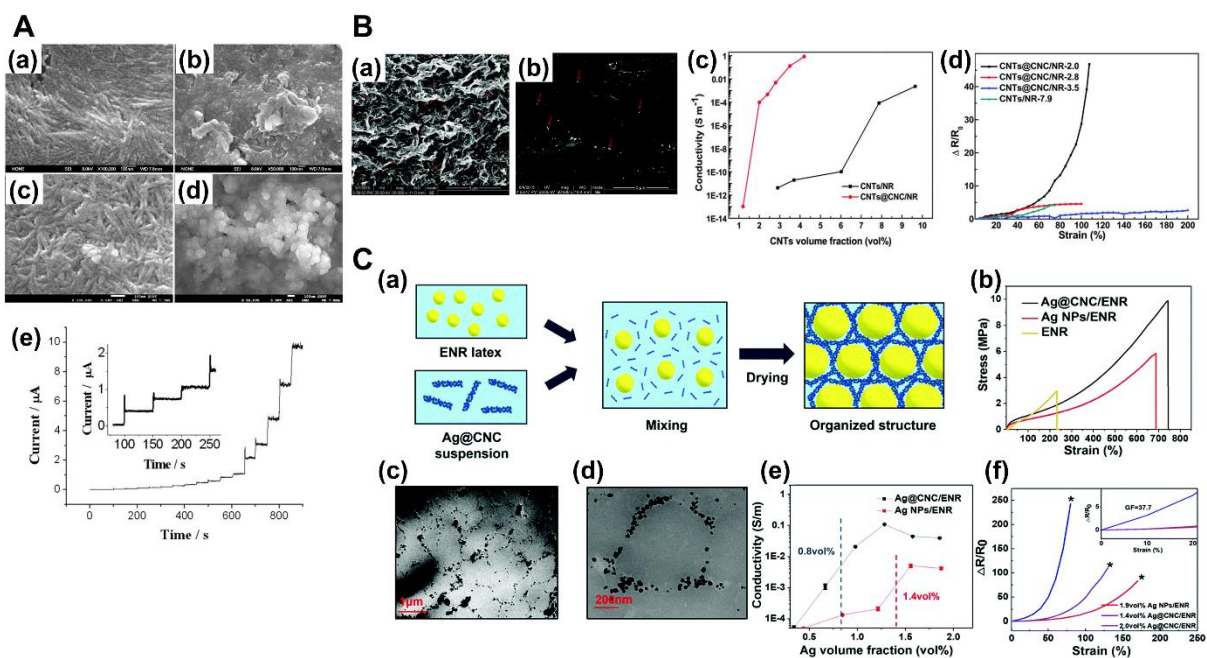


Figure 2.9 Conductive CNC for sensors. (A) SEM images of (a) NCC, (b) the chemically polymerized PEDOT/chloride, (c) the electrochemically polymerized PEDOT/NCC, and (d) the chemically polymerized PEDOT/NCC; (e) Amperometric responses of the electrodeposited PEDOT/NCC modified CPE to successive addition of dopamine into stirring Britton–Robinson buffer (0.2 M, pH 5.0). The working potential was 0.34 V, and the dopamine concentrations added were from 0.2 to 62.0 mM in sequence. Inset, amplified portion of the amperometric response curve. Reproduced from ref 64 with permission from The Royal Society of Chemistry. Copyright 2014.⁶⁴ (B) SEM images of the extracted conductive network skeleton from unvulcanized (a) CNT@CNC/NR and (b) CNT/NR nanocomposites; (c) electrical conductivity of CNT/NR and CNT@CNC/NR nanocomposites as a function of CNT volume fractions and (d) plot of the relative resistance change as a function of applied strain. Reproduced from ref 65 with permission from The Royal Society of Chemistry. Copyright 2016.⁶⁵ (C) (a) Schematic representation of the fabrication process of the organized conductive network in epoxy natural rubber (ENR) matrix. (b) Stress–strain curves of neat ENR, Ag NPs/ENR, and Ag@CNC/ENR composites after vulcanization. (c and d) TEM images of the organized conductive networks in Ag@CNC/ENR nanocomposite. (e) The electrical conductivity of Ag@CNC/ENR and AgNPs/ENR composites as a function of Ag volume fraction. (f) Relative resistance changes of Ag@CNC/ENR and AgNPs/ENR composites as a function of applied strain. Reproduced from ref 66 with permission from The Royal Society of Chemistry. Copyright 2018.⁶⁶

The templated 1D Ag nanohybrid was synthesized in the solid-state and added to epoxy natural rubber (ENR) latex to form an electrically conductive network that yielded a highly sensitive flexible strain sensor. The tensile strength of Ag/CNC/ENR nanocomposites was enhanced by 234.9% compared to neat ENR and exhibited superior electrical conductivity of 0.1 S m^{-1} with a significantly lower percolation threshold of 0.8 vol% compared to the Ag NP/ENR composites (0.005 S m^{-1} , 1.4 vol%). Moreover, it possessed an extremely high sensitivity with a gauge factor of around 304 and excellent durability even after more than 10,000 cycles of bending.

Printable electronics is an emerging field of research where direct metallization and various printing methods offer flexibility, scalability, sustainability, and lower restriction on substrates compared to traditional processes. Although various forms of cellulose have gained increasing attention as promising materials in printable electronics, substrate materials and ink additives, however limited attention has been paid to the use of CNC in printable electronics compared to other cellulosic materials. However, unlike CNF and bacterial cellulose that have limited utility as substrate materials due to the length of the fiber that clog the nozzles, CNC could be employed for a wide range of printed electronics applications, including inkjet-printed conductive ink owing to their nanosized dimension. The advantage of conductive CNC as conductive inks over metallic silver nanowires is that the cost can be considerably reduced as CNC is much cheaper than silver nanowires. CNC not only improves the dispersity of the conductive materials, but its large aspect ratio reduces the concentration threshold for the formation of the electrical percolation network. Hoeng *et al.* elucidated the advantages of CNC

in the inkjet printing of electrically conductive silver patterns.⁶⁷ CNC was not only added to ink as a dispersing and stabilizing agent for silver nanoparticles, but it was coated onto a porous substrate to reduce the ink diffusion. The prepared silver-CNC conductive ink formed conductive patterns with only 3 wt % of silver, which is much lower than the percolation threshold of traditional silver nanoparticle ink (around 20% wt). Also, the printing quality on the CNC coated substrate was improved due to the reduction in ink diffusion. The fabricated silver conductive patterns showed $50 \Omega \text{ sq}^{-1}$ of sheet resistance after annealing at 180 °C and it dramatically decreased to $1 \Omega \text{ sq}^{-1}$ after annealing near the cellulose degradation temperature of 250 °C.

In addition to the applications described previously, conductive CNC can be used for the fabrication of conductive films, co-filler in electrically conductive adhesives (ECAs) to endow electrical conductivity as well as high mechanical strength.^{46, 68, 69}

2.1.3.5 CNC for biomedical applications

Here, various biomedical applications of CNC will be discussed, except antimicrobial application that will be described in Chapter 2.4. CNC has found extensive application in biomedical systems, as CNC can play a role as a biocompatible and biodegradable template such as i) versatile nanocarriers for functional material, ii) efficient scaffolds to reinforce matrices for tissue engineering.⁷⁰⁻⁷² The large specific surface area and tunable surface chemistry of CNC allow the efficient loading of various drugs and biologically active compounds. The potential of CNC for drug delivery was initially reported by Jackson *et al.*⁷³,

where pristine CNC with sulfate ester groups was found to bind hydrophilic antibiotic drugs, doxorubicin hydrochloride (DOX) and tetracycline, and those drugs were completely released in 1 day. They further modified CNC with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), to introduce hydrophobicity that enabled the loading of hydrophobic anticancer drugs, such as docetaxel, paclitaxel, and etoposide. The CTAB-coated CNC not only bound significant quantities of hydrophobic drugs but it could release them over several days in a controlled manner. The prepared nanocomplexes were also bound to KU-7 cancer cells and successfully delivered hydrophobic fluorescent probe. The nature-derived novel drug delivery system was developed using chitosan oligosaccharide grafted CNC.⁷⁴ The reaction between carboxyl groups of TEMPO-oxidized CNC and amino groups of chitosan oligosaccharide was successfully conducted. The procaine hydrochloride was used as a model drug, and prepared chitosan modified CNC exhibited a binding efficiency of 21.5 % with a drug loading of 14 % w/w. An *in-vitro* drug release study revealed a rapid drug release at pH 8 for up to 1 h. The mucoadhesive hydrogel based on CNC for controlled local drug delivery was recently reported by Vakili *et al.*⁷⁵ They optimized the grafting ratio of poly(acrylic acid) (PAA) to CNC in order to improve the mucoadhesive property of PAA by the formation of a hard-core bottle-brush polymer. They developed PAA grafted CNC and drug (cisplatin) complex exhibited a slow drug release and demonstrated non-toxicity against colorectal cancer cells.

The fluorophore-labeled CNC was firstly prepared by Dong and Roman for fluorescence bioassay and bioimaging application.²⁶ The fluorescein-5'-isothiocyanate

(FITC), the most widely used fluorophore, was successfully grafted to the CNC surface to prolong the blood circulation time. This group further reported folic acid-conjugated CNC for cancer targeting.⁷⁶ The CNC was initially labeled with FITC, followed by a reaction with folic acid. The FITC and folic acid conjugated CNC exhibited selective binding to folate receptor-positive mammalian cells, demonstrating the potential for targeted delivery of chemotherapeutic agents to cancer cells (Figure 2.10). The fluorescent poly(amidoamine) (PAMAM) was grafted onto the surface of CNC, and it demonstrated pH-responsive fluorescent properties.⁷⁷ The CNC-PAMAM showed significant blue fluorescent emission, which was governed by the formation of aggregates. This interesting pH-responsive behavior of fluorophore grafted CNC suggested the potential applications in pH-responsive separation, fluorescent-based pH sensing, optical imaging, and catalytic field as nanoreactors.

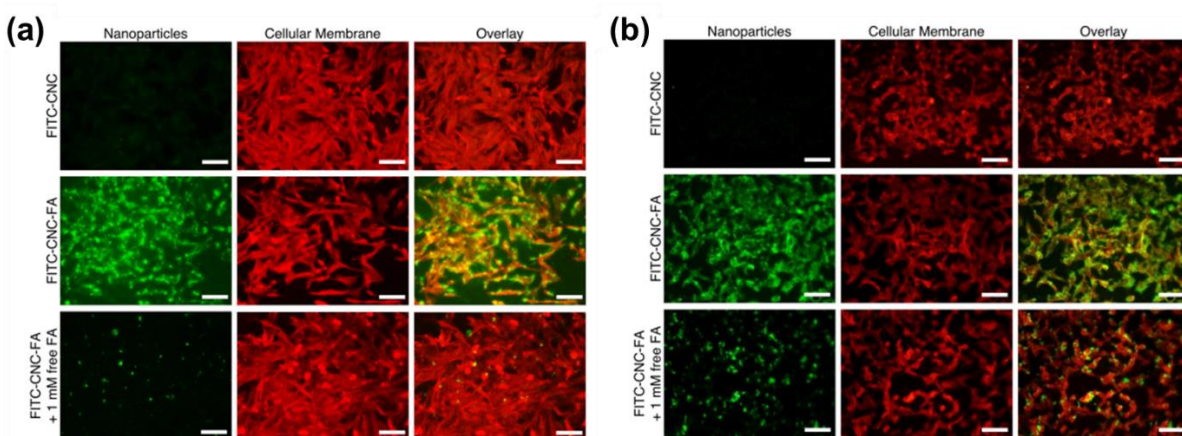


Figure 2.10 Cellular binding/uptake of FITC-CNC and FITC-CNC-folic acid (FA) in the absence and presence (1 mM) of free folic acid by (a) DBTRG-05MG and (b) H4 cells. Scale bar: 100 μm . Adapted with permission from ref 76. Copyright 2014 American Chemical Society.⁷⁶

CNC has received significant interest in tissue engineering since it promotes cell proliferation with the excellent reinforcing ability and unique rheological properties. The potential of CNC in tissue engineering application was firstly described by Dugan *et al.*⁷⁸ They prepared a sub-monolayer of CNC with a high degree of orientation via spin coating. Regardless of the small size of the CNC, the myoblasts arranged themselves along the bulk direction of the CNC orientation. More interestingly, the skeletal muscle myotubes also produced striking radial patterns after the induction of differentiation (Figure 2.11). Recently, two types of CNC aerogels with different surface chemistry were implemented and tested to evaluate the suitability of the CNC aerogels for use as bone tissue scaffolds.⁷⁹ Hydrazone cross-linked aerogels were prepared with either sulfate half-ester group (S-CNC) or phosphate half-ester group (P-CNC) as flexible, porous bone growth templates. In terms of the compressive strength and long-term stability in liquid environments, S-CNC aerogel showed better performance than P-CNC, and it also exhibited an increased bone volume fraction of 50% compared to the control at 12 weeks. CNC showed promise in tissue engineering when incorporated into the polymer matrices, and it was incorporated into polylactide–polyglycolide (PLGA) nanofiber, resulting in potential nanocomposite scaffolds for skin tissue engineering applications.⁸⁰ The CNC reinforced nanofiber membranes showed improved thermomechanical properties and mechanical strengths. The tensile modulus of 7 wt.% CNC-loaded nanofiber membrane was 21.28 MPa, with an ultimate strain of 89.2 ± 5.3 %, which were comparable to the values of human skin. Cell–nanofiber interactions study using 3T3 fibroblasts also revealed that the developed composite possessed better biocompatibility and

fibroblast adhesion, spreading, and proliferation than neat poly(lactic-co-glycolic acid) (PLGA) nanofiber membranes.

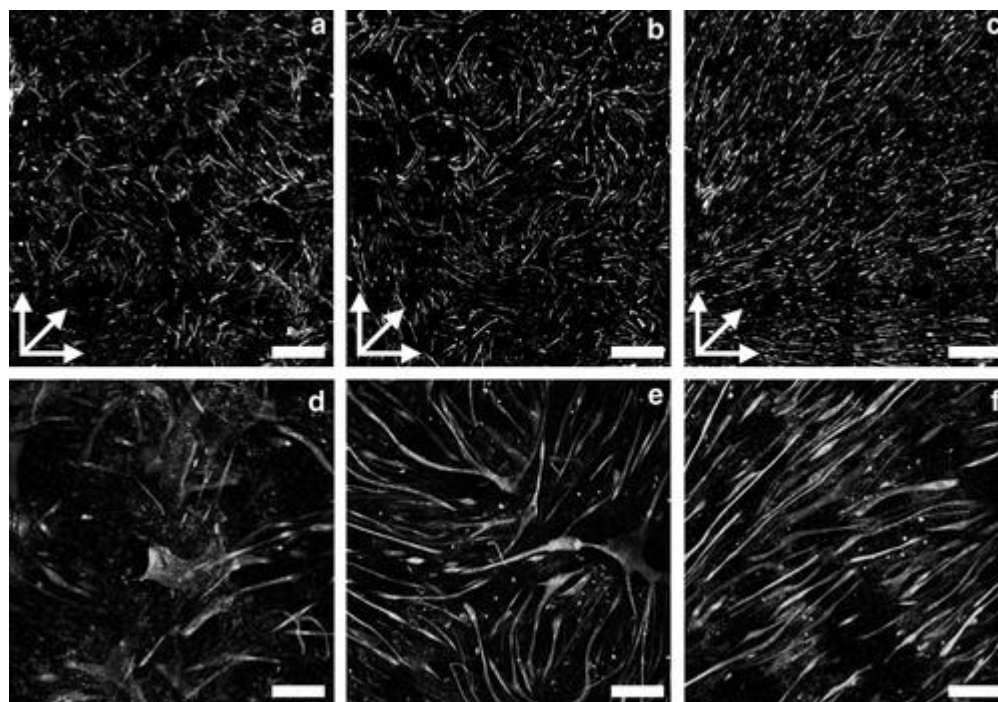


Figure 2.11 (a–c) Large scale tile scans of differentiated myotubes stained for myosin 7 days after induction of differentiation: Myotubes on (a) a glass control surface, (b) a C500 surface-spin coated at 500 rpm, and (c) a C6000 surface-spin coated at 6000 rpm. Arrows indicate the radial axes. Scale bars: 1 mm. (d–f) Higher magnification micrographs of differentiated myotubes stained for myosin: Myotubes on (a) a glass control surface, (b) a C500 surface, and (c) a C6000 surface. Scale bars: 250 μm . Adapted with permission from ref 78. Copyright 2010 American Chemical Society.⁷⁸

2.2 Metal Nanomaterials

2.2.1 The general aspect of metal nanomaterials

Metal nanoparticles have received significant research and industrial interest due to their unique and interesting characteristics, which stem from their extremely small size. The large surface-to-volume ratio makes them chemically reactive, and plasmonic excitation of metal nanoparticles renders characteristic optical properties not attainable in other optical materials.⁸¹ Due to their fascinating properties, metal nanoparticles find applications in a range of fields, including catalysis,⁸² imaging,⁸³ electronics,⁸⁴ sensors,⁸⁵ photonics,⁸⁶ energy harvesting,⁸⁷ antimicrobial,⁸⁸ and biomedical applications.⁸⁹ Furthermore, the development of nanotechnology and material science enable metal nanoparticles to be intentionally engineered to achieve very specific properties by controlling shape, size, and surface chemistry.

Among many metal species, particular emphasis has been placed on the synthesis and utilization of noble metallic nanostructures, such as gold, silver, and copper because of their optoelectrical properties and resistance to oxidation, offering endless possibilities in some applications.⁹⁰ Strong absorption band in the visible and near-infrared region of electromagnetic spectrum is the characteristic property of noble metal nanoparticles, ascribed to the localized surface plasmon resonance (LSPR).⁹¹ As described in Figure 2.12, LSPR is generated by the collective oscillation of conduction electrons on the metal nanoparticles excited by the incident photons at the resonant frequency.^{92,93} The absorbance wavelength and intensity of LSPR can be tuned by controlling the material, size, shape, and surrounding

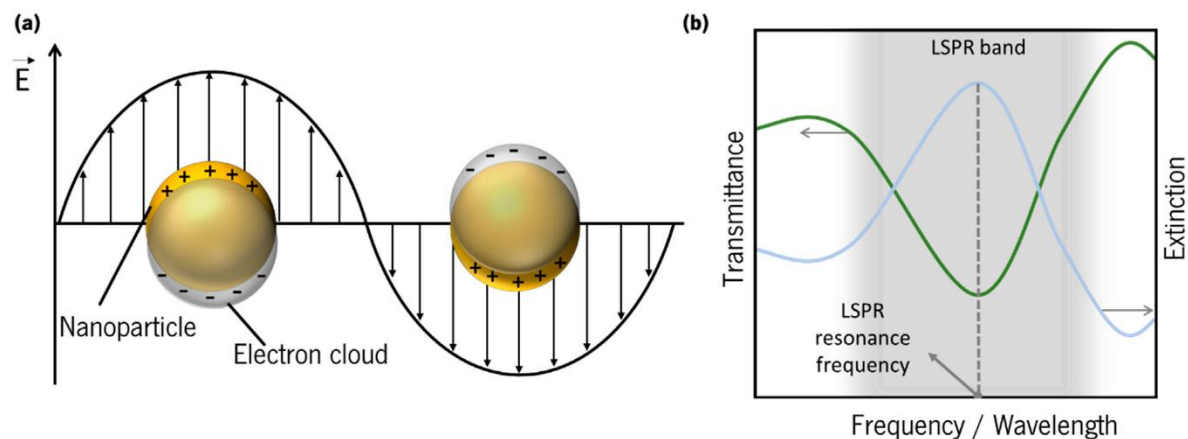


Figure 2.12 (a) Schematics of localized surface plasmons of a metal sphere. (b) Schematics of a typical LSPR band, measured in transmittance mode and extinction spectrum. Adapted with permission from ref 93. Copyright 2021 MDPI.⁹³

medium. This tunable optical (plasmonic) properties allow metal nanoparticles to find applications in a wide range of fields.

In particular, gold is biologically benign and oxidation resistant. Therefore, their unique optical properties can be successfully exploited for various biomedical applications, including therapy and diagnosis of cancers. Over the past three decades, researchers have made significant progress in synthesizing various gold nanostructures and tuning their optical properties to maximize their performance in specific applications.

Aside from the unique optoelectronic properties, the superior electrical conductivity of noble metal nanoparticles makes them attractive in printed electronics, energy harvesting

devices, actuators, and sensors. The antimicrobial activity of metal nanoparticles has also drawn significant research and interest, which will be discussed in Chapter 2.4.2 in detail.

The metal nanoparticle synthesis methods must be carefully designed to obtain the optimized properties. In this regards, colloidal synthesis via wet chemical reduction is widely used as it is convenient, versatile, and scalable. The following sections discuss the synthesis of various metal nanostructures based on wet chemistry.

2.2.2 Fundamental of metal nanoparticle synthesis

Two main approaches are used to prepare metal nanoparticles: top-down and bottom-up. Top-down approaches encompass the methods of preparing particles by breaking the bulk metal into small particles using high energy sources. Mechanical grinding is most frequently used, and other methods are also available. Rapid condensation of metal vapor, laser ablation in a liquid, thermal heating, or plasma excitation of bulk metal followed by its transport with a stream of an inert gas onto a substrate or into a liquid are examples of top-down approaches.⁹⁴
⁹⁵ However, these methods are challenging to produce monodispersed nanoparticles and require high energy consumption and sophisticated equipment resulting in high processing costs.

On the other hand, bottom-up approaches are better in controlling all the processing stages (nucleation, particle growth, and the interactions between nanoparticles) necessary to prepare metallic particles with the desired characteristics, including morphology, size distribution, and stability.⁹⁶ This method starts from ionic precursors with a proper reducing

agent to form nanomaterials by reaction or decomposition of precursor molecules in the liquid phase. There are a variety of experimental parameters that control the properties of prepared nanoparticles, namely, the concentration of reagents, reducing agents, temperature, pH, the rate of reagent addition, addition of pre-formed seeds, types, and concentration of protective agents.⁹⁶⁻⁹⁸

In the wet synthesis of nanoparticles, the first step is the formation of metallic atoms from metal ions by electrons transfer from a reducing agent (Red) to the oxidized metallic species (Me^{n+}).⁹⁶



The driving force of the reaction is the reduction potential difference between the metal and the reducing agent, ΔE^0 , which is associated with the free energy of the redox process according to the well-known relation (Eq. (2.2)). (Table 2-1)

$$\Delta G^0 = -nF\Delta E^0 \quad (2.2)$$

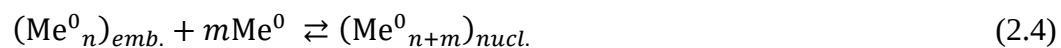
The possibility and rate of reaction can be predicted from the magnitude of ΔE^0 . The reduction can proceed only when ΔE^0 is positive values (practically larger than 0.3–0.4 V for favorable reaction), which means that the reduction potential of the reducing agent need to be more negative than the reduction potential of the metal precursor.⁹⁶ The introduction of ‘seeds’ can be a strategy to control the nucleation rate and properties of synthesized metallic particles. The surface of seeds can play the role of a catalyst that promotes the reduction of the metal species and the nucleation process; therefore, the reduction can proceed even in systems that are less

favorable for the reduction process. The seeds can either be introduced by the rapid reduction of a different metal species,⁹⁹ or in the form of a stable nanoparticle dispersion consisting of the same metal.¹⁰⁰

Table 2-1 Standard reduction potential at 25 °C in aqueous solution.¹⁰¹⁻¹⁰³

Half reaction	Potential	
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69 V	Weaker reducing agent  Stronger reducing agent
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50 V	
$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	+1.18 V	
$\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}$	+0.95 V	
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80 V	
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34 V	
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22 V	
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.000 V	
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.26 V	
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.45 V	

Once the metal atoms are formed, they transform into small metal clusters called embryos, which undergo continuous aggregation-dissociation processes, and eventually, these clusters reach a critical size and form the nuclei, which are the first stable states of the metallic phase in the system.



The size distribution of the nuclei is dependent on various factors, such as the reduction potential of the species, the concentration of reactants, pH, temperature, solvents, and additives. After the formation of nuclei, rapid diffusional growth can occur at the expense of the remaining metal atoms in the solution above the saturation concentration, forming larger size primary nanoparticles.

2.2.3 Shape control in metal nanoparticle synthesis

As described earlier, the intrinsic physicochemical properties of metal nanomaterials are governed by their size, composition, shape, crystallinity, and surface functionality. Particularly, tailoring the shape of a metal nanoparticle has been the subject of decades of research because it is a major driving force in maximizing their unique properties for specific applications. The shape-dependent optical properties of the gold nanoparticle are widely studied, and some typical example are shown in Figure 2.13.¹⁰⁴

In most cases, the synthesis of anisotropic metal nanoparticle synthesis involves separated ‘seeds generation’ and ‘seed growth’ steps because each step requires different reduction conditions. Seeds are starting point for further complicated metal structure development; therefore, they must be monodispersed and exhibit the same crystallographic characteristics.¹⁰⁵ The high-quality seed solution can be obtained using an excess amount of strong reducing agents rendering homogeneous nucleation. On the other hand, the growth stage generally uses weaker reducing agents to avoid the formation of new seeds, and the reducing agent at this step should be strong enough only to allow autocatalytic growth on existing

seeds.¹⁰⁶ Although some simple seedless approaches have been reported by adding a small amount of strong reducing agent to growth solution, they usually result in insufficient morphology control and poor reproducibility.¹⁰⁷

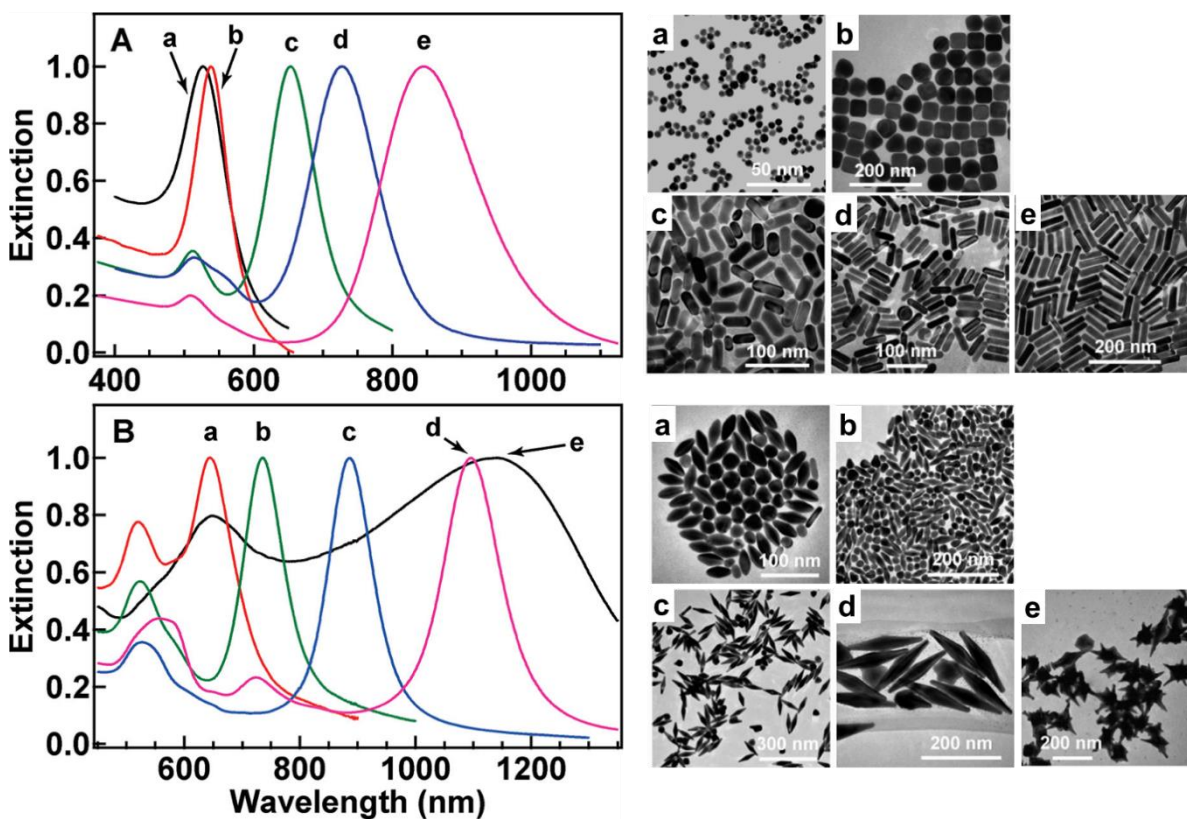


Figure 2.13 Normalized extinction spectra of Au nanoparticles of different shapes and sizes. (A) Spectra a-e correspond to (a) nanospheres, (b) nanocubes, and nanorods with aspect ratios of (c) 2.4 ± 0.3 , (d) 3.4 ± 0.5 , and (e) 4.6 ± 0.8 , respectively. (B) Spectra a-e correspond to nanobipyramids with aspect ratios of (a) 1.5 ± 0.3 , (b) 2.7 ± 0.2 , (c) 3.9 ± 0.2 , and (d) 4.7 ± 0.2 , and (e) nanobranches, respectively. Adapted with permission from ref 104. Copyright 2008 American Chemical Society.¹⁰⁴

The mechanism of shape control involves the different surface energy of crystal facets and binding of capping/ directing agents to specific facets to promote or inhibit growth along them.^{106, 108} The final metal structure is initially governed by the type of prepared seeds, as

shown in Figure 2.14.¹⁰⁹ Each facet of *fcc* crystal structures contain different atomic packing densities rendering different surface energies (γ) ordered as $\gamma(111) < \gamma(110) < \gamma(100)$.¹⁰⁸ During the growth step, metal ions migrate to specific crystallographic planes and participate in the growth to achieve the enlargement of low-energy facets. The standard method to control the shape of the metal nanostructure is by introducing capping agents, such as small organic ligands, polymers, and inorganic salts because it can alter the order of surface energies for different crystal facets and change the growth rates.¹⁰⁹ Certain capping agents, including polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), and bromide, generally provide strong interaction with (100) planes of crystalline silver, gold, palladium, and platinum. Consequently, it promotes the preferential addition of metal atoms to the other crystal facets rather than the tightly passivated (100) plane, leading to selective growth in certain crystal planes. For example, the typical synthesis of silver nanowire starts from the decahedral seeds.¹¹⁰ Since these seed particles consist of twin defects representing the highest energy plane, the silver atoms will be preferentially deposited on those sites resulting in anisotropic growth into pentagonal rods. Then, in the presence of PVP capping agent, the (100) plane along the longitudinal faces can be strongly passivated by PVP adsorption. Therefore, the nanorod grows into a nanowire with the (100) sides and (111) endcaps.

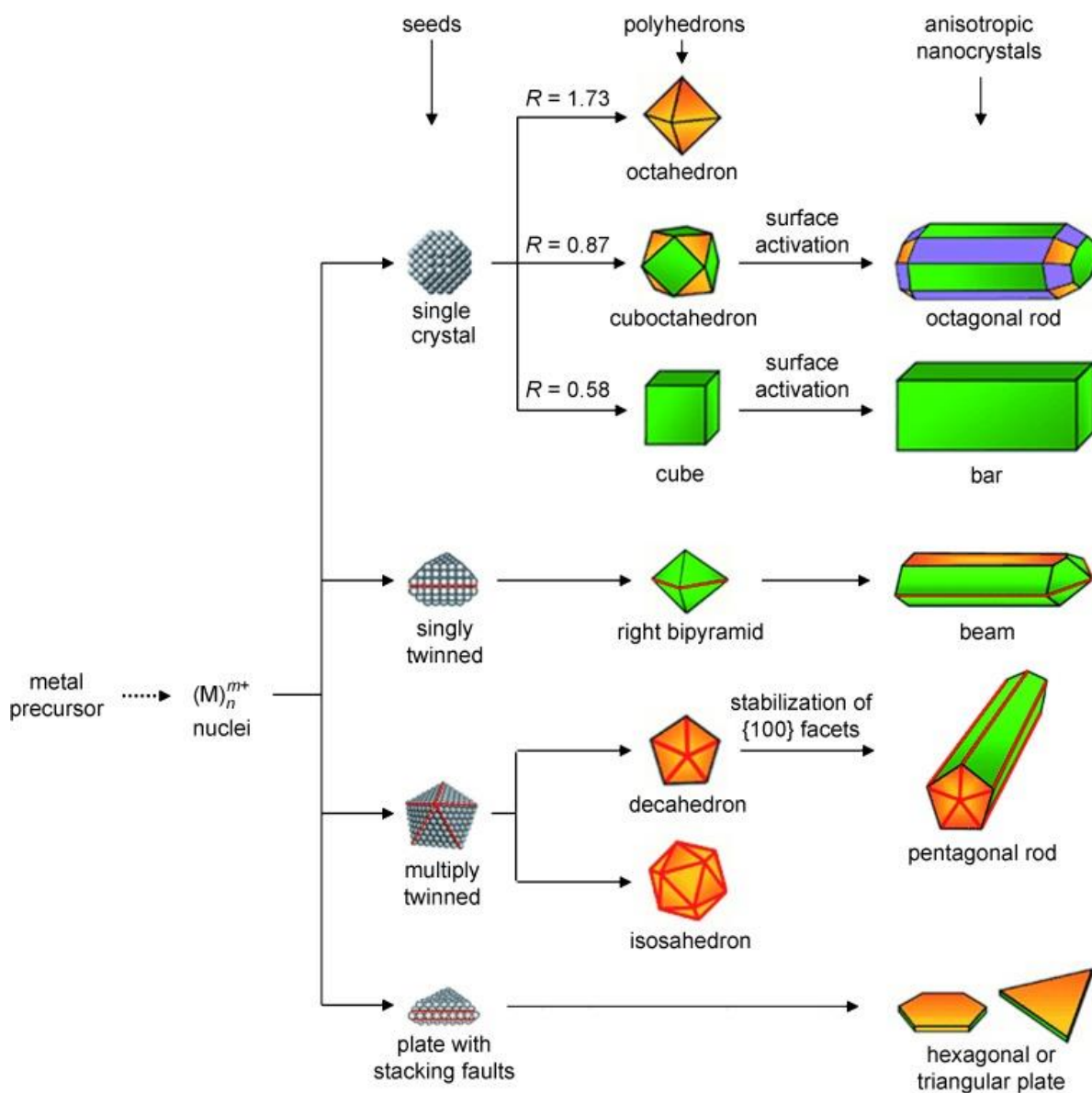


Figure 2.14 Reaction pathways that lead to fcc metal nanocrystals having different shapes. The green, orange, and purple colors represent the $\{100\}$, $\{111\}$, and $\{110\}$ facets, respectively. Twin planes are delineated in the drawing with red lines. The parameter R is defined as the ratio between the growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. Adapted with permission from ref 109. Copyright 2009 Wiley.¹⁰⁹

2.2.4 Metal shell nanostructure synthesis

With the increasing attention on the synthesis of metal nanomaterials, the design of core-shell nanoparticles has been the subject of intense research in recent years, mainly due to their diverse structures as well as electrical and optical properties.¹¹¹⁻¹¹³ Particularly, core-shell nanostructure composed of a dielectric core surrounded by the noble metals layer possesses unique characteristics, such as highly tunable optical absorption features that are even more versatile than homogeneous metal nanoparticles.¹¹⁴ The first synthesis of metallic nanoshells was reported by Halas and colleagues in 1998.¹¹³ They coated silica nanoparticles with a thin gold layer by a decoration of tiny gold seeds followed by the electroless deposition of gold, as shown in Figure 2.15. Since this first reported study, metallic nanoshells have been extensively investigated via several synthetic routes, such as seed-mediated growth,^{113, 115, 116} multistep LBL deposition,¹¹⁷⁻¹¹⁹ thermal evaporation methods,¹²⁰ and sonochemical processes.¹²¹

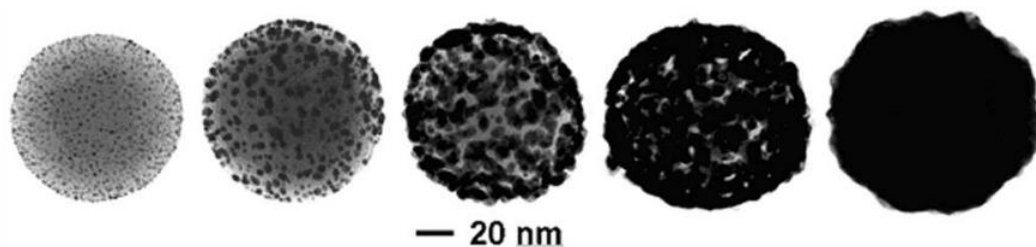


Figure 2.15 Transmission electron microscope images of gold/silica shell/core during shell growth. Adapted with permission from ref 113. Copyright 1998 Elsevier.¹¹³

The standard fabrication process for metal nanoshells is straightforward: (1) preparation of functionalized core nanoparticles, (2) synthesis of small-sized seed metallic

nanoparticles, (3) decoration of the surface of prepared core nanoparticles with very small size metal seeds, (4) growth of metal nanoshell by additional chemical reduction onto the seed. Based on this, the detailed approaches for wet chemistry-based fabrication of metal nanoshell structure can be classified into three categories: (1) *Ex-situ* seed-mediated method,^{112, 113, 116, 122} (2) *In-situ* seed-mediated method,¹²³ (3) direct metal shell deposition method.^{124, 125}

The most common method for metallic nanoshell synthesis is the homogeneous seed-mediated method, the same approach proposed by Oldenburg *et al.* in 1998. In this method, the seeds are separately prepared, and it is then introduced to core particles to decorate them. Brinson *et al.* adopted this procedure to prepare gold nanoshells on silica and hematite core particles.¹²² They used carbon monoxide as a reducing agent and demonstrated thin, uniform shell layers on core nanoparticles. This approach indicated that current liquid-phase reduction methods have limitations in achieving continuous shell layers and suggested the potential to transform the manufacturing process from a batch to a continuous flow process using a gas-phase reducing agent. Heterogeneous seeds can also be used to fabricate the complete metal shell. Silver nanoshell from the gold seeds decorated silica nanoparticle was synthesized by Brito-Silva *et al.*¹¹⁶ They controlled the stirring rate, which is a critical parameter to attain a homogeneous distribution of fully grown nanoshells and found that the presence of catalysts, ammonium hydroxide in this study, required the use of fast stirring rates to minimize the effect of external nucleation.

The seed could also be generated by the *in-situ* method without the separated seed particle preparation. Liu *et al.* reported an improved seed-mediated growth method to

synthesize mono-disperse $\text{SiO}_2@\text{Ag}$ core-shell particles.¹²³ The seeds were synthesized by absorbing reducing agent Sn^{2+} onto the silica nanoparticles, followed by Ag^+ reduction. After then, the addition of PVP allows the formation of complete silver shells by controlling the isotropic growth of silver nuclei during the additional electroless metallization of silver (Figure 2.16).

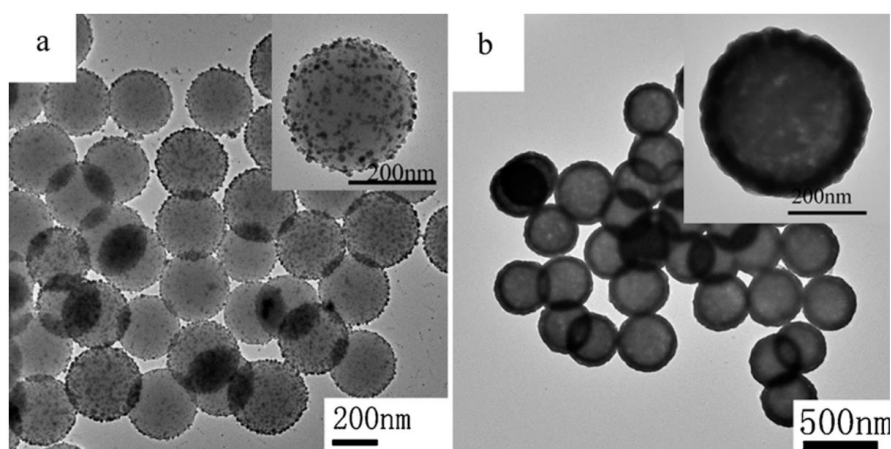


Figure 2.16 TEM images of products: (a) silver nuclei decorated silica spheres; (b) $\text{SiO}_2@\text{Ag}$ core-shell particles with 50 nm thick shell. Adapted with permission from ref 123. Copyright 2011 Elsevier.¹²³

Instead of introducing seeds, some researchers have focused on the direct metal shell deposition method, which allows a one-pot synthesis of metallic nanoshells. Storti *et al.* studied the simple preparation method to obtain nanometer-sized gold nanoshells on amino-functionalized silica nanoparticles at high temperatures.¹²⁵ The amino groups on the silica surface were used as nuclei sites to assemble gold nanoshells during the redox reaction with sodium citrate reducing agent. The final diameter of a complete gold nanoshell was below 30 nm, with a gold layer of 6 nm. A cost-effective, fast, and scalable route for copper-coated

nanoparticles was suggested by Mondin *et al.*¹²⁴ They first prepared mercaptosilane functionalized core particles to utilize the -SH groups, which promotes a selective metal deposition during the electroless plating process due to its high affinity towards metal ions. This approach revealed that it could be applied to both silica and alumina core nanoparticles resulting in the uniform and conformal copper coating, as shown in Figure 2.17.

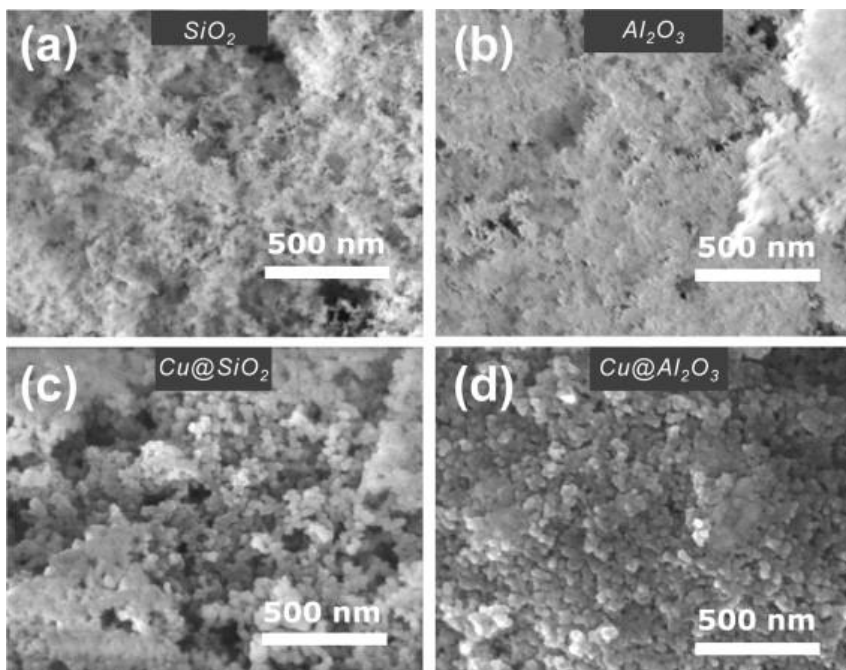


Figure 2.17 SEM images of SiO₂ nanoparticles (a) before and (c) after the copper electroless metallization. SEM images of Al₂O₃ nanoparticles (b) before and (d) after the copper electroless metallization. Adapted with permission from ref 124. Copyright 2013 Elsevier.¹²⁴

2.3 Preparation of Conductive CNC[§]

Thus far, there is a scarcity of reviews that is devoted to the preparation of conductive CNC and their applications as compared to other sectors since CNC is inherently an insulator.¹²⁶ Nevertheless, CNC possesses many attractive characteristics, making it a promising material for the preparation of conductive nanocomposite:

- (i) the nanosized CNC with a high aspect ratio can lower the percolation threshold via the formation of electrical networks with reduced functional material loading.¹²⁶
- (ii) the abundance of reactive surface hydroxyl groups on CNC facilitates simple chemical modification to obtain the desired electrical properties.¹²⁷
- (iii) the strong mechanical properties enable self-standing and high strength materials to be fabricated without additional additives.¹²⁸
- (iv) the high carbon content of CNC and its nanosize dimensions makes it an ideal precursor to prepare porous carbon-based electrodes via a high-temperature pyrolysis.⁶³

Additionally, CNC allows for water-based processes, owing to their high stability in aqueous suspension, which facilitates the use of environmentally friendly processes to produce conductive materials. Due to these advantages, there is an increased interest in the preparation

[§] This chapter is partially adapted from “Lee, Y., Zhang, H., Yu, H. Y., & Tam, K. C. (2022). Electroconductive cellulose nanocrystals—Synthesis, properties and applications: A review. *Carbohydrate Polymers*, 289, 119419” with permission from Elsevier.

of conductive CNC for advanced engineering applications, such as energy storage devices, sensors, and printed electronics.

CNC, which is an intrinsically insulating material, can be transformed into one that possesses electrically conductive properties by utilizing various modification strategies that harness their exceptional characteristics. The use of CNC as a template material not only improves the strength of the composite but also utilizes the aqueous-based processing due to their superior dispersity in water and abundance of surface hydroxyl groups. The approaches for the preparation of conductive CNC can be grouped into four categories, as illustrated in Figure 2.18. Although most of the researches has employed conductive polymeric coating on the CNC surface to yield fully coated surfaces, other approaches, such as metallic coating, carbonization, and hybridization with carbon nanotube (CNT), have been explored due to their attractive electrical properties and stability. Each strategy has its advantages and disadvantages in terms of preparation, cost, stability, optical property, biocompatibility, and environmental risk, as well as the level of conductivity.

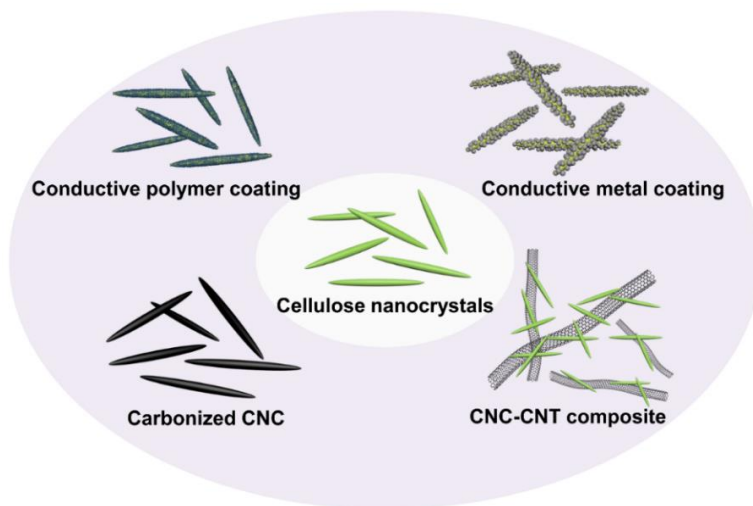


Figure 2.18 Schematic illustration describing the generalized approaches to prepare electrically conductive CNC.

2.3.1 Conductive polymer coating

The electrical properties of conductive polymers originate from their conjugated π -electron backbone. Due to some of the attractive properties of conductive polymers, such as polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethyldioxythiophene) (PEDOT), many of them have been extensively studied.¹²⁹ Conductive polymers are flexible and they possess excellent electrical, optoelectrical, photovoltaic properties. Another advantage of conductive polymers is that their properties can be easily tuned through doping or post-treatment, which permits us to tailor the materials to meet the desired performance for a given application.¹³⁰

Due to these unique properties, conductive polymers have been applied in thin-film transistors,¹³¹ photovoltaic cells,¹³² organic light-emitting diodes,¹³³ supercapacitors,^{134, 135} fuel cells,¹³⁶ sensors,¹³⁷ anti-corrosion materials,¹³⁸ and many other applications. There are many

studies dedicated to the fabrication of conductive polymer composites, where the conductive polymer and substrate material are used as the matrix.¹³⁹ Recently, CNC has gained increasing attention as a sustainable template material for preparing conductive polymer composites due to its high surface area, dispersion stability, and excellent mechanical properties.¹⁴⁰ The high specific surface area and abundance of active moieties on the surface of CNC make it an excellent template for the grafting or coating of conductive polymers. Additionally, the high aspect ratio of CNC lowers the percolation threshold for the conduction of electrons, while its strong mechanical strength provides structural reinforcement. The methods of combining conductive polymers and CNC can be divided into *in-situ* and *ex-situ* methods, depending on the presence of CNC during the polymerization (Figure 2.19A).

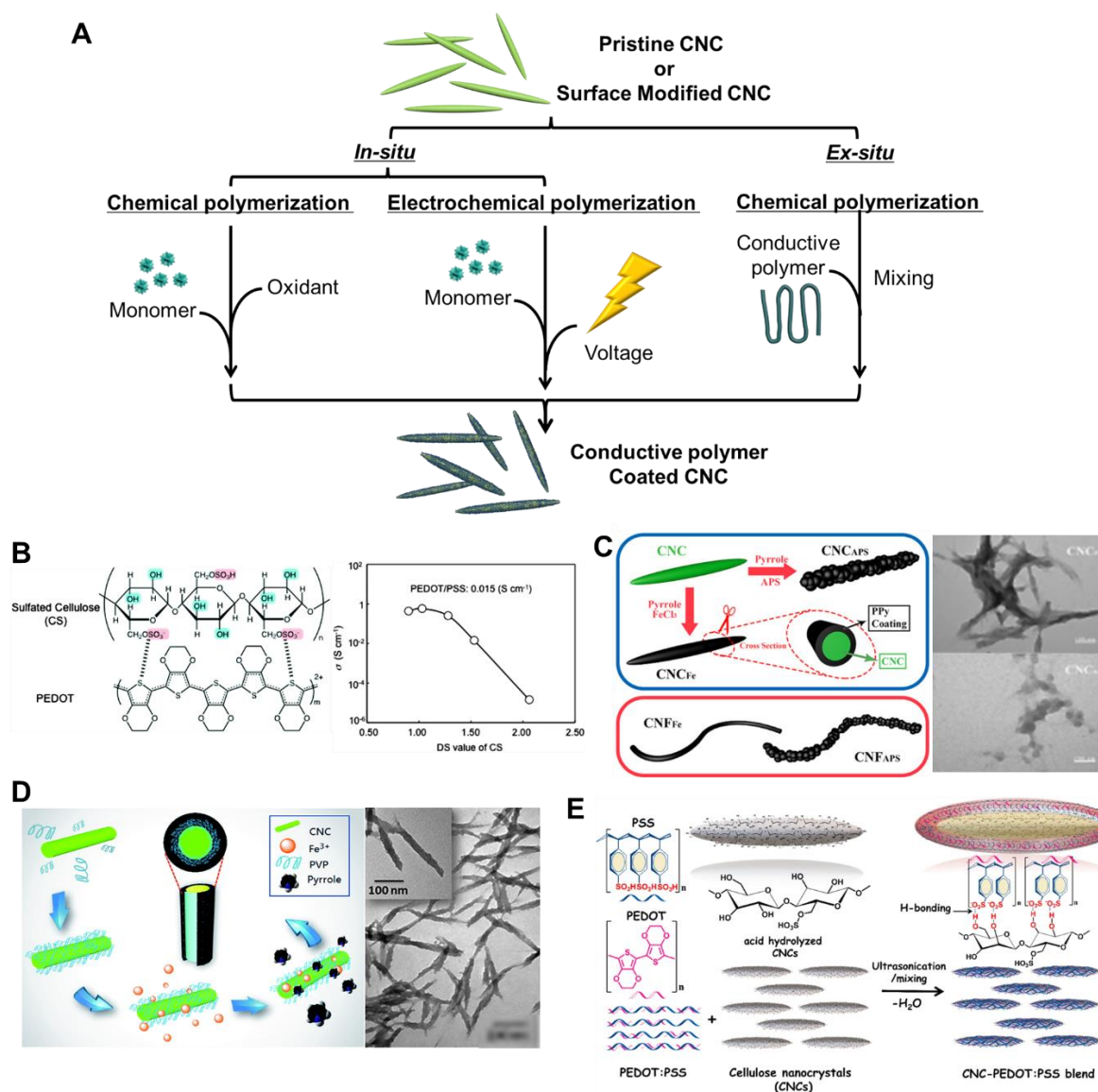


Figure 2.19 (A) Schematic of the preparation of conductive polymer coated CNC. (B) Structure and conductivity of sulfated cellulose and PEDOT. Reproduced from ref 141 with permission from The Royal Society of Chemistry. Copyright 2014.¹⁴¹ (C) Schematic representation of the synthesis of CNC-PPy, and CNF-PPy nanocomposites; also TEM images of CNC-PPy_{Fe}, and CNC-PPy_{APS}. Reprinted with permission from ref 142. Copyright 2019 American Chemical Society.¹⁴² (D) Schematic illustration and TEM images for PPy/PVP/CNC. Reproduced from ref 47 with permission from The Royal Society of Chemistry. Copyright 2014.⁴⁷ (E) Schematic illustrating the association between PEDOT:PSS and CNC. Reproduced with permission from ref 69. Copyright 2019 Springer.⁶⁹

For *in-situ* methods, conductive polymers are polymerized in the presence of CNC to form a core-shell structure, where the conductive polymer is coated on the CNC. The two typical polymerization techniques to fabricate conductive polymeric coating on CNC are chemical and electrochemical polymerizations. Chemical polymerization is the most commonly used technique to prepare core-shell conductive polymer coated CNCs because the process is scalable.¹⁴³ In chemical polymerization, CNC is dispersed in a variety of solvents (water, protonic acids, or a mixture of organic solvents and polar solvents). Monomers of a specific conductive polymer are then added to the CNC suspension. Ammonium persulfate (APS) or ferric chloride (FeCl_3) are typical oxidants used to initiate the polymerization of the monomers to form conductive polymer coated CNC. After the polymerization, the reaction is terminated and the products are subject to various purification techniques, such as ultrafiltration, centrifugation, or dialysis. Many factors, such as CNC surface chemistry, oxidant, solvent, reaction temperature, dopant type, CNC/monomer mass ratio, and oxidant/monomer molar ratio affect the polymerization and properties of conductive polymer coated CNC, and they determine the performance of the conductive nanocomposites.

Favorable surface chemistry of the CNC is necessary to promote the interaction between the functional groups on its surface (hydroxyl, carboxylic, or sulfuric) and conductive polymer (NH_2 on PANI and PPy, heterocyclic sulfur on PEDOT). The sulfate half ester groups and hydroxyl groups on pristine CNC can act as binding sites for the conductive polymer coating without pre-treatment of the CNC surface. Horikawa *et al.* demonstrated the doping effect of sulfate groups on the cellulose polymer in PEDOT using different degrees of sulfate

groups (DS).¹⁴¹ They fabricated sulfated cellulose with DS values of 0.9, 1.03, 1.28, 1.53, 2.06, and observed that at a DS of 1.03, the best doping effect for PEDOT and highest conductivity of 0.576 S cm^{-1} was observed, which was 38 times greater than the reference PEDOT: PSS sample prepared using the same polymerization method (Figure 2.19B). Beyond the DS of 1.03, the conductivity began to decrease, and this was attributed to the polymorphic structure of the highly sulfated cellulose, which hindered the arrangement of 3,4-Ethylenedioxythiophene (EDOT) monomers on the CNC surface. Han *et al.* prepared PPy coated CNC through the chelation of metal ion and hydrogen bonds between the free OH groups of the CNC and amino groups of PPy chains.¹⁴² They used pristine CNC without any surface modification and found the optimal synthetic conditions for the uniform PPy coating with different oxidants (Figure 2.19C). Although the inherent functional groups on CNC provide adequate intermolecular interactions between CNC and the monomer, the addition of functional groups through surface modification facilitates better stability and adsorption of the monomer/polymer onto the CNC surface. In a study by Wu *et al.*, carboxylic acid groups were functionalized onto the surface of CNC via 2,2,6,6-Tetramethylpyperidine-1-oxy radical (TEMPO) mediated oxidation for the adsorption of PPy, where the optimal *in-situ* polymerization conditions were elucidated.¹⁴³ They found that a pyrrole/OH ratio of 16 yielded an optimum conductivity of $\sim 4.5 \text{ S cm}^{-1}$. At this concentration, there was sufficient PPy to cover the entire nanorod through hydrogen bonding between carboxylated CNC and PPy. They also reported an advanced method to obtain uniform PPy coating by applying polyvinylpyrrolidone (PVP) interlayer instead of chemical modification of CNC.⁴⁷ Individual

CNC was coated with the amphiphilic PVP before polymerizing the pyrrole monomers on the PVP/CNC complex (Figure 2.19D). Using a PVP/CNC mass ratio of 10, they were able to produce a highly conductive (36.9 S cm^{-1}) and capacitive (322.6 F g^{-1}) nanocomposite. In addition, the PPy/PVP/CNC nanocomposite displayed smooth and uniform morphology compared to the PPy coating on pristine CNC. It is believed that amphiphilic PVP binds to hydrophilic CNC surface and provides a hydrophobic surface for the coating of PPy. The carbonyl groups on PVP bind to the pyrrole monomers via hydrogen bonding with the NH groups, while the PVP chains prevent the agglomeration of PPy through steric hindrance. The choice of oxidant for the polymerization of conductive polymer also plays a critical role in the fabrication of conductive polymer composites. APS and $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$, as well as other derivatives are the most commonly used oxidants.^{64, 144} The different oxidants have different effects on the morphology and electrical properties of the conductive polymers. It is observed that APS produced conductive polymers with spherical shapes, while FeCl_3 formed rod shape nanoparticles under similar reaction conditions, and the particles oxidized by APS were approximately ten times larger than those produced with FeCl_3 .^{145, 146} This could be associated with the higher reduction potential of APS (2.00) compared to FeCl_3 (0.77), resulting in different reaction rates and aggregation of polymerized particles.¹⁴⁷ Additionally, the primary doping effect from oxidants should be considered to achieve the desired performance of the products. It is suggested that sulfate ion from the APS oxidant acts as a dopant through electrostatic interaction with PEDOT.¹⁴⁸⁻¹⁵⁰ FeCl_3 is also known to act as a dopant for conductive polymers.^{64, 151, 152} Additionally, it is believed that Fe^{3+} ion can chelate with the NH

groups on the conductive polymer and OH groups on CNC, thereby enhancing the interaction between the polymer and template.¹⁴² The polymerization condition was normally performed at low temperature (0–5 °C) in order to reduce the reaction rate and control the particle size.¹⁵³ The polymerization time of CNC based conductive polymer composites can vary between 30 min to 72 h, and typically, the polymerization times for PPy and PANI were between 1 and 24 h, compared to several hours to several days for PEDOT.¹⁵⁴

Electrochemical polymerization is another synthetic method commonly applied to *in-situ* polymerization, however it is less popular than chemical polymerization. The limitation of suitable conductive polymers and the requirement of an electrochemical cell make this method less versatile.¹³⁰ Despite its drawbacks, electrochemical polymerization has been widely studied because electrochemically produced conductive polymers generally displayed superior conductivity compared to chemically prepared conductive polymers.¹⁵⁵ A typical procedure for electrochemical polymerization of conductive nanocellulose requires an electrolyte containing the CNC dispersion and monomer in a three-electrode cell.^{64, 156} The polymerization begins when the required potential difference is applied, and the monomer is polymerized on the CNC deposited on the surface of the positive working electrode. Due to the limited area for the polymer deposition, electrochemical polymerization is more challenging to scale-up compared to chemical polymerization. However, the process is much faster, typically at the time scale of minutes to tens of minutes. The properties of the synthesized polymer are dependent on the electrode system, applied charge, time, the type of monomer, solvent, temperature, and electrode system.¹⁵⁷⁻¹⁶¹ Ravit *et al.* used electrochemical polymerization to

prepare CNC/PEDOT composite, and it was reported that the polymerization at 1.2 V for 5 mins resulted in a dense network morphology.¹⁵⁶ At higher potential differences, the morphology revealed the presence of agglomeration, which was attributed to the over oxidation of PEDOT. The properties of electrochemically and chemically polymerized CNC/PEDOT were compared by Fan *et al.*, where the chemically polymerized nanocomposites possessed a particle-like, globular microstructure, while the electrochemically polymerized CNC/PEDOT displayed a more fibrous network-like structure.⁶⁴ It is believed that in chemical polymerization, the negative chloride ions from FeCl₃, were incorporated as dopants into PEDOT to facilitate the polymerization in the bulk solution and on the surface of CNC. In comparison, electrochemical polymerization used CNC as the only dopant; therefore, PEDOT was polymerized around CNC, preserving the morphology of the pristine CNC rods. In addition to the morphology, electrical properties of the modified PEDOT/CNC from different polymerization methods were compared, and it was shown that the electrochemically prepared PEDOT/CNC exhibited lower charge transfer resistance (R_{ct}) than its counterpart.

In the *ex-situ* method, the conductive polymer was separately prepared or purchased as a commercial product (Clevios PH1000, Baytron P). The conductive polymer adheres to the CNC surface via a simple mixing and blending method. Again, the surface functionalities of CNC are responsible for the stable and robust interactions with the conductive polymers. *Ex-situ* methods are typically applied to CNC/PEDOT composites to lower the electrical percolation threshold and enhance its mechanical properties. PEDOT cannot be dissolved in most solvents; thus, poly(4-styrenesulfonic acid) (PSS) is generally associated with PEDOT as

an effective counter-ion and stabilizer.¹⁶² Untreated PEDOT: PSS has a particle-like structure, with distinct PEDOT rich regions distributed throughout the PSS insulating layers.^{163, 164} Due to the insulating PSS region surrounding PEDOT, pristine PEDOT: PSS possesses a relatively low electrical conductivity ($<1 \text{ S cm}^{-1}$), and secondary doping through harsh treatment with sulfuric acid or organic solvents with high boiling points is required to enhance its conductivity.¹⁶⁴ Tkalya *et al.* revealed that the templating of CNC lowered the electrical percolation threshold of PEDOT:PSS.¹⁶⁵ They prepared CNC/PEDOT:PSS-based polystyrene (PS) composites via a simple mixing method followed by freeze-drying and compression molding. The PEDOT:PSS in the composite was bound onto the CNC surface and this PEDOT:PSS coated CNC network in the PS matrix resulted in the formation of electrically conductive pathway. The percolation threshold of PEDOT:PSS in the CNC/PEDOT:PSS-based PS composite was extremely low, such as at 0.4 wt% (0.42 vol%) compared to 2.2 wt% (2.31 vol%) in the absence of CNC. This study shows that the addition of a minimal amount of nonconducting CNC facilitates the formation of conductive networks within the composite materials together with a smaller amount of the more expensive conducting polymers. Alam *et al.* analyzed the morphological characteristic of CNC/PEDOT:PSS from blended nanocomposite films, where the CNC/PEDOT:PSS blended films self-organized into a vertically layered stack structure with the CNC coated by PEDOT:PSS polymer chains through PSS adsorption on the CNC surfaces (Figure 2.19E).⁶⁹ Due to a continuous percolation network of PEDOT in the films and the enhanced molecular ordering of PEDOT chains, the conductivity of CNC/PEDOT:PSS blends was equivalent to the conventional PEDOT:PSS

even with high insulating CNC content of 50 wt%. The *ex-situ* method was also applied to prepare CNC/PPy nanocomposite for electronic applications.⁶² PPy nanofibers were incorporated into CNC aerogels acting as a nanosized substrate. The resulting 3D lightweight hybrid aerogel with high porosity and flexibility possessed excellent capacitance retention at high charge-discharge rates, which is suitable for their use as supercapacitors.

In conclusion, conductive polymer and CNC hybrid materials have been widely studied due to its relatively low cost, ease of preparation, and the existence of many strategies to control its properties. The preparation methods and the type of conductive polymers to prepare conductive polymer composites can be selected according to the required properties and performance of the end-use applications.

2.3.2 Conductive metal coating

CNC coated with conductive metals provides the highest level of electrical conductivity, which is suitable for various high-end applications due to the intrinsically high bulk conductivity of the metal. Metal coatings on CNC are usually prepared by the attachment of pre-synthesized metal nanoparticles or direct metallic ion reduction onto the surface of modified CNC as shown in Figure 2.20A. The CNC surface should have chelating sites or high surface charges to anchor the metallic ions and metal nanoparticles; therefore, chemical modification of CNC surface,^{67, 166, 167} or polymer coating on CNC^{46, 168, 169} were used to prepare CNC templates for metal coating. The choice of the reducing agent is also very critical to control the size and distribution of the metallic nanoparticles. A necessary requirement is

that the reduction potential of the reducing agent should be sufficiently negative compared to the reduction potential of the metallic precursor to form the atomic metal.⁹⁶ In terms of conductive metals, noble metals, such as silver, gold, and copper are commonly used for electronic applications due to their superior electrical conductivity, chemical and thermal stability. Recently, many researchers have reported the fabrication of metallic nanoparticles on CNC surface, but most of the researches mainly focused on traditional applications, such as catalysts,^{167, 169, 170} biosensors,^{167, 168} and antibacterial^{171, 172} rather than utilize their electrical conductivity as a conductor. There are only a few reported studies that produced metal-coated CNC for their conductive properties. Silver is the most widely used conductive metal for this purpose owing to its high chemical stability, superior electrical conductivity, and relatively high resistance to oxidation.

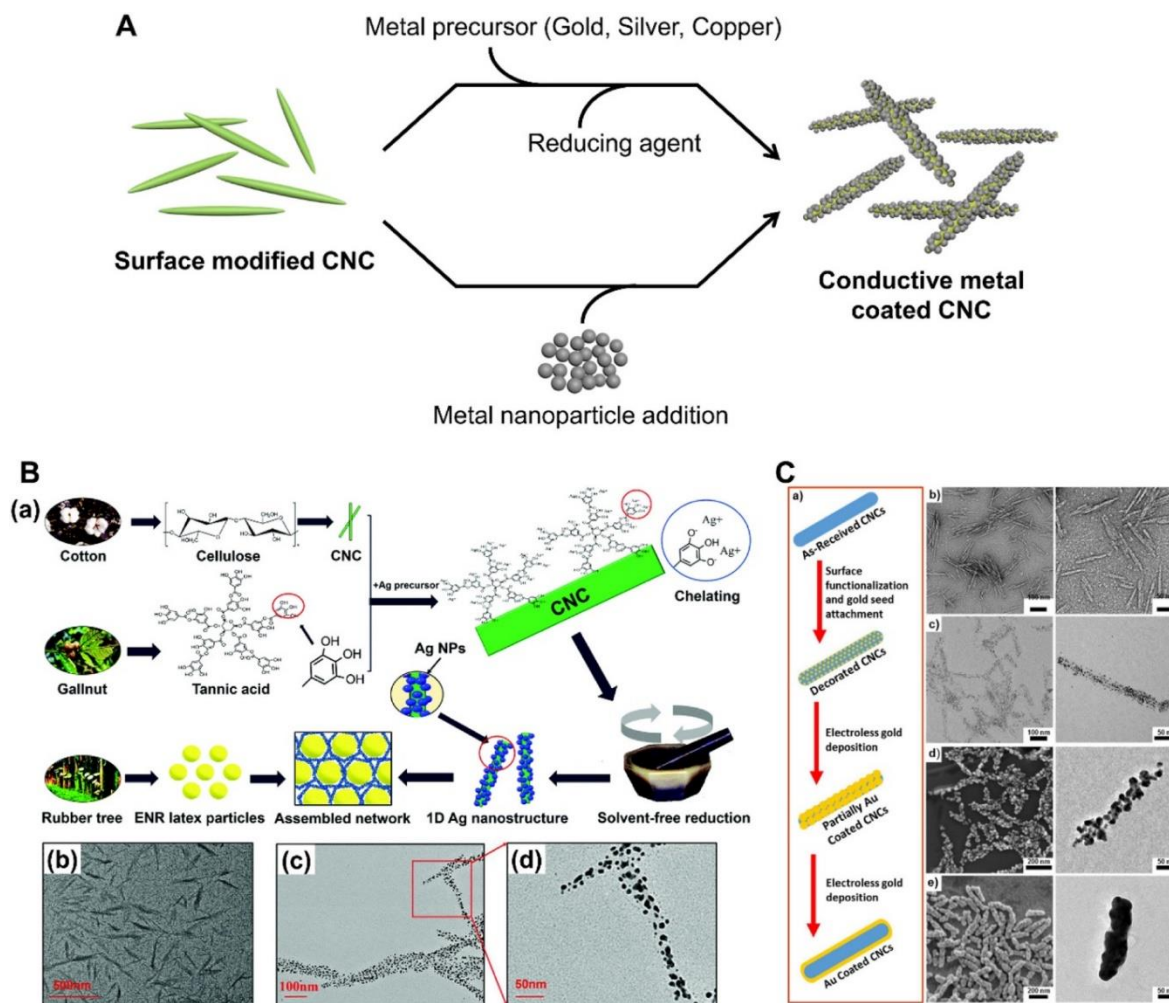


Figure 2.20 (A) Schematic of the preparation methods of conductive metal coated CNC. (B) (a) Schematic illustration for the solvent-free synthesis of the templated Ag@CNC 1D nanohybrid and the assembled organized network; TEM images of CNC (b) and Ag@CNC 1D nanohybrid (c and d). Reproduced from ref 66 with permission from The Royal Society of Chemistry. Copyright 2018.⁶⁶ (C) Schematic representation of the gold coating process; corresponding SEM and TEM images. Reproduced with permission ref 173. Copyright 2018 American Chemical Society.¹⁷³

TEMPO-oxidation is the most common method to introduce permanent carboxylate chelating groups onto the CNC surface. This strategy is remarkably versatile for wet-chemistry because carboxylated-CNC exhibits high dispersity in water owing to the relatively stable

negative charge in basic pH conditions.^{2, 41} Hoeng *et al.* developed silver conductive ink for inkjet printing using TEMPO-oxidized CNC scaffold as a stabilizing agent.⁶⁷ The silver nitrate was reduced by NaBH₄ in the presence of carboxylated CNC to produce nano-silver coated CNC. The highly charged oxidized CNC surface stabilizes the silver ink, and it remained stable for >1 day due to the electrostatic repulsive forces. The high aspect ratio of the CNC also lowers the required silver content to 3% by reducing the percolation threshold. Meulendijks *et al.* adopted the sophisticated silver reduction strategy to produce a high degree of silver nanoparticle coverage on the CNC surface.¹⁶⁶ They first attached tin(II) ions as a reducing agent onto the TEMPO-oxidized CNC, followed by silver reduction to form seed nanoparticles anchored to the CNC surface that acts as nucleation sites for further silver deposition. After the two-step metallization procedure, CNC was entirely covered with silver nanoparticles and the Ag-decorated CNC yielded a high conductivity of $2.9 \times 10^4 \text{ S cm}^{-1}$ after photonic sintering at 500 V and 4.0 J cm^{-2} for 600 μs .

Due to its relatively simple preparation procedure, the polymer-coated CNC (instead of oxidized CNC) has also been used for the attachment of silver nanoparticles. CNC coated with polydopamine (PDA) and PVP was used for silver nanoparticle deposition.⁴⁶ PVP is amphiphilic without charges, and it acts as a coupling agent to facilitate the uniform coating of the PDA layer on CNC. The PVP interlayer is not only advantageous for suspension stability of CNC@PVP@PDA but it is also beneficial for the further formation of uniform silver nanoparticles onto the CNC surface. The prepared CNC@PVP@PDA@Ag was added to a conventional electrically conductive adhesive (ECA) as a co-filler, which decreased the

resistivity by building an effective conductive path. Liu *et al.* synthesized a 1-dimensional silver nanohybrid using a facile and environment-friendly solid-state method (Figure 2.20B).⁶⁶ They used the CNC template with tannic acid as a chelating and reducing agent to form silver nanoparticles via a mortar-milling at room temperature. Reduced silver nanoparticles were anchored onto the CNC surface through the surface charge and chelating effect of tannic acid and CNC. The synthesized Ag@CNC hybrid was added to rubber latex to fabricate nanocomposite with a higher electrical conductivity of 0.1 S m^{-1} compared to silver nanoparticles directly added to the latex dispersion. The improved conductivity of CNC composite was achieved from the lower percolation threshold due to the organized electrical pathway within the CNC scaffold.

However, most reported studies revealed morphological defects that limit the benefit of a 1-D CNC template. Unlike the continuous conductive polymer coating strategy, individual metal nanoparticles attached to CNC will lead to the discontinuous electron transfer pathway. In this context, a continuous metal-coated CNC is required to achieve a high conductivity even without the sintering process. There are only a few reported studies on the continuous metal nanoshell synthesis on individual CNC. Semenikhin *et al.* prepared gold nanoshells on aminated CNC via a wet chemistry approach and they characterized the properties of gold-coated CNC.¹⁷³ To modify the surface of CNC for gold nanoparticle decoration, four sequential steps for surface functionalization methods were used to introduce the amine groups. Afterward, 1–3 nm size gold seed particles were attached to the CNC surface, followed by the electroless deposition of gold to produce a continuous shell structure on individual CNC

(Figure 2.20C). The synthesized gold nanoshell-bearing CNC displayed two distinctive plasmon resonance bands that confirmed the CNC-gold core-shell structure. A more elaborate synthesis of gold nanoshell on CNC was conducted using electrostatic interaction among CNC, reducing agent, capping agent, and gold precursor.¹⁷⁴ They coated the surface of CNC with poly-(diallyldimethylammonium chloride) (PDADMAC), which has quaternary ammonium groups providing a high positive charge. During the controlled gold reduction process, ascorbic acid reducing agent was absorbed onto the PDADMAC coated surface. Limiting the gold reduction region minimizes the generation of gold nanoparticles in the bulk solution. Also, the electrostatic attachment of hexadecyltrimethylammonium bromide (CTAB) to the reduced gold particle induces a unidirectional smooth gold nanoshell growth. Although the electrical properties were not reported, the structure of the continuous and uniform metal coating developed in this work suggests the enormous potential of CNC as a template material for metal shell coating, which is applicable for a wide range of applications, including electronics.

However, metal-coated CNC as conductive materials is less investigated as it is more challenging to control the synthesis to achieve a continuous electron transfer network. Nonetheless, it is a promising strategy to produce highly conductive, effective, and environmental-friendly conductors for advanced applications. Therefore, we hope that researchers will be motivated to pursue this after reading this review as the fabrication of the conductive metal-CNC hybrid system offers many attractive potential applications.

2.3.3 Carbonized CNC

The use of renewable biomass as a sustainable carbon source to prepare materials with excellent electrochemical properties has been extensively investigated since it is an environmentally benign and cost-effective method.¹⁷⁵⁻¹⁸⁵ Among many potential natural resources, CNC derived carbon material is suitable for various applications, such as the adsorption of large molecules, catalyst supports, supercapacitors, and batteries. Because CNC is nanosize with a large specific surface area, it can easily form porous structure, which is suitable for charge storage. Moreover, by removing the organic components, CNC can be directly converted to carbonaceous nanorod at high temperature under an inert atmosphere (Figure 2.21A). Also, their electrochemical properties can be modulated by simple strategies, such as oxidation or heteroatom doping to generate more reactive sites. Therefore, the porous carbonaceous materials derived from CNC have attracted significant research interest, especially as an electrode material for application in energy storage and conversion.

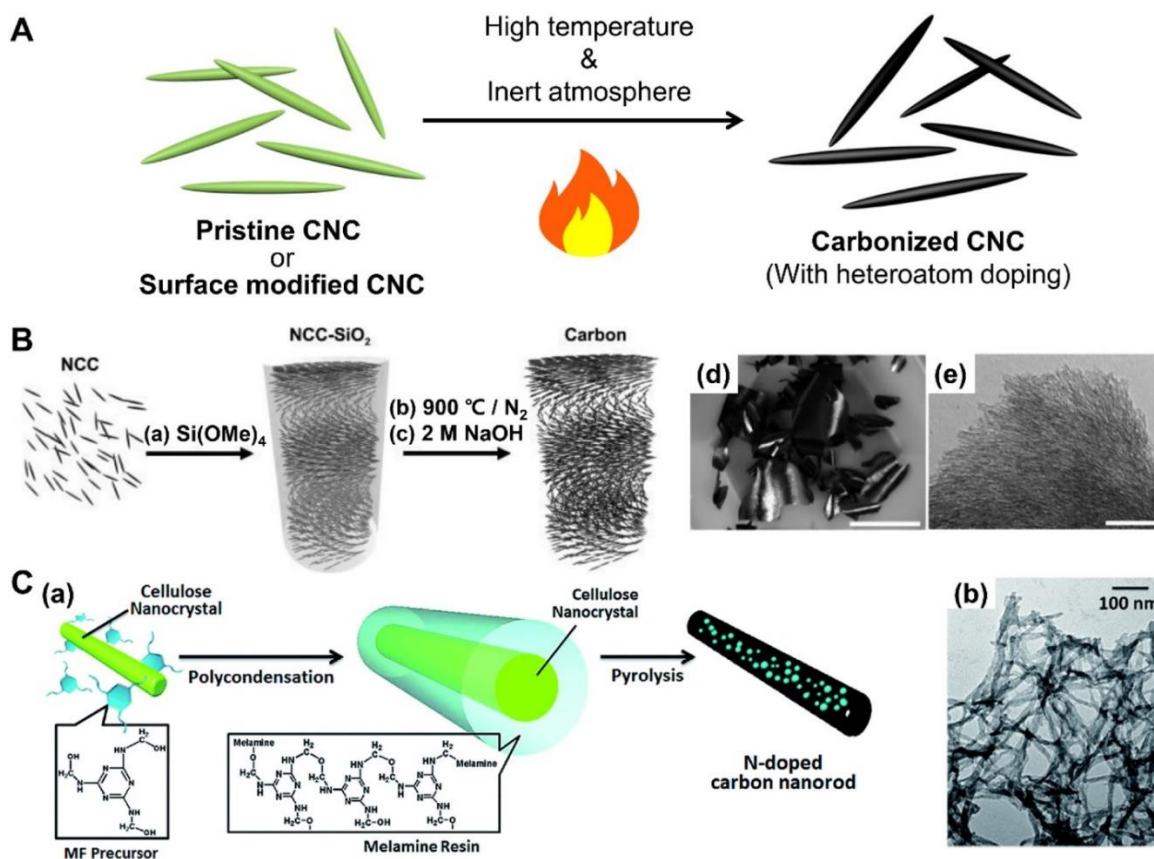


Figure 2.21 (A) Schematic of the preparation methods of carbonized CNC. (B) Synthesis of chiral nematic mesoporous carbon. (a) NCC prepared by hydrolysis with sulfuric acid is mixed with TMOS and slowly evaporated to form chiral nematic NCC–silica composite films. (b) NCC–silica composite films are pyrolyzed in an inert atmosphere at 900 °C to generate carbon–silica composite films. (c) Silica is removed from the carbon–silica composite films using 2 M NaOH to generate chiral nematic mesoporous carbon. (d) Photograph of mesoporous carbon sample (scale bar = 2 cm). (e) TEM image of mesoporous carbon sample (scale bar = 200 nm). Reproduced with permission from ref 186. Copyright 2011 WILEY-VCH.¹⁸⁶ (C) (a) Schematic illustration of the 2-step synthesis of nitrogen-doped carbon nanorods; also (b) the TEM image of nitrogen-doped carbon nanorods prepared at 900 °C. Reproduced from ref 187 with permission from The Royal Society of Chemistry. Copyright 2015.¹⁸⁷

Shopsowitz *et al.* first reported the fabrication of mesoporous carbon film as an effective electrode material for supercapacitors that possessed a high specific surface area

using a CNC template.¹⁸⁶ The pyrolysis of CNC-silica composite followed by silica etching yielded a chiral nematic film templated by CNC (Figure 2.21B). The surface area and pore volume of mesoporous carbon were greatest when 65 wt% of CNC was used due to the long-range chiral nematic structure of individual CNC prior to carbonization. The optimal mesoporous carbon possessed a specific capacitance of 170 F g^{-1} at 230 mA/g and a conductivity of $1.3 \times 10^{-2} \text{ S cm}^{-1}$ at 25°C . This electrical conductivity value increased linearly with increasing temperature due to changes of electron mobility yielding property similar to a semiconductor. The porous carbon materials from CNC could be easily doped with heteroatoms to enhance their electrochemical properties by using low-cost and straightforward methods for high-performance energy applications. Highly porous nitrogen (N) doped carbonaceous nanorod was produced from melamine-formaldehyde resin (MF) coated CNC (Figure 2.21C).¹⁸⁷ *In-situ* polymerized MF coating on CNC carbon precursor serves as a N doping source after one-step pyrolysis, producing carbon nanorods with promising capacitive performance compared to pristine carbonized CNC. They found that the best carbonization temperature was 900°C in terms of capacitive performance from moderate nitrogen doping content, hierarchical porous structure, and high specific surface area. The optimal capacitance of 352 F g^{-1} at 5 A g^{-1} was achieved from the nitrogen-doped carbon rod electrode, and it also displayed robust cycling stability. Pang *et al.* reported nitrogen and sulfur dual doped nanoporous carbon from the self-templated CNC to obtain a relatively high doping content.⁶³ CNC was uniformly coated with aqueous polyrhodanine (PR) solution as the doping source, instead of using two separate doping sources to introduce two heteroatoms sulfur (S) and

nitrogen (N), followed by the addition of tetraethyl orthosilicate (TEOS). After evaporation of water from the dispersion, it yielded self-standing films that were pyrolyzed, retaining the chiral nematic ordered self-assembly structure of CNC. The “dual-doping” strategy significantly improves the chemisorption of lithium polysulfides for lithium-sulfur batteries system. It also enhances the conductivity of the carbon material to 0.78 S cm^{-1} compared to a value of 0.04 S cm^{-1} from non-doped CNC-derived carbon due to the increased doping content resulting in favorable kinetics. Li *et al.* developed the freestanding carbonaceous material with a hierarchical porous structure using the pyrolysis of CNF integrated CNC.¹²⁸ After the fabrication of CNF/CNC hybrid film through solution mixing and solvent evaporation, Al_2O_3 protective layer was deposited on the CNF/CNC dry film by atomic layer deposition (ALD). A two-level hierarchical porous structure, consisting of a macro-porous framework from CNF and micro/mesopores from CNC, could be preserved during carbonization due to the thin protecting layer of Al_2O_3 which was then removed by an etching process. The fabricated freestanding films possessed a high specific surface area of over $1200 \text{ m}^2\cdot\text{g}^{-1}$ and a two-level hierarchical porous structure, which resulted in fast ion transport in the film. Zhu and Shen carbonized ordered CNC into porous carbon materials with higher graphitic crystalline domain at a relatively low temperature of 1000°C .¹⁸⁸ They prepared CNC films by evaporating water from the CNC dispersion in the oven and pyrolyzed the dried CNC in argon gas environment. The short-range ordered hexagonal carbon lattice from aligned cellulose glucose chains and percolated long carbon nanofiber were characterized by molecular dynamic simulations and *in-situ* TEM measurements. The CNC derived mesoporous carbon not only displayed an ideal

structure, but it also possessed a superior electrochemical performance as a sodium ion battery (SIB) anode material, including the high reversible capacity of 340 mA h g^{-1} at 100 mA/g , excellent rate, and good cycling stability.

CNC is considered an attractive carbon source for preparing highly advanced electrode material at a low price even though only a very limited number of researches have used CNC to achieve this goal. We believe that the use of CNC for the fabrication of carbonaceous material will grow with the increasing demand for sustainable nanomaterials and advanced energy storage devices.

2.3.4 CNC/CNT hybrid system

Carbon-based materials, including carbon black, CNT, and graphene, have been widely studied due to their promising electrical and thermal conductivity as well as outstanding mechanical strength. Among many forms of carbon materials, CNT has been recognized as a promising electronic material as the mass production of CNT has become possible. CNT can be classified into two types, depending on their structure, which are the single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). SWCNT is made up of only one single layer of a two-dimensional hexagonal lattice of carbon atoms, which is rolled up to form a hollow cylindrical structure, and MWCNT consists of nested SWCNT.^{189, 190} CNT possesses unique properties, such as high intrinsic current mobility, exceptional tensile strength, and elastic modulus due to their nanostructure and strong bonds strength between the carbon atoms. However, CNT readily agglomerates to form large undesirable aggregates due to van der

Waals forces, which require the use of toxic chemicals and expensive processes.¹⁸⁹ Also, CNT itself cannot be self-standing and must be incorporated into other supporting materials to form the electrode in some applications, like supercapacitors. To overcome these challenges for advanced electronic applications, CNC can be incorporated into the CNT nanocomposites (Figure 2.22A). This type of CNT-CNC nanocomposite uses a different approach compared to the conductive polymer coating, metal coating, or carbonization methods in terms of the role of CNC in the composite, but it is a remarkably effective strategy.

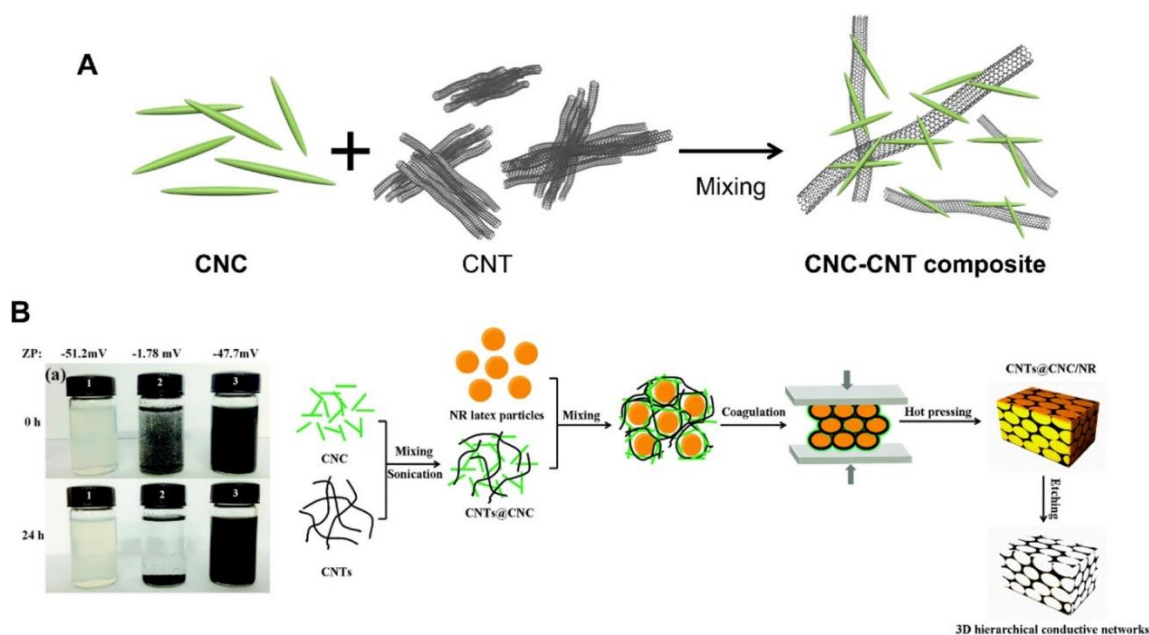


Figure 2.22 (A) Schematic of the preparation methods of CNC-CNT composite. (B) Digital camera pictures along with the z-potential of CNC, CNT and CNT@CNC nanohybrid aqueous suspension under neutral conditions before and after standing for 24 h; also the schematic illustrating the fabrication of CNT@CNC/NR nanocomposites. Reproduced from ref 65 with permission from The Royal Society of Chemistry. Copyright 2016.⁶⁵

Wang *et al.* introduced CNC into natural rubber (NR)/CNT composites to produce highly stretchable, sensitive, and reversible strain sensors.⁶⁵ CNT@CNC nanohybrid

suspension was mixed with NR latex to fabricate nanocomposite, followed by demulsification with H₂SO₄ and drying. The amphiphilic CNC considerably enhanced the suspension stability of CNTs in aqueous media and allowed the CNT@CNC nanohybrids to be selectively located between the NR latex microspheres, which are organized into a continuous 3D conductive structure as shown in Figure 2.22B. CNT@CNC/NR nanocomposites possess a much lower percolation threshold (1.6 vol%) and higher conductivity than CNT/NR nanocomposites (7.0 vol%) due to the 3D hierarchical conductive networks. Yang and Shi reported on the development of combined lightweight, highly porous, and flexible CNC aerogels with various capacitive nanomaterials for supercapacitor devices.⁶² PPy-coated MWCNT (PPy-CNT) was incorporated into crosslinked CNC aerogels consisting of aldehyde-modified CNC and hydrazide-modified CNC to form a self-standing structure. An optimum ratio of 1.5:1 for the capacitive nanoparticle:CNC was required to produce a stable dispersion. The dispersed nanomaterials retained the crosslinked structure during the freeze-drying process and resulted in a considerably high mass ratio of active material in the aerogels. The 3D cellulose aerogel electrodes exhibited significant capacitance retention at high charge-discharge rates and a low internal resistance of 0.59 Ω for PPy-CNT cells. They also have prepared an aerogel-based current collector with high capacitance using CNC, MWCNT, and *in-situ* polymerized PPy, which was flexible and compressible.¹⁹¹ CNC-MWCNT hybrid aerogels were fabricated through the crosslinking of CNC by combining suspensions consisting of MWCNT, bile acid dispersant, and cross-linkable CNC. Then, the PPy was *in-situ* polymerized in the presence of CNC-MWCNT aerogels to prepare PPy loaded CNC-MWCNT aerogels. The fabricated

aerogel-based electrodes possessed an excellent capacitance of 2.1 F cm^{-2} , an active mass loading of 17.8 mg cm^{-2} , and a mass ratio of active material/current collector of 0.57.

CNC significantly improves the dispersity of CNT, making it possible to prepare free-standing structure. Although there are a limited number of studies on CNC-CNT composites compared to BC-CNT and CNF-CNT, we believe the availability of commercial scale CNC and CNT would propel the development and application of CNC-CNT composites with high performance and also sustainability.

2.4 Antimicrobial Systems

2.4.1 Current antimicrobial systems and problems

Infectious diseases caused by bacteria, fungi, and viruses are a threat to public health worldwide. These disease-causing agents can be transferred, directly or indirectly, from the environment or one person to another, causing illness and death in the community.¹⁹² Antimicrobials are a group of compounds used to treat and prevent these infections by killing or inhibiting the growth of microorganisms. Antimicrobials can be classified into three distinct groups: (i) Antibiotics, which specifically prevent or treat infections caused by bacteria; (ii) antifungals, which selectively target fungal or yeast infections; and (iii) antivirals, which restrict the entry and replication of viral agents.¹⁹³

Bacteria are single-celled organisms with a length of 1–10 μm and width of 0.2–1 μm .¹⁹⁴ They can be found practically everywhere on the earth and play important roles in the ecosystem. Most bacteria are harmless to humans, and some of them are even beneficial. Many bacteria are normally found in the gut and play a role in the digestion of food and absorption of nutrients.¹⁹² However, there are also bacteria that are highly infectious and can cause deadly diseases. These bacteria can be transmitted from infected animals to people, as well as from infected humans to healthy ones. They have caused significant morbidity and mortality in human since the beginning.

Penicillin, discovered by Alexander Fleming in 1928, is the world's first and one of the most widely used antibiotics.¹⁹⁵ The discovery of antibiotics marked a significant turning point

in the prevention of some diseases, and offers a tool to fight against infectious bacteria. Antibiotics kill bacteria by disrupting an essential process or a structure in the cells, resulting in their destruction or inhibition of their growth. Antibiotics are generally categorized as either bactericidal or bacteriostatic based on their antibacterial action.^{196, 197} While bactericidal antibiotics kill the bacteria by damaging and inhibiting the cell wall synthesis, bacteriostatic antibiotics prevent their further growth by inhibiting DNA replication and protein synthesis.¹⁹⁶ However, the antibacterial action can vary with the amount of dose. When an antibiotic is used in low doses, it could act as a bacteriostatic agent, whereas a high dose of bacteriostatic antibiotic may act as a bactericidal agent.

Fungi are unicellular or multicellular eukaryotic organisms that are present in various environments,^{198, 199} and most fungi are saprophytic. However, a few fungal species are pathogenic and cause many infections and allergies in humans.²⁰⁰ In most cases, fungal infections affect only the skin or nails to an uncomfortable degree. However, some can cause life-threatening illnesses, such as meningitis, pneumonia, and blood infections. Antifungal drugs generally target the fungal cell membrane and cell wall that surround and protect the fungal cell or cellular functions.¹⁹⁸

Viruses simply consist of nucleic acid, either RNA or DNA, with a protein coat.^{201, 202} Unlike other microorganisms, a virus cannot replicate alone; it can only replicate within a living host organism such as animals, plants, fungi, and bacteria. A viral infection involves the incorporation of a viral genetic material into a host cell, followed by the replication of that material to generate new viruses. These new viruses are released to the external environment

by destroying the host cell. Therefore, viral replication often causes severe damage to the host organism. However, antivirals, unlike most antibiotics, do not kill their target pathogen. They only prevent its replication to reduce the duration and severity of viral infections.²⁰² Vaccination is the primary method to prevent viral infections using inactive viral particles, which helps the immune system recognize and attack a specific virus.²⁰³

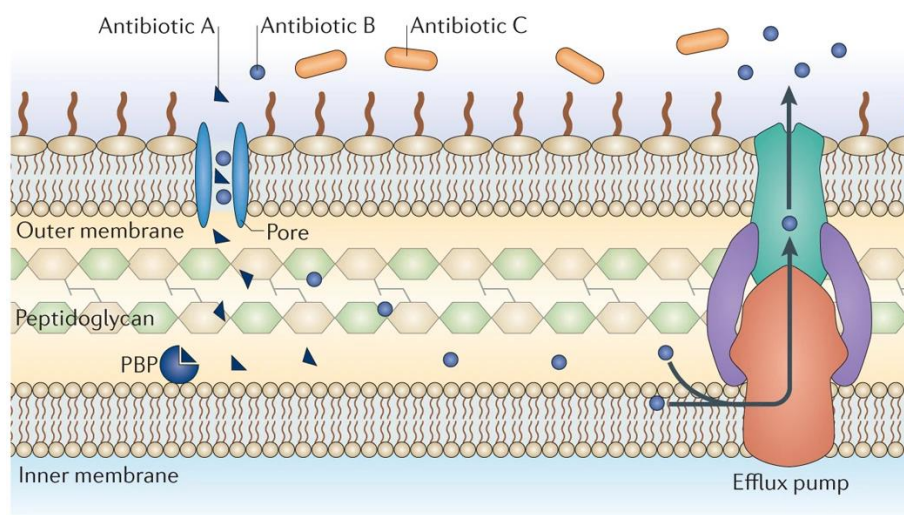
In addition to these chemotherapeutic antimicrobial agents, biocides are also used to control and kill harmful microorganisms. Biocides are chemical substances and are used as disinfectants, antiseptics, and preservatives. Biocides are mainly categorized into two types: oxidizing and nonoxidizing.^{197, 204, 205} Oxidizing biocides, such as chlorine dioxide and hydrogen peroxide are based on halogens. They kill microorganisms by causing the irreversible cell damage through electrochemical oxidation. Nonoxidizing biocides involve highly toxic organic chemicals or surfactants. They work through various processes such as inactivation of enzymes, cell lysis, and stress on intracellular pH.²⁰⁵ These biocides are used for various purposes, including water treatment, antifouling paints, plastics, wood, cosmetics, and food.^{197,}

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Although these valuable antimicrobials save lives, their indiscriminate use has led to the emergence of several antimicrobial-resistant pathogens. As a result, many antimicrobial agents are no longer effective, which is threatening the global public health. In 2014, the World Health Organization (WHO) stated that antimicrobial resistance is a “serious threat is no longer a prediction for the future, it is happening right now in every region of the world and has the potential to affect anyone, of any age, in any country.”²⁰⁷ The deaths attributable to

antimicrobial resistance are projected to increase to 10 million by 2050 with the cumulative loss of USD 20–35 trillion.²⁰⁸ While antimicrobial resistance poses a severe threat to public health, the antibiotic resistance is particularly urgent.²⁰⁹ Approximately 5 million deaths have been estimated to be associated with antibiotic resistance in 2019.²¹⁰ Despite making intensive efforts and massive investments in developing new antimicrobial agents, it is still insufficient to tackle the rapid emergence of drug-resistant bacteria.²¹¹

Figure 2.23 demonstrates the intrinsic resistance mechanisms of bacteria, which involve the followings: (1) limiting drug uptake, (2) active drug efflux, (3) drug inactivation, and (4) alteration of drug targets.^{212, 213} While the intrinsic resistance usually stems from limiting the uptake, drug efflux, and drug inactivation, the bacteria can become resistant owing to drug-target modification.²¹² The development of antibiotic resistance involves the following steps.²¹⁴ First, the bacteria acquire the resistance against single and multiple drugs through the horizontal gene transfer and spontaneous mutation of existing genes. These bacteria then express the resistant gene that can survive antimicrobial drug treatment. These resistant bacteria grow and become widespread. Some bacteria further transfer their drug resistance to other bacteria. This antibiotic selection pressure occurs whenever microorganisms are exposed to the medicine but not eliminated, resulting in the emergence of antimicrobial resistance. Because of the increasing antimicrobial resistance and associated challenges, the development of effective and novel antimicrobial agents is attracting more attention. We will now discuss a promising antimicrobial system comprising metal nanoparticles and CNC.



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Figure 2.23 Intrinsic mechanisms for antimicrobial resistance. Here, β -lactam antibiotic is used to target a penicillin-binding protein (PBP). Unlike antibiotic A, which reaches its target and inhibits peptidoglycan synthesis, antibiotic B is efficiently removed by efflux after entering the cell. Antibiotic C cannot cross the outer membrane and therefore is unable to access the target PBP. Adapted with permission from ref 215. Copyright 2015 Springer Nature.²¹⁵

2.4.2 Metal nanoparticles as antimicrobial agents

Metals have been used as antimicrobial agents for thousands of years.^{216, 217} Copper or silver was used for food preservation, water disinfection, and as medicine to prevent infection. Until the Second World War, metals were used to combat diseases such as dysentery. However, as the golden era of antibiotics began, the use of metals for these applications rapidly decreased.¹⁹⁵ Unfortunately, in less than a century after the discovery of penicillin, antimicrobial resistance has become a severe threat to global health. The WHO has already warned that we are approaching a post-antibiotic era where even common infections and minor

injuries can bring death.²¹⁸ As a result, metals are again attracting attention as a viable solution to overcome this post-antibiotic era.

The physical and chemical properties of metal nanoparticles differ from their bulk substances owing to their small size and high surface-to-volume ratio. The remarkable antimicrobial activity of metals results from the synergistic combination of multiple mechanisms.^{211, 219-221} Figure 2.24 demonstrates the major pathways of physical interaction between metal nanoparticles and bacterial cells. Firstly, metal nanoparticles can bind and disrupt a bacterial cell wall/membrane, causing leakage of cytoplasmic components. Since both Gram-positive and Gram-negative bacteria cell walls and common viruses have a negative surface charge, metal nanoparticles and/or metal ions tend to interact with these microorganisms via electrostatic interaction.^{202, 219} These interactions exert localized stress on the cell membrane potential and integrity, impairing the membrane function and eventual cell death. Another critical role of metal nanoparticles is inhibiting enzyme activity and DNA synthesis.²¹¹ Small metal nanoparticles and metal ions can bind to intracellular components such as enzymes, DNA, and ribosomes upon membrane permeation. This interaction impairs their function and disturbs cellular metabolism such as respiration, DNA synthesis, and ATP production. The reactive oxygen species (ROS) or oxygen-free radicals generated from metal nanoparticles also damage cellular and viral components. ROS are highly reactive chemicals containing oxygen molecules, including hydrogen peroxide (H_2O_2), hydroxyl radical ($\text{HO}\bullet$), and superoxide anion (O_2^-). They generate severe oxidative stress and cause damage to biological macromolecules, including nucleic acids (RNA and DNA), lipids, and proteins.

Consequently, the disrupted cell membranes release the cell content by forming holes and/or pits, leading to cell lysis.

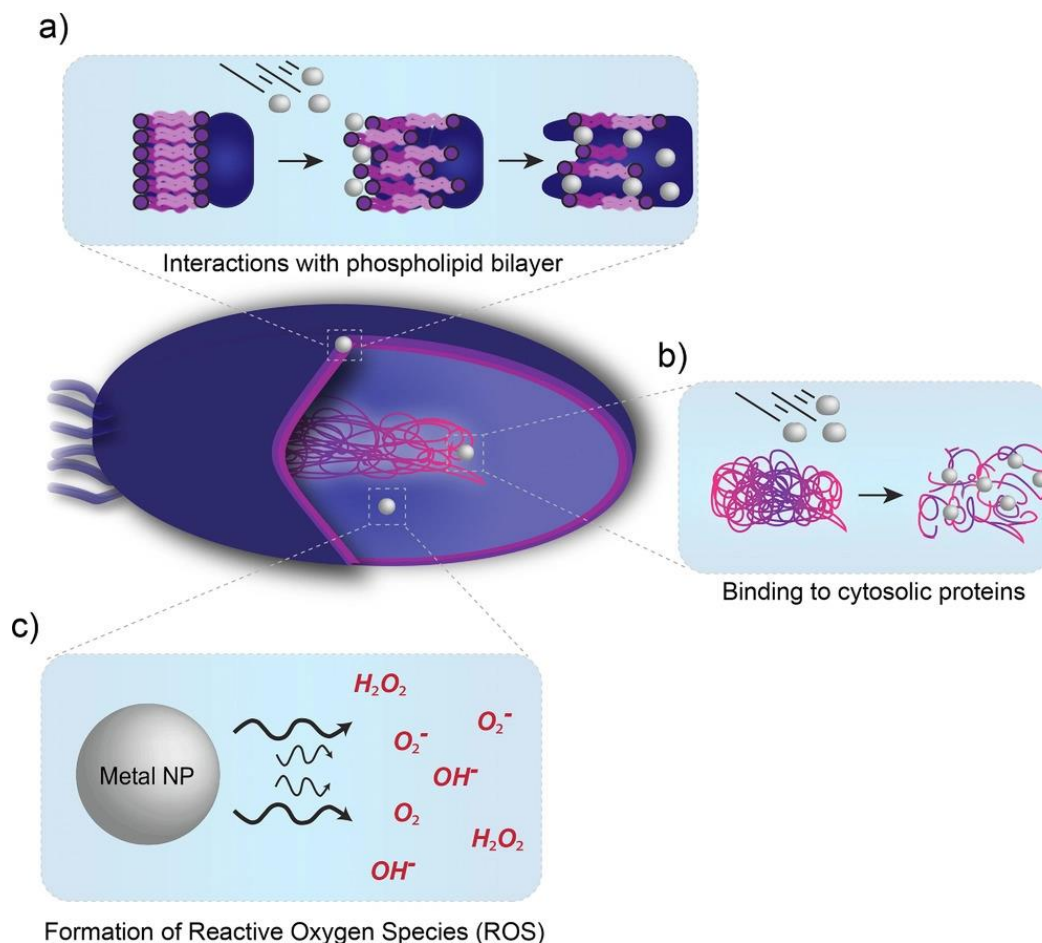


Figure 2.24 Schematic describing the antimicrobial mechanism of metal nanomaterials by a) destabilizing the phospholipid bilayer of the cell, causing cell lysis; b) binding to cytosolic proteins, such as DNA, triggering cell death; and c) producing ROS, leading to increased oxidative stress and cell instability. Adapted with permission from ref 220. Copyright 2018 Wiley.²²⁰

Healthy microorganisms use biochemical mechanisms to resist metal toxicity, including efflux, reduced uptake, chemical modification, metabolic by-pass, and repair of damaged components.¹⁹⁵ However, this resistance is not sufficient to compensate for the attack by metal

nanoparticles having a much smaller size than the bacteria and a large specific surface area. Furthermore, metal nanoparticles generate a focal source of metal ions that are continuously being released. As a result, the locally concentrated toxic metal ions can cause severe damage to microorganism cells.²¹⁹ This efficient antimicrobial performance of metal nanoparticles allows various metals and metal oxides, such as silver (Ag),^{222, 223} gold (Au),²²⁴ copper and copper oxides (Cu, Cu₂O, and CuO),^{223, 225} zinc oxide (ZnO),²²⁶ magnesium oxide (MgO),²²⁷ titanium dioxide (TiO₂),²²⁸ and iron oxide (Fe₂O₃)²²⁹ to be used as antimicrobial agents. In particular, some nonessential metals such as Ag, Hg, and Te can be devastating to most microorganisms even at very low concentrations.²³⁰

To design effective antimicrobial metal nanoparticles, various factors should be considered, such as their size, shape, and surface charge. Smaller metal nanoparticles generally exhibit higher antimicrobial property than larger nanoparticles due to their higher surface energy owing to a larger surface-area-to-volume ratio.²³¹ Therefore, smaller metal nanoparticles can produce more ROS that damage essential biomolecules. They are also advantageous in penetrating microbial cell walls. Interestingly, some studies have demonstrated that larger nanoparticles have a higher toxicity than smaller ones, indicating that there are more critical factors than the size alone.²³² If a nanoparticle is spherical, which is the most common shape, the assumption that smaller nanoparticles are more toxic would usually be valid. However, the antimicrobial activity of highly crystalline nanometals with specific surfaces such as cubes, rods, plates, and tubes is more complicated because different crystal facets exhibit different toxicities.²³³⁻²³⁵ Pal *et al.* compared the antibacterial properties of silver

nanoparticles having different shapes against Gram-negative bacteria.²³⁴ Because of the (111) lattice plane, the truncated triangular silver nanoplates possessed a stronger bactericidal activity than spherical and rod-shaped silver nanoparticles, both in liquid systems and on agar plates. The surface charge of metal nanoparticles is another crucial factor that controls the toxicity of antimicrobial metal agents. Positively charged metal nanoparticles promote the electrostatic interaction with negatively charged surface of microorganisms, leading to efficient membrane disruption and viability reduction. Four different silver nanoparticle suspensions were prepared using different capping agents and their antibacterial activity against *bacillus* was investigated.²³² The silver nanoparticles clearly showed a surface charge-dependent toxicity. Silver nanoparticles with a positive surface charge of +40 mV exhibited superior toxicity compared to those of the other prepared nanoparticles. The lowest toxicity was observed when citrate-capped nanoparticles (−38 mV) were used. Apart from these abovementioned factors, there are other factors that govern the antimicrobial property, such as solubility, agglomeration, and oxidation states. Therefore, these factors should also be considered when designing and developing efficient and effective antimicrobial metal nanoparticles for target applications.

2.4.3 Application of CNC in antimicrobial systems

The use of CNC and modified CNC as antimicrobials has received significant interest because they are biocompatible, biodegradable, and chemically accessible for modification.^{71,}
²³⁶ Antimicrobial CNC can be grouped into two categories on the basis of loaded antimicrobial

materials: i) metal-functionalized CNC; ii) antimicrobial drug carrier CNC. Considerable research efforts have been devoted to fabricating CNC-reinforced antimicrobial composites because of their excellent mechanical properties and nontoxicity.²³⁷⁻²⁴⁴ However, we will not cover details of them here because the primary role of CNC in those studies is just reinforcing agents rather than imparting/enhancing antimicrobial activity.

As discussed earlier, metal nanoparticles such as gold, silver, copper, and zinc oxide exhibit excellent antimicrobial activity. To prepare antimicrobial metal nanoparticles, the synthesis of small and stable nanoparticles is essential because smaller nanoparticles are generally more effective than larger ones. However, due to the high surface energy of smaller metal nanoparticles, they readily agglomerate and aggregate resulting in the loss of active surface area, which, in turn, decreases their applicability. Therefore, a large amount of capping agents is used as stabilizers to prevent metal nanoparticle aggregation in colloidal synthesis. Although typical capping agents such as surfactants and polymers are commonly used, most of them are potentially toxic, nonbiodegradable, and difficult to remove. CNC could be utilized as sustainable stabilizers in metal nanoparticle synthesis. CNC not only prevents the aggregation of metal nanoparticles by immobilizing nanoparticles onto their surface, but also promotes the nucleation of nanoparticles from the metal precursor, resulting in narrow size distribution.²⁴⁵ This synergetic effect of sustainable CNC enable the synthesis of stable and small metal nanoparticles, which could be used as promising antimicrobial metal agents.

The initial study on antimicrobial metal-functionalized CNC has mainly focused on utilizing silver, a well-known strong antimicrobial agent. Yu *et al.* demonstrated one-pot

synthesis of silver nanoparticle-coated CNC through the Fischer esterification and redox reactions beginning from the acid hydrolysis of commercial microcrystalline cellulose (MCC).²⁴⁶⁻²⁴⁸ The prepared CNC/Ag nanocomposites were deposited with silver nanoparticles (20–40 nm in diameter), and they displayed excellent thermal stability and good antibacterial activity against Gram-negative *E. coli* and Gram-positive *S. aureus*. They also exhibited potential miscibility with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PLA matrix as a bifunctional nanofiller in the preparation of antibacterial and biodegradable polymer nanocomposites. Shi *et al.* demonstrated that the adoption of modified CNC as a capping agent could improve the antibacterial activity of silver nanoparticles.¹⁷² They prepared polydopamine-coated CNC (PD-CNC) to enhance the adhesion property of CNC toward silver. The synthesized PD-CNC showed outstanding chelating ability and excellent reduction property for silver ions, resulting in well-dispersed silver nanoparticle-coated CNC in an aqueous solution without using toxic reducing agents. Owing to the superior dispersion stability of AgNP-PD-CNC, they can eliminate both Gram-positive *E. coli* and Gram-negative *B. subtilis* with a four-time lower minimum inhibitory concentration (MIC) than that of the pure silver nanoparticle system (Figure 2.25).

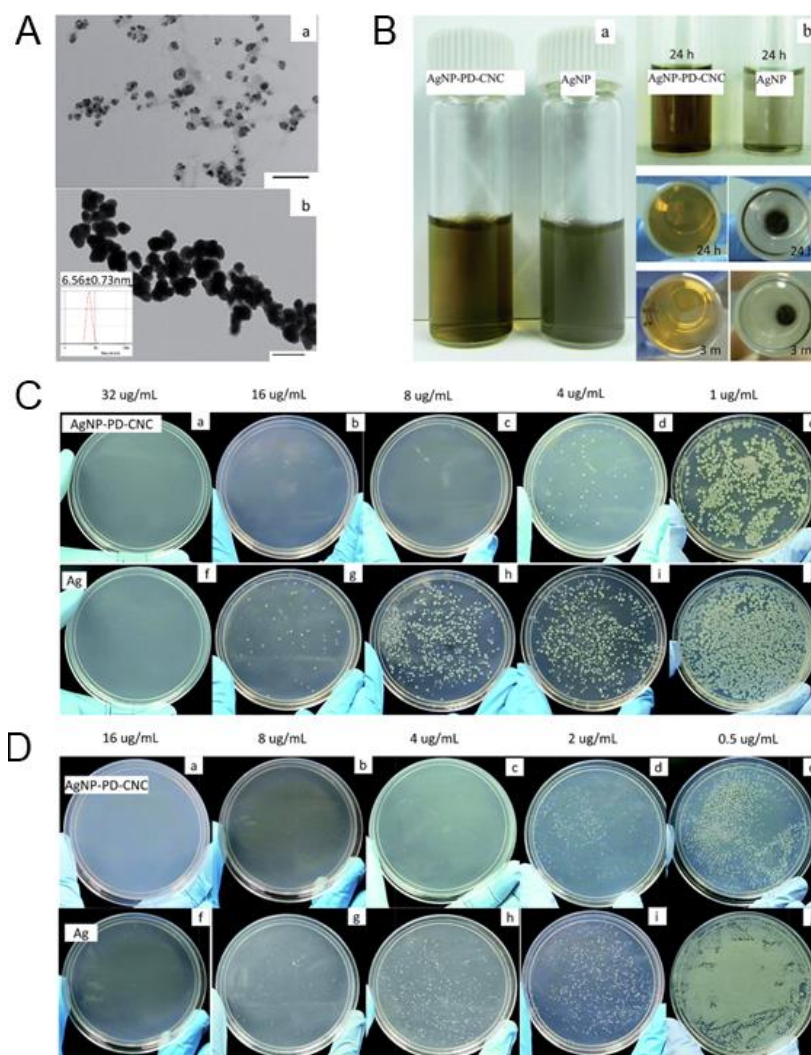


Figure 2.25 (A) TEM images of AgNP-PD-CNC (a) and pure AgNPs (b). Inset presents size distribution of AgNPs by DLS. Scale bar: 100 nm. (B) AgNPs and AgNP-PD-CNC solution (a) after preparation and (b) after one day and 3 months. Antimicrobial activity of AgNP-PD-CNC and AgNPs against (C) *E. coli* and (D) *B. subtilis*. Adapted with permission from ref 172. Copyright 2015 Royal Society of Chemistry.¹⁷²

Similarly, Wang *et al.* revealed the critical role of CNC in the synthesis of antimicrobial silver nanoparticles to enhance their antimicrobial performance.²⁴⁵ The negatively charged CNC substrate absorbed Ag^+ by electrostatic interaction, resulting in a high local concentration of

silver ions around the CNC, which promoted the nucleation of silver nanoparticles in the presence of a glucose reducing agent. The generated silver nanoparticles with the CNC stabilizer exhibited much lower MIC against not only *E. coli* and *S. aureus*, but also multidrug-resistant (MDR) *E. coli* and *S. aureus* owing to the outstanding dispersibility. Their study implies that CNC-stabilized silver nanoparticles could overcome the current antimicrobial resistance crisis by significantly improving the antimicrobial activity. The remarkable reinforcing effect of CNC-complexed silver nanoparticles was also confirmed by Ma *et al.*²⁴⁹ They synthesized 3–6-nm silver nanoparticles onto the CNC surface through wet-chemical synthesis with glucose. The prepared CNC-Ag was combined with the PLA matrix to fabricate a green antibacterial composite with poly(butylene adipate-co-terephthalate) (PBAT) flexibilizer. The addition of CNC-Ag nanohybrids increased both the crystallization rate and storage modulus (E') of the nanocomposites and endowed them with outstanding antibacterial activity against both Gram-positive and Gram-negative bacteria. This excellent reinforcing effect of CNC with metal nanoparticles is particularly advantageous when it is applied to wound dressing and tissue engineering applications because of their biocompatibility and biodegradability. Abdelgawad *et al.* recently developed a novel carrageenan (CAR)-based antibacterial cryogel system as a functional wound dressing material.²⁵⁰ Carboxymethylated CNC (CM-CNC) were initially prepared as a reducing and capping agent, followed by silver nanoparticle synthesis via a solid-state method. Incorporating CNC decorated with silver nanoparticles and epichlorohydrin (EPH) as a crosslinking agent to CAR resulted in the formation of a porous cryogel. This cryogel showed enhanced swelling, improved mechanical

compression strength, and controlled and sustained release of silver with 100% reduction in the population of *E. coli* and *S. aureus*, which are desired characteristics for wound dressing agents. Shuai *et al.* revealed that the immobilization of silver nanoparticles on CNC endowed the nanocomposite with long-term antibacterial properties.²⁵¹ They prepared silver nanoparticles on CNC (CNC@Ag) by an in situ growth method to improve the dispersibility of the nanoparticles, followed by their incorporation into a poly-L-lactide (PLLA) matrix to prepare an antibacterial scaffold for bone repair. The uniform distribution of CNC@Ag in the scaffold promoted the antibacterial activities by the controlled release of Ag⁺ for more than 28 days that significantly improved the mechanical properties through enhanced load transfer efficiency in the scaffold.

Combining ZnO with CNC was initially demonstrated by Yu *et al.*²⁵² They employed a one-pot synthesis route to prepare the CNC and ZnO hybrids (CNC/ZnO) by employing electrostatic interaction between carboxyl groups on CNC and Zn²⁺ ions. The CNC/ZnO nanohybrids showed outstanding thermal stability, high antibacterial activity, and photocatalytic activity resulting from strong interactions between CNC and ZnO nanoparticles. They also synthesized sheet-like²⁵³ and flower-like²⁵⁴ ZnO nanocrystals with a CNC template by controlling the concentrations of Zn²⁺ ions and solution pH (Figure 2.26). The prepared CNC/ZnO nanohybrids were applied to the fabrication of antimicrobial nanocomposites using solution casting²⁵⁵ and electrospinning.²⁵⁶ The results indicated that CNC/ZnO nanohybrids have various advantages, including enhanced hydrophilicity, barrier properties, mechanical strength, and thermal stability, besides possessing excellent antibacterial properties.

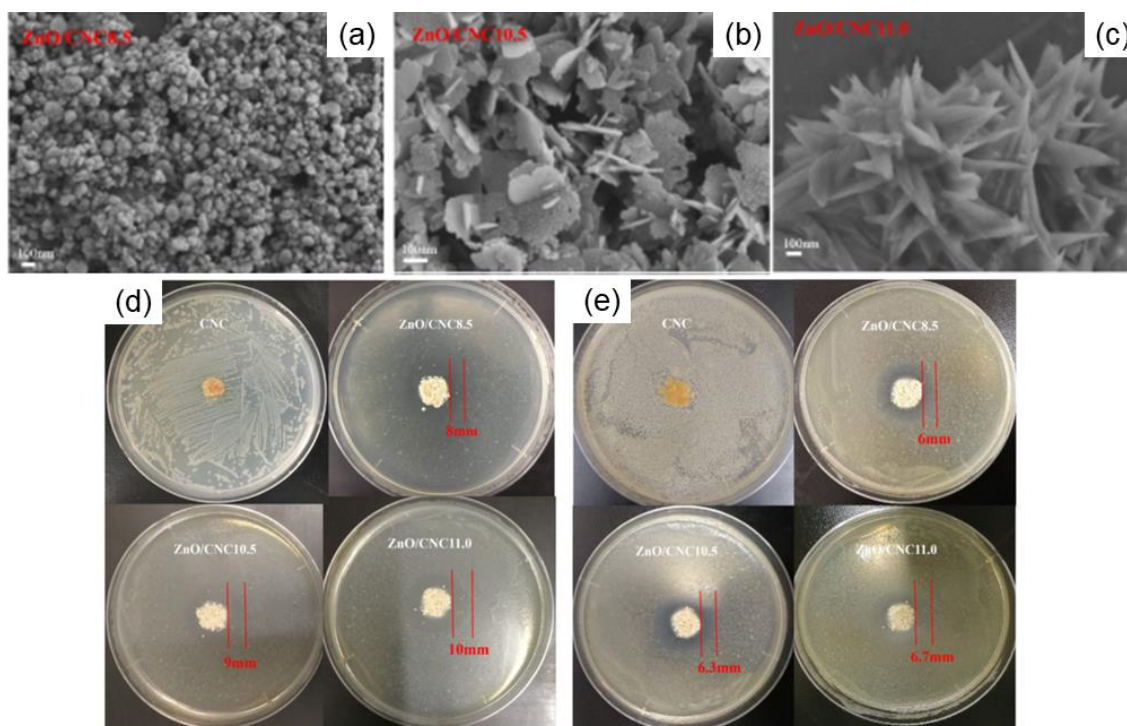


Figure 2.26 (a–c) FE-SEM images of CNC and ZnO/CNC hybrids. Antibacterial ability of CNC and ZnO/CNC hybrids against (d) *E. coli* and (e) *S. aureus*. Adapted with permission from ref 254. Copyright 2019 Elsevier.²⁵⁴

Jia *et al.* developed ZnO and CNC composites (ZnO/CNC) to suppress the aggregation of ZnO nanoparticles and protect the paper surface from antimicrobials.²⁵⁷ The paper treated with ZnO/CNC (K/CNCN/ZnO) showed superior antimicrobial activity against five different fungi (*Aspergillus niger*, *Aspergillus Versicolor*, *Rhizopus nigricans*, *Saccharomycetes*, and *Mucor*) and two bacteria (*E. coli* and *S. aureus*) compared to that exhibited by unmodified ZnO-applied samples (K/ZnO). (Figure 2.27)

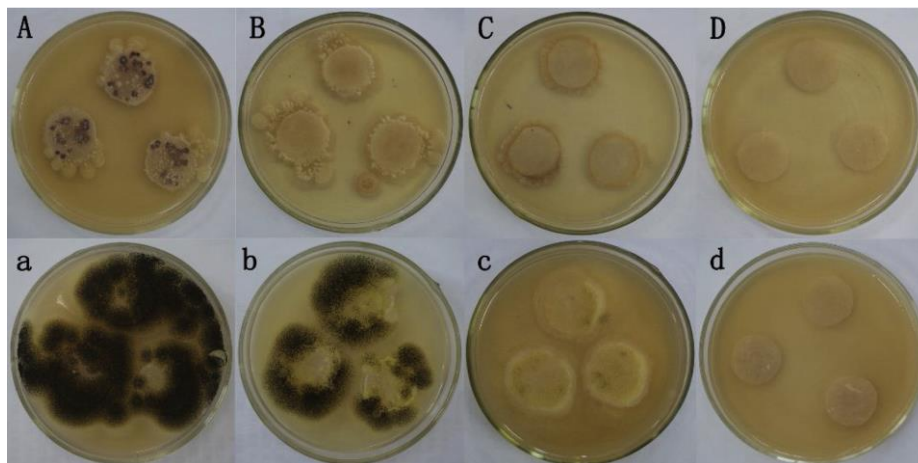


Figure 2.27 Antimicrobial observation of paper specimens coated by K/ZnO (B and b), K/CNC/ZnO-1 (C and c) and K/CNC/ZnO-2 (D and d) against fungi and bacteria spore suspension compared with uncoated paper (A and a). A–D are the results of three-day cultivation; a–d are the results of one-month cultivation. Adapted with permission from ref 257. Copyright 2019 Elsevier.²⁵⁷

The excellent antibacterial activity of TiO₂ nanoparticles onto the CNC template was demonstrated by Zhan *et al.*²⁵⁸ Electrostatic interaction between negatively charged CNC and positively charged Ti(OH)₃⁺ species increases the stabilizing surface energy and prevents TiO₂ nanocrystal aggregation. Compared with other TiO₂ studies, the TiO₂ synthesis method proposed by Zhan *et al.*²⁵⁸ was more straightforward and afforded nanoparticles with much smaller sizes (3–4 nm) and a very high antibacterial efficiency.

CNC can also act as a promising antimicrobial drug carrier. Their excellent water dispersibility enables the effective delivery of hydrophobic drugs. In addition, the antimicrobial drug loading on the CNC surface increases the local concentration of drugs, thereby elevating the antimicrobial activity.²⁵⁹ Zoppe *et al.* loaded tyrosine sulfate mimetic ligands onto the CNC surface, instead of a traditional gold nanoparticle template having

potential toxicity.²⁶⁰ Interestingly, pristine CNC, obtained by sulfuric acid hydrolysis from different cellulosic sources, exhibited decent inhibitory activity against alphaviral infection owing to the anionic surface sulfate groups (Figure 2.28). Further enhanced viral inhibition was attained after exchanging the surface sulfate groups of CNC for tyrosine sulfate mimetic groups. Moreover, CNC grafted with tyrosine sulfate mimetic ligands displayed no cytotoxicity, even at high concentrations. Their study suggests the potential of CNC as viral inhibitors as they have multiple binding sites for target-specific functionalization and create a high local concentration of binding ligands.

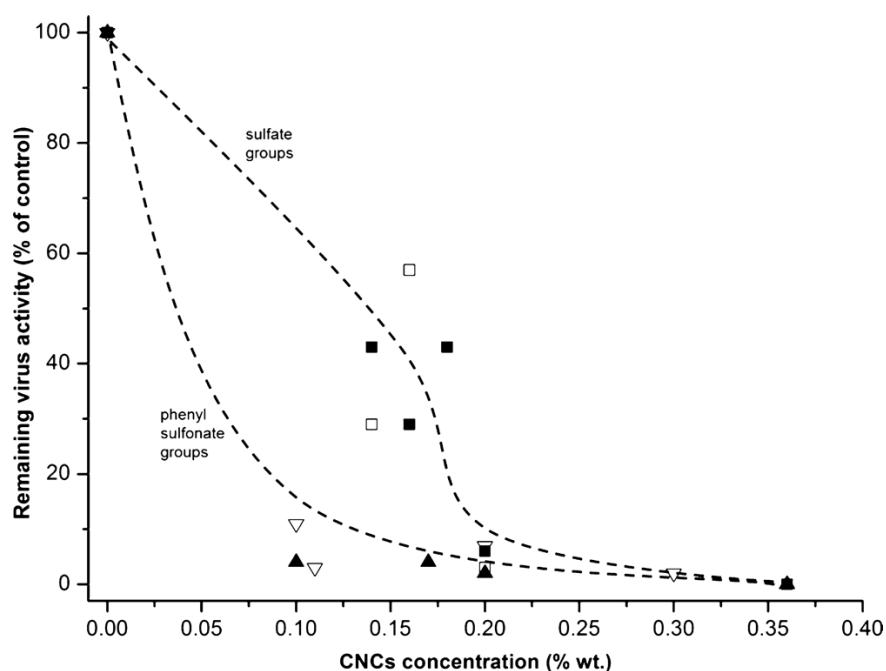


Figure 2.28 Influence of cotton CNC bearing sulfate or phenyl sulfonate groups as a function of concentration on the inhibition of VA7-EGFP infection *in vitro*. Legend: Cotton CNC batch 1 (■) and batch 2 (□), cotton-SPTC (▲), and cotton-EBEA (▽). Adapted with permission from ref 260. Copyright 2014 American Chemical Society.²⁶⁰

Antimicrobial polyrhodanine-coated CNC (CNC@PR) was developed by Tang *et al.*²⁷ The CNC template endowed CNC@PR with excellent colloidal stability in aqueous media that lasted over several months. Notably, the prepared CNC@PR demonstrated a lower MIC against both *E. coli* and *B. subtilis* than that exhibited by other spherical silica–polyrhodanine nanocomplexes because of its rod-shaped structure and larger surface area (Figure 2.29). This result confirmed that the CNC template can improve the antimicrobial activity because of its nanosized, rod-like, and core-shell structure.

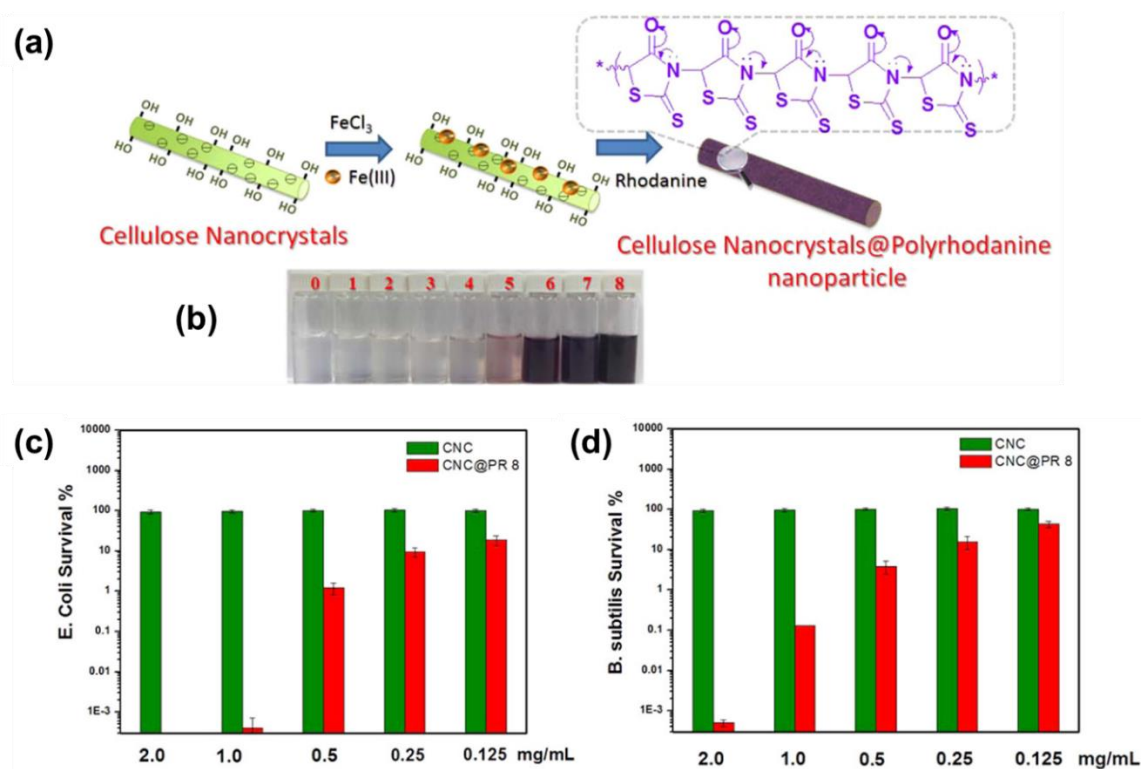


Figure 2.29 (a) Schematic illustration of in situ polymerization of CNC@PR nanoparticles; (b) pictures taken with a digital camera showing color change of 0.1 wt % CNC@PR suspensions under different reaction conditions; antimicrobial assessment of pristine CNC and CNC@PR 8 suspensions toward (b) *E. coli* and (c) *B. subtilis*. Adapted with permission from ref 27. Copyright 2015 American Chemical Society.²⁷

Ma *et al.* demonstrated that CNC could enhance the poor dispersity of hydrophobic curcumin in water, which allowed the preparation of antioxidant and antibacterial films.²⁶¹ TEMPO-oxidized CNC were firstly modified by cetrimonium chloride (CTAC) to impart hydrophobicity, followed by the successful curcumin binding. The prepared curcumin-loaded CNC were then incorporated into the tara gum/PVA matrix to fabricate antibacterial films. The resulting films showed improved mechanical and barrier properties as well as distinct inhibition zones for *S. aureus*, indicating excellent antibacterial activity against Gram-positive bacteria. Li *et al.* demonstrated natural antibacterial agents and biopolymer-based antibacterial nanocomposites for application in green packaging.²⁶² They grafted the antibacterial rosin, extracted from pines, to the CNC surface and then incorporated it into the PHBV matrix. The rosin-grafted CNC showed improved compatibility and dispersibility in the PHBV matrix, resulting in enhanced mechanical properties and barrier performances. The antibacterial activity of the prepared composite was confirmed by the formation of a clear inhibition zone and an outstanding antibacterial rate (>99%). The fabricated green antibacterial composite was used to extend the shelf-life of grapes by up to 11 days, which demonstrated its potential as a packaging material.

2.5 Summary

An overview of the CNC, metal nanoparticles, conductive CNC, and the antimicrobial system has been presented in this chapter. As discussed in the first part of the review, CNC is an attractive nanomaterial not only because of its inherent properties, such as sustainability, mechanical strength, dispersibility, and biocompatibility but also its accessibility for modification. Various CNC modification methods have been extensively explored, and modified CNCs have found wide applications in many fields. However, the majority of works involve complicated and expensive synthetic methods. Among many available methods to impart the desired properties to CNC, the most straightforward one is the formation of functional material coatings on CNC. Therefore, we will aim to develop the functional coating on CNC for several advanced applications.

As presented in the second part of the review, much research effort has been devoted to metal nanomaterials related to their synthesis, characteristics, and applications. However, the study on metal nanoparticle modified CNC is relatively unexplored compared to other modified CNCs. Although there are some studies to prepare metal-coated CNCs, most of them required inefficient synthetic steps resulting in low metal nanoparticle loading. This issue limits the application of metal-coated CNC to specific applications, such as a catalyst. Therefore, there is a need to develop metal shell-coated CNC for a broad range of applications, including electronics. Furthermore, the synergistic effect between the high aspect ratio of CNC and electrical conductivity would be a fascinating subject that will enhance the electrical conductivity of composite making it attractive for some applications.

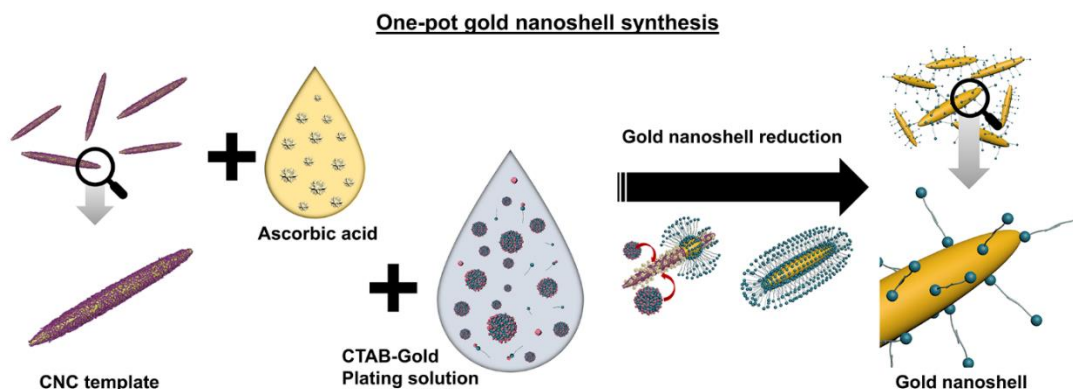
The antimicrobial metal-coated CNC is also a compelling research subject due to the current antimicrobial resistance and the excellent antimicrobial activity of metal nanoparticles. From the literature review, there exists a research gap between expensive silver-based systems and less effective zinc-based systems. To address this gap, we aim to develop a highly effective antimicrobial system based on copper and CNC with low-cost materials that possesses significant antimicrobial performance.

Chapter 3^{**}

Interfacial Control of the Synthesis of Cellulose Nanocrystal Gold Nanoshells

In this chapter, cellulose nanocrystal (CNC) with gold nanoshell was prepared using a polymer-coated CNC as a template. A seed mediated shell growth approach (*ex-situ*) was employed, gold nanoparticles (AuNPs) of two sizes were prepared, and the effect of the size of AuNP on the shell quality (smoothness, evenness, and continuity) was elucidated. Additionally, a novel one-pot synthesis approach (*in-situ*) was evaluated for the preparation of the gold nanoshell, where polymer-coated CNCs with adsorbed ascorbic acid were used to reduce Au ions to form a metallic gold shell on CNC. The surface coverage was manipulated by adding different amounts of plating solutions. The formation and morphology of gold nanoshells were evaluated by zeta potential measurements, dynamic light scattering, UV–vis spectroscopy, and transmission electron microscopy (TEM). The catalytic performance of the CNC-gold nanostructures for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was governed by the surface area of gold shells.

^{**} This chapter is adapted from a paper “Lee, Y., Nasser, R., & Tam, K. C. (2020). Interfacial Control of the Synthesis of Cellulose Nanocrystal Gold Nanoshells. *Langmuir*, 36(38), 11215-11224” with permission from American Chemical Society



3.1 Introduction

The control over size and shape of metal nanoparticles during synthesis is extremely important due to the size and shape dependence of many properties at the nanoscale.²⁶³⁻²⁷⁰ Several methods have been proposed for the synthesis of 1D metallic nanostructures including, wet chemical synthesis based on a seed mediated growth mechanism,²⁷¹ solution phase methods based on capping agents,²⁷² reverse micellar or soft template,²⁷³ polyol process,²⁷⁴ electrochemical deposition,²⁷⁵ step edge decoration method,²⁷⁶ photochemical method,²⁷⁷ chemical oxidation method,²⁷⁸ self-assembly in supercritical conditions,²⁷⁹ top down methods based on nanolithography,²⁸⁰ and hard template methods using nanoporous solid templates, such as alumina membranes,²⁸¹ hematite particles,²⁸² CNC.¹⁷³

With the increased attention devoted to the synthesis of metallic nanomaterials, organic-metallic nanostructures have been extensively studied due to their diverse structures, tunable properties, and multiple applications.²⁸³ One category of organic-metallic nanostructures is metallic nanoshell. These nanoparticles consist of a dielectric or

semiconducting core coated with a nanometer layer of metallic shell.¹¹³ Among them, gold nanoshells are of special interest due to their potential applications in various fields, such as biosensing,²⁸⁴ surface enhanced Raman and infrared absorption spectroscopies^{285, 286} and photothermal cancer therapy²⁸⁷ since they are biocompatible, chemically inert, and possess good optical properties and catalytic activity.^{122, 173}

CNC, a rod-like crystalline nanoparticle derived from forest and agro-biomass, has attracted increasing attention because of their unique properties, such as large surface area, excellent mechanical properties, high aspect ratio, facile surface modification, thermal stability, renewability, and biodegradability. Thus, it is a promising material for the preparation of hybrid nanostructures.¹ CNCs are being explored as templates for the synthesis of functional organic-metallic nanostructures via the deposition of a metal layer.²⁸⁸⁻²⁹⁰ Among the metals, one dimensional (1D) CNC-gold nanostructures have attracted increasing attention in recent years due to their tunable optical properties.^{264, 265}

Previous attempts to prepare a continuous layer of gold shell on CNCs were not successful, resulting in only discrete and heterogeneous gold shells.^{291, 292} Recently, Semenikhin *et al.*¹⁷³ reported a fabrication procedure consisting of a complicated surface functionalization protocol followed by a multi-step shell growth process. They used a method originally proposed by Halas and co-workers¹¹³ namely: (1) functionalization of hard template (CNC) surface, (2) synthesis of small-sized seed metallic nanoparticles, (3) attachment of the seeds to the hard template (CNC), and (4) growth of the shell in a solution commonly referred as K-gold. After the removal of the sulfate half-ester groups, they performed periodate

oxidation followed by reductive amination to prepare the surface of CNCs for the shell growth steps (2-4). This complex and time-consuming chemical synthesis of CNC nanoshells may limit their applications.

To facilitate the fabrication of CNC gold nanoshells (Gold nanoshells), we adopted an alternative approach by first coating the CNC with a polymer layer through a simple electrostatic adsorption, bypassing the complicated surface functionalization steps necessary to prepare the CNCs for the attachment of gold precursor. Two different strategies were employed and compared in preparing the gold coating on the CNC template, namely a conventional seed-mediated *ex-situ* method and a novel *in-situ* one-pot synthesis. In *ex-situ* synthesis, we prepared two AuNPs of different sizes coated with different capping agents (trisodium Citrate (TSC) and tetrakis(hydroxymethyl) phosphonium (THPC)) and investigated the effect of AuNP size on the morphology of Au nanoshells. To simplify the CNC nanoshell synthesis, we used a one-pot synthesis approach to precisely control the growth of the gold shell by harnessing the electrostatic interaction between the various species, which to the best of our knowledge, is reported for the first time. By adjusting the pH above the pK_a of our reducing agent, we induced the dissociation and formation of an anionic reducing agent. We then adsorbed the anionic reducing agent onto the positively charged polymer-coated CNCs to localize the reduction reaction of gold ions on the CNC surface. Different amounts of gold plating solution were then added dropwise. A cationic surfactant, hexadecyltrimethylammonium bromide (CTAB) was used as the directing and capping agent to control the shell growth process. It could adsorb on the reduced gold surface to direct the

gold ions in the formation of the gold shell. Varying degrees of surface coverage were achieved using different amounts of gold plating solutions. The impact of different morphologies of CNC-gold nanostructures was evaluated by examining the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

3.2 Experimental section

3.2.1 Materials

Cellulose nanocrystals (CNCs) were provided by CelluForce Inc (average diameter 7.5 nm, average length 150 – 350 nm, nitrogen content 0.023%, sulfur content 0.884%). Poly(diallyldimethylammonium chloride) (PDADMAC) 20 wt% solution in water; (MW=100,000-200,000 g.mol⁻¹), hexadecyltrimethylammonium bromide (CTAB) ≥99%, gold(III) chloride trihydrate (HAuCl₄·3H₂O) ≥99.9%, trisodium Citrate dihydrate (TSC) 99.8%, sodium borohydride (NaBH₄) ≥98%, tetrakis(hydroxymethyl)phosphonium chloride solution (THPC) 80%, sodium hydroxide ≥97%, L-ascorbic acid 99% were purchased from Sigma-Aldrich. Potassium Carbonate, formaldehyde 37%, and 4-nitrophenol (4NP) ≥99.5% were obtained from AMRESCO, Fisher Chemical, and Fluka, respectively. All the chemicals were analytical grade and used without further purification. All aqueous solutions were prepared with Milli-Q grade (18.2 MΩ cm⁻¹) purified water.

3.2.2 Preparation of the PDADMAC wrapped CNCs (CNC-PDADMAC)

In order to obtain the optimum ratio between CNC and PDADMAC, different volumes of PDADMAC solution ((1, 2, 3, 4, 5, and 6 mL), 20 wt% in water) were added to the CNC suspension (200 mL, 0.1 wt%) under sonication. The sonication was continued for 1 h followed by stirring overnight at room temperature and purification by repeated ultrafiltration.

3.2.3 *Ex-situ* Gold Nanoshells synthesis using THPC-AuNPs and TSC-AuNPs

THPC-AuNP suspension was prepared according to Duff *et al.*²⁹³ Briefly, the NaOH solution (0.3 mL, 1 M) was added to Milli-Q water (47 mL). Aqueous THPC solution (12 μ L, 80%) was diluted with Milli-Q water (1 mL), and mixed with NaOH solution under stirring. After 5 min of stirring, the speed of stirring was increased, followed by the rapid addition of HAuCl₄ solution (1.9 mL, 25 mM). The final gold nanoparticle suspension was stored at 4°C for 2 weeks prior to use. TSC-AuNP suspension was prepared according to Graber *et al.*²⁹⁴ Under vigorous stirring, HAuCl₄ solution (1 mL, 25 mM) was added to Milli-Q water (100mL). After 1 min, 1 mL of trisodium citrate solution (1 mL, 1wt%) was added, followed by the addition of NaBH₄ solution (1 mL, 0.075 wt% in 1 wt% trisodium citrate solution). The gold nanoparticle suspension was stirred for 5 min and then stored at 4°C. The decoration of CNC-PDADMAC with two different AuNPs was performed as follows. In order to optimize the decoration process, different amounts of gold seed nanoparticle suspension (1-11 mL) was mixed with CNC-PDADMAC suspension (1 mL, 0.25 wt%) under sonication. The mixture

was stirred overnight, and the excess amount of AuNPs was removed by ultrafiltration. The final CNC-PDADMAC-AuNPs were re-dispersed in Milli-Q water (20 mL) by sonication. HAuCl₄ solution (3 mL, 25 mM) was added to aqueous K₂CO₃ solution (200 mL, 0.0018 M), and the mixture was stirred for 30 min to prepare gold plating solution. The solution was then kept in a dark place for a minimum of 24 h prior to use. Gold nanoshell was formed on CNC via the electroless deposition of gold plating solution using formaldehyde as the reducing agent. First, gold plating solution (0.5-2.5 mL) was added to CNC-PDADMAC-AuNPs suspension (200 μ L), followed by the addition of formaldehyde (15 μ L, 37%) and immediate vortexing. After 3 h, the same shell growth procedure was performed on samples to prepare complete gold nanoshells, and samples with the lowest zeta potential (highest gold coverage) were selected for further analysis.

3.2.4 *In-situ* Gold Nanoshell synthesis

CTAB gold plating solution was prepared via the following procedure. First, HAuCl₄ solution (2 mL, 25 mM) was diluted with Milli-Q water (200 mL). CTAB (7.289 g) was added to dilute HAuCl₄ solution, and the mixture was stirred overnight and stored at 30 °C. *In-situ* gold nanoshells on CNC were prepared by a one-pot synthesis. An ascorbic acid solution (5 mL, 0.05 M) was mixed with diluted CNC-PDADMAC suspension (50 mL, 0.04 wt%), and the pH of the solution was adjusted to ~5 (above $pK_a = 4.2$) by adding NaOH (1 M) solution. The mixture was stirred for 1 h at 30 °C to promote electrostatic interaction between CNC-PDADMAC and ascorbic acid. Then the CTAB gold plating solution (20, 50 and 100 mL) was

added to the mixture via a syringe pump (40 mL h^{-1}) under mild stirring at 30°C . The resultant CNC-gold nanostructures were purified by repeated centrifugation and redispersed in 7 mL Milli-Q water (7 mL).

3.2.5 Evaluation of the catalytic performance of CNC-PDADMAC-Gold nanoshells

The catalytic activity of different CNC-gold nanostructures prepared with different amounts of CTAB gold plating solution was evaluated by the reduction of 4-NP to 4-aminophenol (4-AP) using NaBH_4 . In a reduction reaction, a fixed molar ratio of $[\text{Au}]:[\text{4NP}]:[\text{NaBH}_4] = 1:100:10000$ was used for all the reactions. Typically, NaBH_4 (19 mg) was added to an aqueous 4NP solution (10 mL, 0.5 mM), and then the mixture (0.1 mL) was transferred to a quartz cell, followed by the addition of different volumes of CNC-gold nanostructure suspensions into the quartz cell (to keep the fixed molar ratio of $[\text{Au}]:[\text{4NP}]:[\text{NaBH}_4] = 1:100:10000$) with immediate mixing for 2 s. The reaction was conducted at room temperature and the kinetics of the reaction was monitored by UV-vis absorption measurement in 250-500 nm range over time.

3.2.6 Characterization

The PDADMAC coating on CNC and ascorbic acid adsorption on CNC-PDADMAC were confirmed by FTIR spectroscopy (PerkinElmer Spectrum Two™ FTIR Spectrometer). Freeze-dried samples were mixed with KBr and then compressed into pellets. The wave

number range was 4000-500 cm^{-1} with a resolution of 4 cm^{-1} . A total of 16 scans were accumulated to reduce the noise. The size distribution and zeta potential measurements were carried out using a Malvern Zetasizer Nano ZS90. The samples were dispersed in Milli-Q water at neutral pH and sonicated in bath sonicator for 10 min before the measurement at 25°C. Average values of at least three measurements were reported and the range represents the standard error. Due to the non-spherical shape of CNCs, the reported sizes correspond to a hydrodynamic diameter of a sphere with the same translation diffusion coefficient. Ultraviolet-visible (UV-vis) was recorded using a Cary 100 UV-visible spectrophotometer, and Milli-Q water was used for the sample preparation. The morphologies of gold nanoshells were examined by Philips CM10 transmission electron microscope (TEM) with an acceleration voltage of 60 keV. The samples used for TEM measurement were prepared by placing a drop of suspension on a copper grid (200 mesh coated with copper) and drying it overnight at room temperature.

3.3 Results and discussion

PDADMAC is a water-soluble polymer with quaternary ammonium groups, which makes it an excellent candidate for coating the surface of CNC. It is crucial to determine the optimum ratio between CNC and PDADMAC, where no aggregation of the coated CNC occurred and only individual coated CNCs were present. Optimization of the ratio of PDADMAC and CNC revealed that the 1:2 weight ratio of CNC:PDADMAC was the optimal ratio (showed the highest zeta potential), which was used in subsequent experiments (Figure

3.1). The highest zeta potential can be interpreted as the maximum coverage of the negatively charged CNCs by PDADMAC polycations.

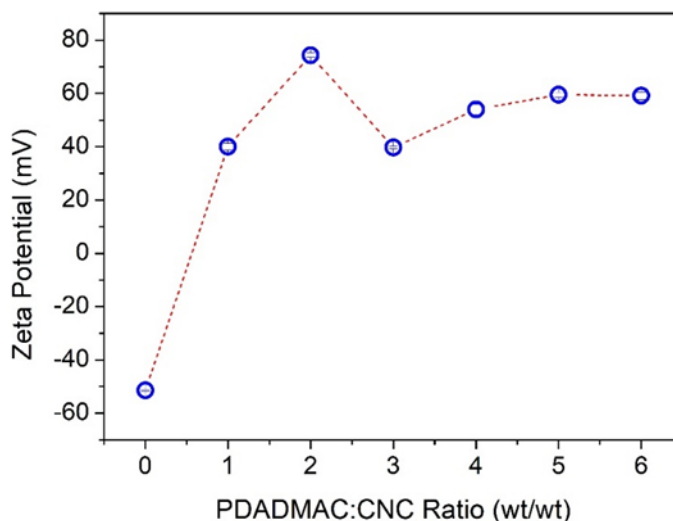


Figure 3.1 Zeta potential of CNC-PDADMAC suspensions comprising different ratios of PDADMAC:CNC after three times of ultrafiltration.

FTIR analysis of freeze-dried CNC-PDADMAC suspension after three ultrafiltration cycles also confirmed the successful wrapping of CNC by PDADMAC. The peaks at 2865 cm^{-1} and 1475 cm^{-1} in CNC-PDADMAC FTIR spectra (these peaks are not observed for pristine CNC spectra) could be assigned to the methyl ($-\text{CH}_3$) stretching and quaternary ammonium group ($-\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_2$) bending vibration of pyrrolidinium rings of PDADMAC, respectively (Figure 3.2).²⁹⁵

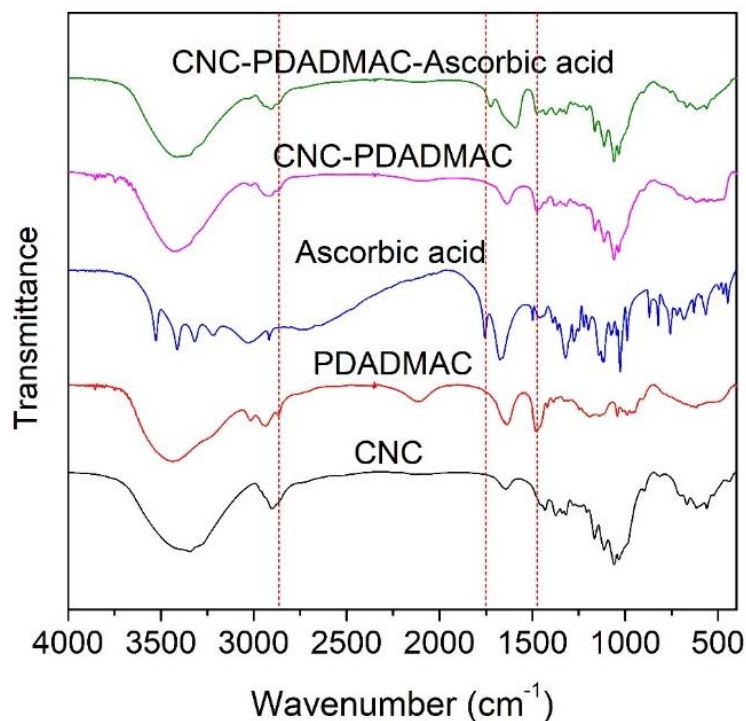


Figure 3.2 FTIR spectrums of pure CNC, PDADMAC, ascorbic acid, CNC-PDADMAC, and CNC-PDADMAC-Ascorbic acid.

In order to optimize the decoration process, different amounts of AuNP (1-11 mL) was mixed with CNC-PDADMAC dispersion (1 mL, 0.25 wt%). By attaching AuNPs to the surface of CNC, the zeta potential began to decrease due to the accumulation of negatively charged hydroxide ions on AuNPs. The zeta potential of the decorated CNC-PDADMAC (CNC-PDADMAC-AuNP) suspension versus the amounts of AuNP suspensions revealed an initial reduction followed by a plateau for both AuNP sizes (Figure 3.3).

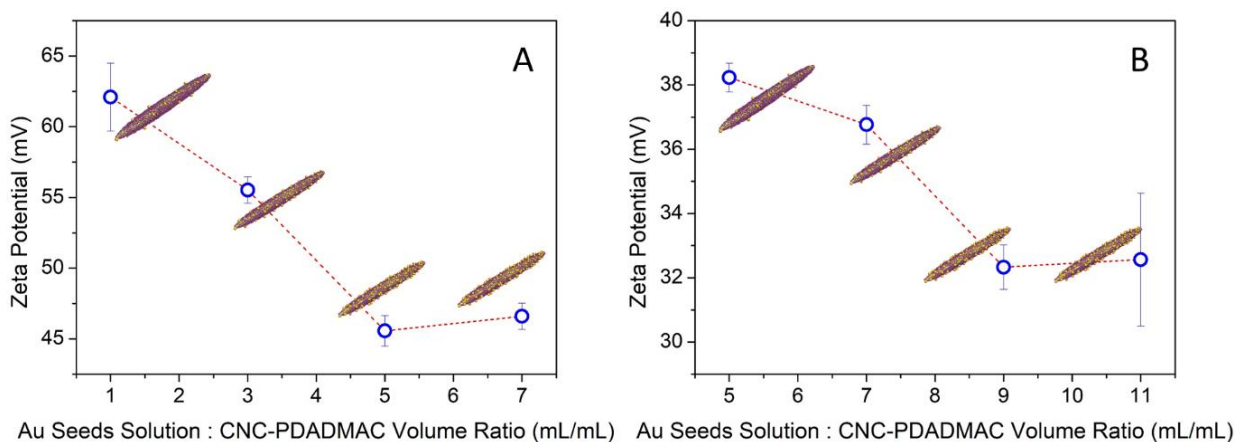


Figure 3.3 Zeta potential of CNC-PDADMAC-AuNPs prepared by adding different volumes of gold seed solution capped by (A) THPC and (B) TSC.

By increasing the amounts of AuNP, the number of adsorbed AuNPs on the CNCs increased until it became saturated, where no additional AuNPs could be bound to the CNCs. As a result, 7 and 9 mL were selected as the optimum volume for TCS-AuNPs and THPC-AuNPs, respectively (Based on the optimum volumes, average number of AuNPs on each CNC was calculated to be about 25 and 1000 for TSC capped AuNPs and THPC capped AuNPs, respectively). The extent of gold coverage on the surface of CNC-PDADMAC was identified from the zeta potential of the suspension. Increasing the coverage of the highly positive surface of CNC-PDADMAC ($+62.1 \pm 1$ mV) with gold led to the reduction in the zeta potential due to the accumulation of hydroxide ions on the gold surface (Table 3-1).^{296, 297} The same shell growth procedure was conducted on samples for preparing a uniform shell on the surface of CNC. Samples with the lowest zeta potentials were selected for further investigations.

Table 3-1 Zeta potential of CNC-PDADMAC-Aushells prepared by the *ex-situ* method

Capping Agent	Round of Shell Growth	Amount of gold plating Solution				
		0.5 mL	1.0 mL	1.5 mL	2.0 mL	2.5 mL
TSC	1 st	22.3 ± 0.5	25.9 ± 0.4	7.9 ± 0.3	-18.1 ± 0.1	-0.8 ± 0.2
	2 nd	19.2 ± 0.2	4.6 ± 0.3	-11.8 ± 1.1	-9.5 ± 0.2	-7.7 ± 0.2
THPC	1 st	2.0 ± 0.9	15.5 ± 0.3	2.4 ± 0.2	0.0 ± 0.2	24.9 ± 1.6
	2 nd	7.6 ± 0.5	-12.6 ± 0.5	-18.5 ± 0.2	-1.7 ± 0.2	-12.3 ± 0.5

Electroless gold deposition on the heterogeneous nucleating sites provided by gold seed nanoparticles led to an interconnected continuous gold shell around CNC-PDADMAC-AuNPs. A schematic illustrating this process is shown in Figure 3.4. TEM images of CNC-PDADMAC-AuNPs (Figure 3.4A,D) confirmed the attachment of AuNPs to the CNC-PDADMAC. As a result of the heterogeneous nucleation during electroless deposition, CNC-PDADMAC-AuNP surface was coarsened (Figure 3.4B,E). The second shell growth step resulted in interconnected gold nanoshells (Figure 3.4C,F).

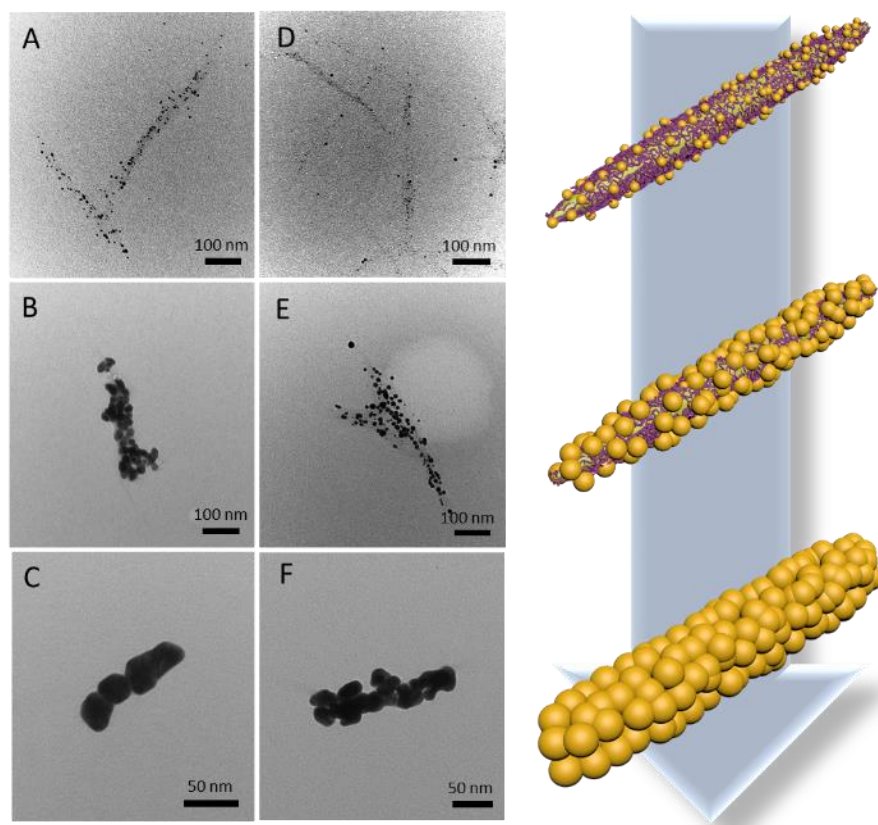


Figure 3.4 TEM images of (A, D) CNC-PDADMAC-AuNP, (B, E) CNC-PDADMAC-gold nanoshell after the first round of shell growth, and (C, F) CNC-PDADMAC-gold nanoshell after the second round of shell growth. CNC-gold nanostructures were prepared by (A–C) TSC-capped AuNPs and (D–F) THPC-capped AuNPs.

Shell growth by electroless deposition of gold on CNC-PDADMAC-AuNP prepared by TSC capped AuNPs led to a smoother surface compared to THPC AuNPs (Figure 3.5A,B). The TSC capped AuNPs appeared to be beneficial for preparing a more even surface in the shell growth process compared to THPC capped AuNPs. There are two main differences between TSC capped and THPC capped AuNPs. First is the size where THPC capped AuNPs are smaller (1-3 nm) than TSC capped AuNPs (2–10 nm). Second is the charge of the capping

agents which impart positive surface charges to THPC capped AuNPs and negative surface charge to TSC capped AuNPs. In the decoration process of positively charged CNC-PDADMAC with AuNPs, TSC capped AuNPs can more conveniently bind to the surface via electrostatic interactions. Higher concentration of TSC capped AuNPs with larger size on the surface of CNC-PDADMAC (Figure 3.4A,B) led to a smoother surface after the shell growth process. On the other hand, by using small gold seeds, two situations might be present during the shell growth process. The first is that some seeds whose size is larger than the critical value (determined by thermodynamics) grow first, and then Ostwald ripening among gold particles of different sizes results in an incomplete and uneven shell.¹²³ The second is that some gold seeds grow but end up being dislodging from the surface leading to an uneven shell.²⁹⁸ The zeta potential of nanoshells after the second round of shell growth were -9.5 ± 0.2 mV and -18.5 ± 0.2 for gold nanoshells prepared by TSC capped AuNPs and THPC capped AuNPs, respectively (Table 3-1).

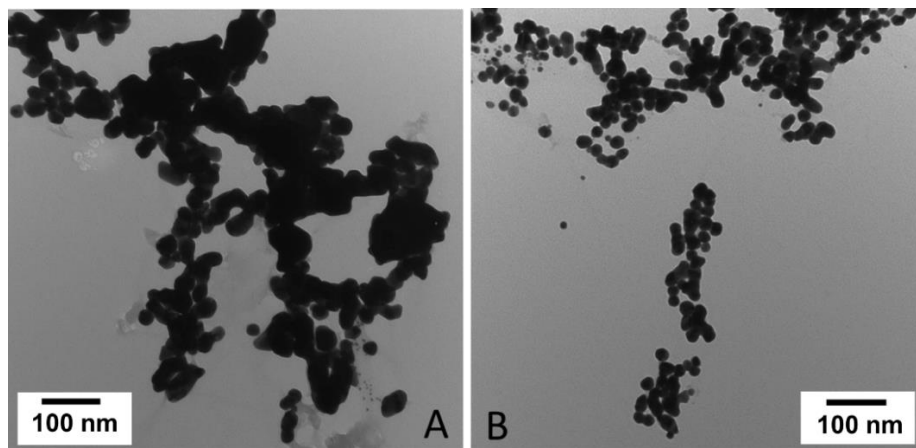


Figure 3.5 TEM images of aggregates of CNC-gold nanoshells prepared from CNC-PDADMAC-AuNPs. (A) TSC capped AuNPs and (B) THPC capped AuNPs.

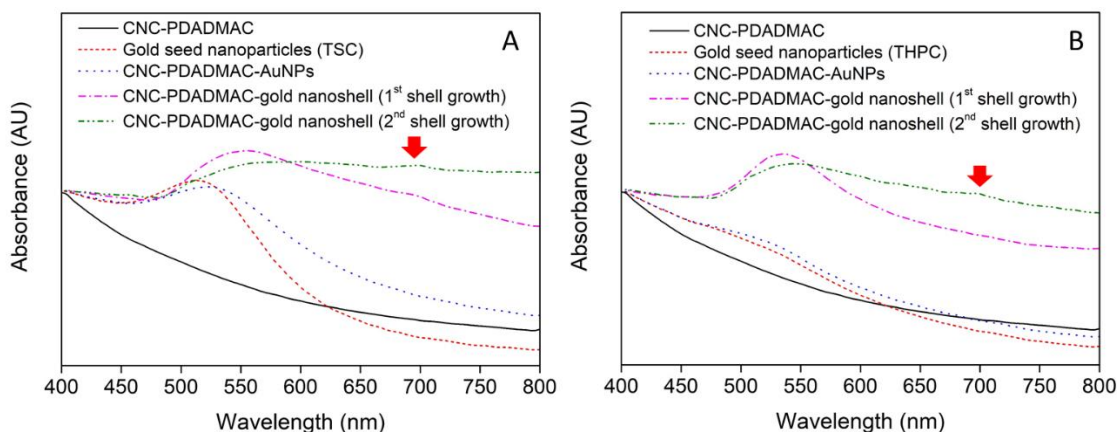


Figure 3.6 UV-vis absorption spectrums of CNC-gold nanostructures prepared by TSC AuNPs (A) and THPC Au NPs (B). Red arrows point to near-infrared peaks appeared after shell growth.

The shape evolution of the product in each step could be studied by UV-vis spectroscopy due to the strong shape dependence of the surface plasmon resonance of CNC-gold nanostructures.^{113, 122, 264} Figure 3.6 shows the absorption spectra of nanostructures prepared with the *ex-situ* method. The spectrum of CNC-PDADMAC followed a monotonically decay profile with increasing wavelength due to the Rayleigh scattering of the nanoparticles.²⁹⁹ A peak at 520 nm in the spectra of gold seed nanoparticles is consistent with the absorption of gold nanoparticles.²⁹³ Due to the larger size, this peak was more obvious for TSC capped AuNPs than the THPC AuNPs. This peak became broader in the CNC-PDADMAC-AuNPs spectra due to the plasmon coupling of closely spaced AuNPs.¹⁷³ The formation and growth of the gold nuclei on the nanoparticle surface after the first round of shell growth reduced the spacing between these nuclei that increased the interparticle plasmon coupling and a red-shift in plasmon resonance (Figure 3.6).¹²² As the growing nuclei started to coalesce, the plasmon resonance peak broadened, which is related to the distribution of aspect

ratios of the coated nanoparticle (Figure 3.6).¹¹³ The characteristic plasmon resonance of a complete shell is associated the emergence of a peak in the near-infrared range with only a small shoulder of the initial visible range peak. As evident from Figure 3.6, a peak appeared at 700 nm (red arrow) after the second round of shell growth with a rather large shoulder in the visible range. The near-infrared peak is more pronounced for the nanoshells prepared with TSC capped AuNPs, and these UV-vis absorption spectra corresponded to an assembly of complete and incomplete nanoshells.

To improve the nanoshell fabrication process, a convenient and repeatable protocol consisting of a one-pot shell growth approach was employed. Ascorbic acid, a mild reducing agent, was used to reduce Au^{III} salts in the growth stage. To minimize the undesirable nucleation in the bulk solution, anionic ascorbic acid was adsorbed onto CNC-PDADMAC.

To promote the adsorption of ascorbic acid on CNC-PDADMAC, the pH of the suspension was adjusted to ~5 (above pK_a of ascorbic acid, 4.2), where the ascorbic acid dissociated into ascorbate anions that electrostatically bound to the positive surface of CNC-PDADMAC.³⁰⁰ To confirm the presence of ascorbate anions on the surface of CNC-PDADMAC, FTIR was performed on freeze-dried powder of CNC-PDADMAC after 1 hr of mixing with ascorbic acid at 30 °C and pH ~ 5 with three cycles of ultrafiltration. Strong absorption at 1755 cm⁻¹ in the FTIR spectrum of ascorbic acid is attributed to the C=O stretching.³⁰¹ The same peak with a slight shift towards lower wavenumbers was observed in the CNC-PDADMAC-Ascorbic acid FTIR spectrum (Figure 3.2). Zeta potential of CNC-PDADMAC-Ascorbic acid suspension also decreased compared to CNC-PDADMAC

suspension, confirming the presence of ascorbic acid on the surface of CNC-PDADMAC (Figure 3.7).

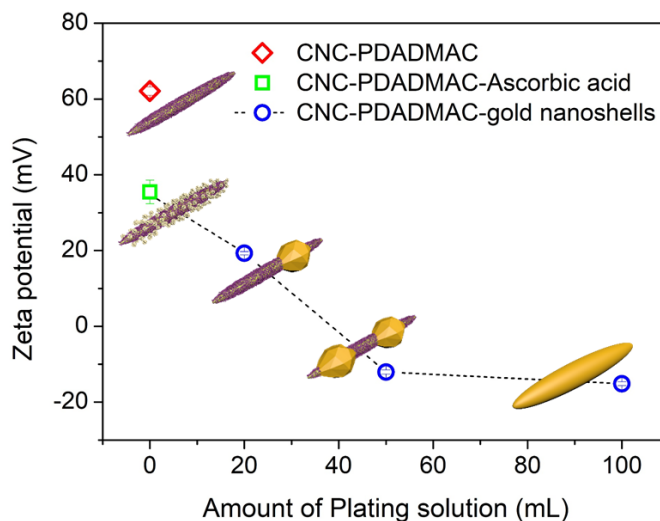


Figure 3.7 Zeta potential of CNC-gold nanostructures prepared by the *in-situ* method.

CTAB was added to the CNC-PDADMAC suspension with gold ions, and it was used as the directing and capping agent in the shell growth process. It has been proposed that CTAB headgroup would bind to the surfaces of gold along the length of the pentahedrally twinned nuclei²⁸⁰ compared to the gold surfaces at the ends of the nuclei.^{264,302} At the same time, CTAB electrostatically repels the PDADMAC coated CNC surface. As a result, further reduction of gold ions occurs on the bare CNC-PDADMAC surface leading to a unidirectional shell growth. It has also been suggested that bilayer assembly of CTAB to rod-shaped micelle provides a soft template for the shape control.^{263, 303} CTAB gold plating solution was added dropwise to the CNC-PDADMAC-Ascorbic acid suspension to prevent the undesirable nucleation in the bulk solution. The slow addition of gold plating solution served to promote the unidirectional

growth of gold, and the low temperature (30 °C) decreased the reduction reaction rate and minimized the undesirable gold nucleation in the bulk solution.^{270, 304} Temperatures lower than 30 °C would result in the crystallization and the precipitation of CTAB.³⁰⁴

Various experimental conditions were explored to identify the optimum condition. First, decorated CNC (CNC-PDADMAC-AuNPs) prepared by TSC capped AuNPs (50 mL, 0.04 wt%) was mixed with ascorbic acid (5 mL, 0.05 M). The pH was not adjusted and was around 2. Then, CTAB gold plating solution (100 mL) was added dropwise (40 mL h⁻¹). Figure 3.8 shows the TEM image of the resulting CNC gold-nanostructures. Some bare CNC-PDADMAC nanoparticles were observed along with some free gold nanoparticles. The detachment of AuNPs from the CNC-PDADMAC surfaces led to the formation of free gold nanoparticles. The growth of these free gold nanoparticles consumed the available gold ions in the solution resulting in some bare CNC-PDADMAC nanoparticles. Cross-linking between some CNC Aushells also was observed in this sample.

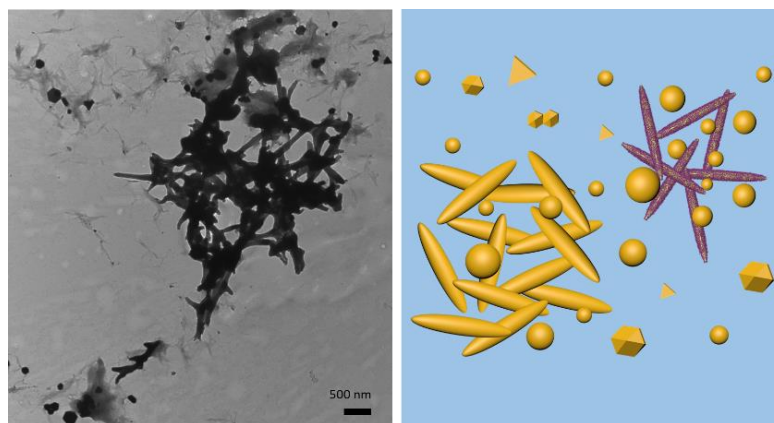


Figure 3.8 TEM image of CNC gold-nanostructures prepared by CNC-PDADMAC-AuNPs in the *in-situ* method.

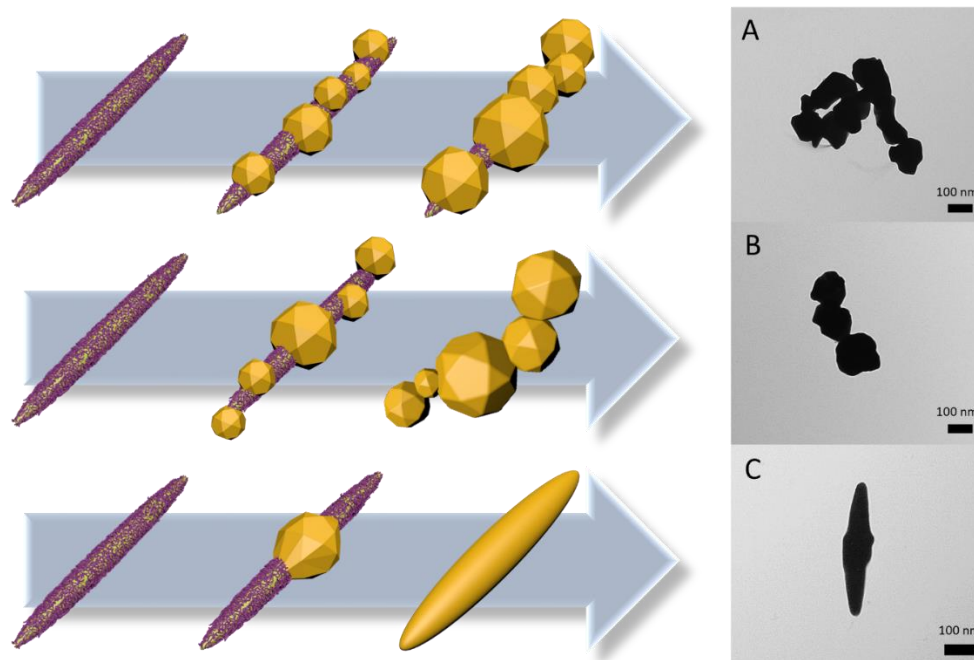


Figure 3.9 TEM images of CNC-gold nanostructures prepared by different reaction conditions: (A) pH~2 at 30°C, (B) pH~5 at 80 °C and, (C) pH~5 at 30 °C.

The effect of pH and temperature on the morphology of Aushells were also investigated. In one experiment CNC-PDADMAC suspension (50 mL, 0.04 wt%) was mixed with an ascorbic acid solution (5 mL, 0.05 M) without adjusting the pH (pH was around 2). The mixture was stirred for 1 h at 30 °C and then CTAB gold plating solution (100 mL) was added to the mixture by a syringe pump (40 mL h⁻¹) under mild stirring at 30 °C. In the other experiment, after mixing CNC-PDADMAC suspension (50 mL, 0.04 wt%) and ascorbic acid solution (5 mL, 0.05 M), pH was adjusted to around 5 and then CTAB gold plating solution (100 mL) was added to the mixture by a syringe pump (40 mL h⁻¹) under mild stirring at 80°C. TEM images of resulting CNC-gold nanostructures are shown in Figure 3.9. Rough,

incomplete, and discontinuous surface morphology was observed in the TEM images of the Aushells prepared without adjusting the pH, Figure 3.9A. TEM image of the Aushells prepared at 80°C showed a complete but very rough and uneven surface morphology, Figure 3.9B. Morphology of the Aushell prepared by adjusting the pH to 5 and at 30°C was presented in Figure 3.9C for comparison.

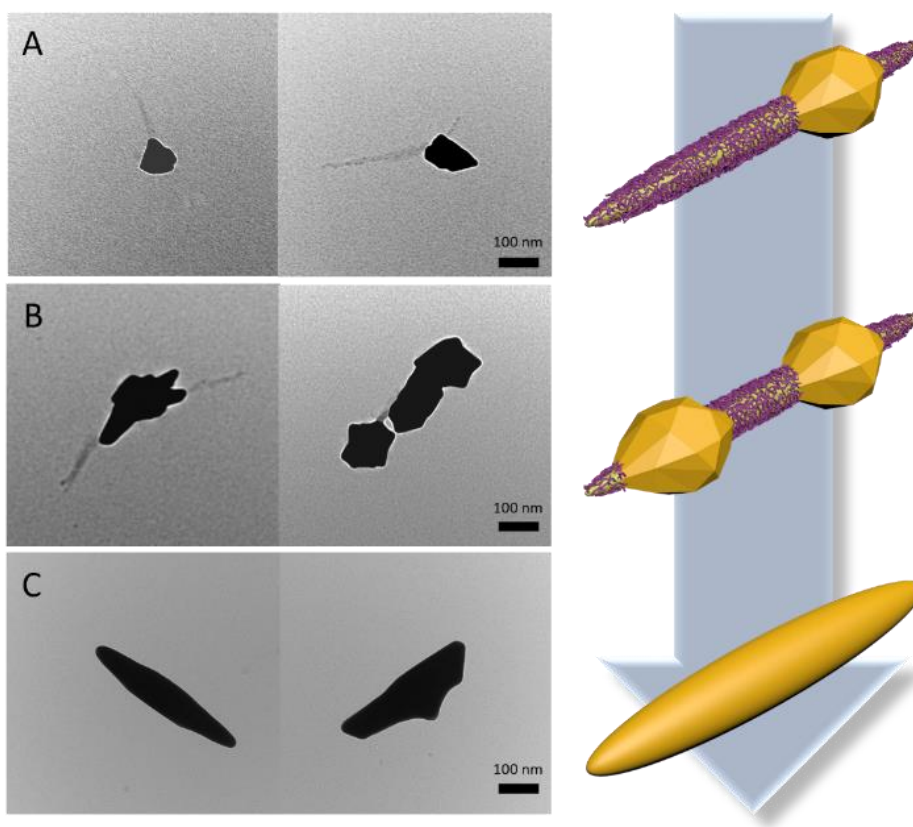


Figure 3.10 TEM images of CNC-gold nanostructures prepared by the *in-situ* method after adding 20 mL (A), 50 mL (B), and 100 mL (C) CTAB plating solution.

Figure 3.10A–C shows the TEM images of CNC-gold nanostructures prepared by adding 20 mL, 50 mL and 100 mL CTAB plating solution to CNC-PADADMAC-Ascorbic

acid suspension. By slowly adding the CTAB plating solution, few nuclei were formed on the CNC-PADADMAC-Ascorbic acid surface that grew into a complete and continuous shell. The surface of the resulting CNC-gold nanoshells prepared by this method was much smoother compared to the surface of CNC-gold nanoshells fabricated using the seed mediated approach reported in this study and previously.¹⁷³ TEM images of several individual CNC-gold nanoshells along with an aggregate of CNC-gold nanoshells are presented in the Figure 3.11.

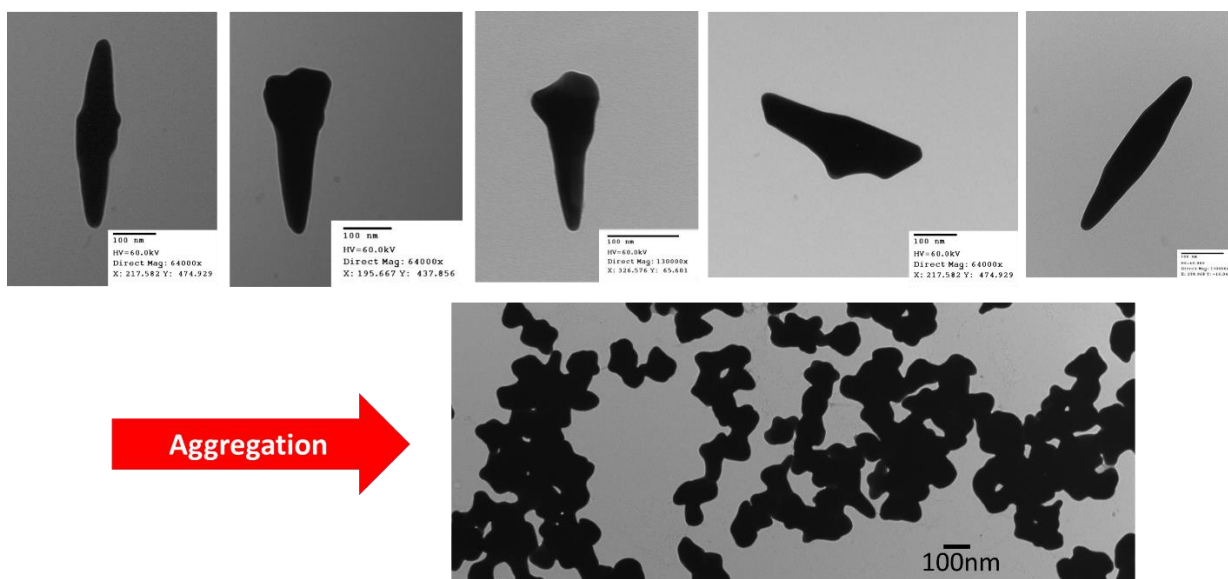


Figure 3.11 TEM images of a few individual CNC-Aushells along with an aggregate of several CNC-Aushells. Scalebars are 100 nm.

The evolution of zeta potential of the gold nanostructure prepared by the *in-situ* method is shown in Figure 3.7. After the adsorption of the ascorbate anions on the positive CNC-PDADMAC surface ($+62.1 \pm 1$ mV), the zeta potential decreased to $+35.5 \pm 3$ mV. By adding CTAB gold plating solution that increased the coverage of CNC-PDADMAC, the zeta

potential decreased even further (Figure 3.7) due to the accumulation of hydroxide ions on the gold surface (after repeated centrifugation to remove CTAB).^{296, 297} The zeta potential of the final CNC-PDADMAC-Gold nanoshell was -15.1 ± 0.5 mV. The hydrodynamic size of pristine CNC increased from 95.0 ± 1.8 to 128.4 ± 3.5 after the adsorption of PDADMAC. The hydrodynamic size of the final CNC-PDADMAC-gold nanoshell was 232.4 ± 1.8 nm, confirming that CNC-PDADMAC-gold nanoshells were individually dispersed in solution.

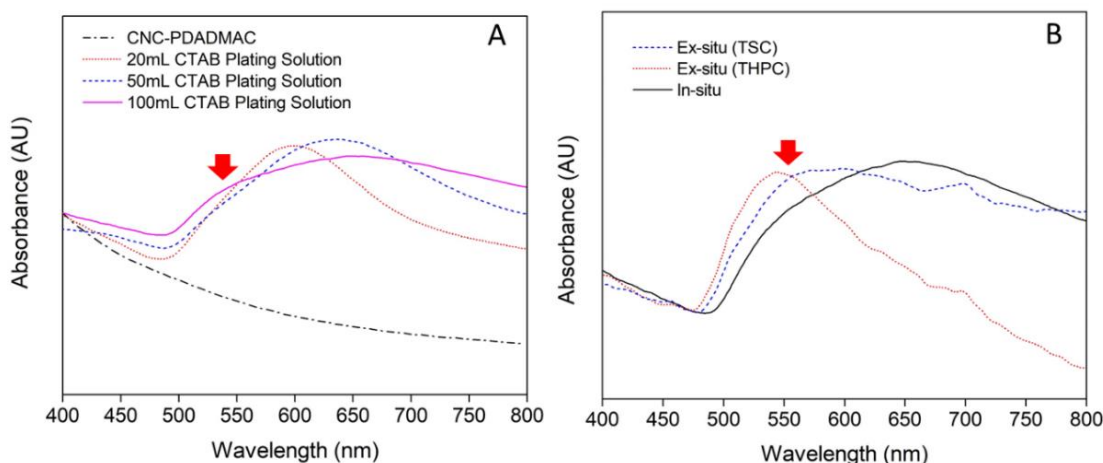


Figure 3.12 UV-vis absorption spectrums of CNC-gold nanostructures prepared by *in-situ* method (A) and gold nanoshell prepared by *ex-situ* and *in-situ* method (B). Red arrows point to the small shoulders remaining from the visible peaks after shell formation.

UV-vis absorption spectra of the nanostructures prepared by the *in-situ* method are summarized in Figure 3.12. The formation and growth of gold nuclei on the nanoparticle surfaces with the addition of CTAB plating solution, resulted in the increased interparticle plasmon coupling and a red-shift in the conventional plasmon resonance of gold nanoparticles (from 520 nm to 600 nm by adding 20 mL of CTAB plating solution)¹²² (Figure 3.12A). As

described earlier, the characteristic plasmon resonance of a complete shell is the general shift of the initial visible wavelength peak to near-infrared leaving only a small shoulder of the initial visible peak (red arrow in Figure 3.12A). This precise plasmon resonance was observed after the addition of 100 mL of CTAB plating solution.

Comparison of the absorption spectra of the *ex-situ* and *in-situ* methods revealed that the *in-situ* method led to more uniform Gold nanoshells with complete and continuous coating (Figure 3.12B).

Figure 13 illustrates the proposed mechanism for the formation of gold nanoshells. After the addition of CTAB to HAuCl_4 solution, chloride ions are replaced by bromide ions, and AuBr_4^- ions are stabilized within CTAB micelles. After the addition of the CTAB plating solution, AuBr_4^- ions were adsorbed on the surface of CNC-PDADMAC through the electrostatic interaction with the quaternary ammonium groups of PDADMAC. Then, ascorbic acid reduces the AuBr_4^- to Au^0 atoms on the surface of CNC-PDADMAC.^{168, 305} At the same time, CTAB acts as a directing agent by adsorbing to the surface of gold nuclei, providing a one-dimensional platform for the growth of gold shell. The hydrophobic tail of CTAB leads to the formation of a bilayer, with the cationic headgroup of the first monolayer facing the gold surface.³⁰² Consequently, an anisotropic growth of gold occurs on the surface of CNC-PDAMAC nanoparticles. Repeated centrifugation was performed to remove the CTAB molecules from the CNC-PDADMAC-gold nanoshells as much as possible. After removing CTAB, CNC-PDADMAC-gold nanoshells were not stable in the suspension for a long time.

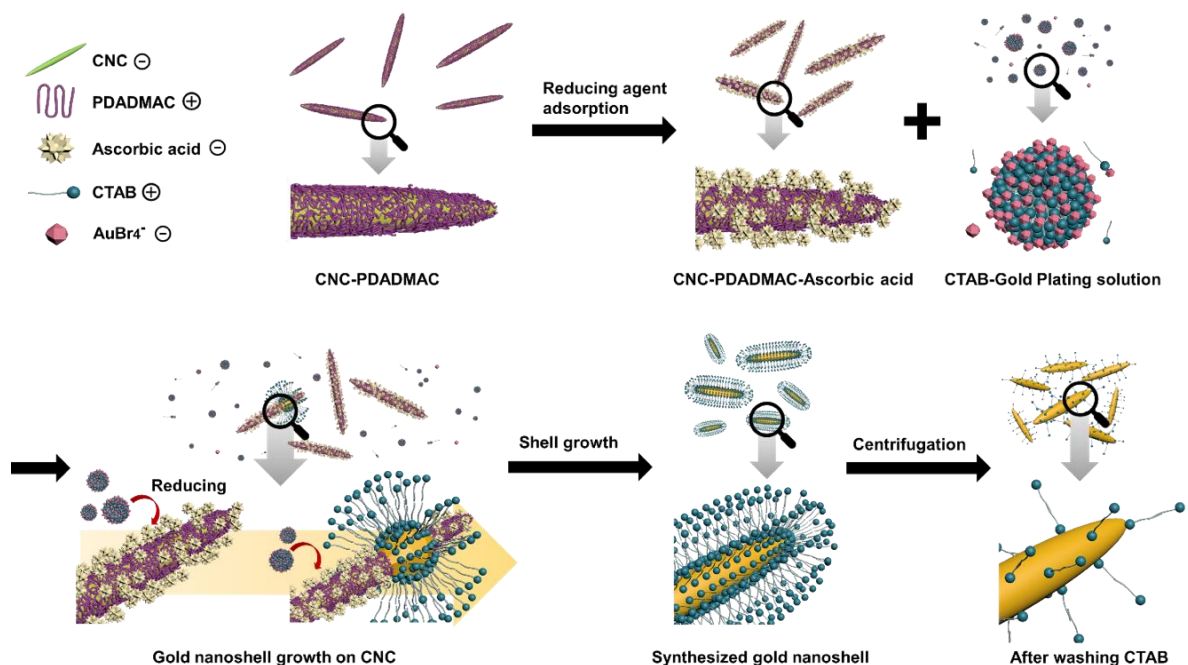


Figure 3.13 Schematic illustration of the proposed mechanism for the formation of CNC-PDADMAC-gold nanoshells by the *in-situ* method.

The reduction of 4-nitrophenol (4-NP) has been used as a model reaction to evaluate the catalytic activity of various nanoparticle systems.^{306, 307} Here, the reduction of 4-NP by NaBH_4 to 4-aminophenol (4-AP) was employed to examine the catalytic activity of CNC-gold nanostructures prepared by the *in-situ* method. The deprotonation of 4-NP produces 4-nitrophenolate ions that possess a strong absorption peak at 400 nm. After the reduction of 4-NP by NaBH_4 , the intensity of this peak decreased and a peak at 300 nm emerged corresponding to 4-AP. The kinetics of the reaction catalyzed by different CNC-gold nanostructures were analyzed by the time-dependent UV-vis absorption spectra of the reaction mediums as shown in Figure 3.14. Since the excess amounts of NaBH_4 was present in the reaction mediums (100 equivalents per 4-NP), a first-order Langmuir-Hinshelwood kinetics

was expected. The linear behavior of $\ln(A_t/A_0)$ as a function of reaction time, where A_0 and A_t are the initial absorbance and absorbance at time t for 400 nm peak, confirmed the first-order Langmuir-Hinshelwood kinetics for this reaction in the presence of all CNC-gold nanostructures. The apparent rate constant, k_{app} was calculated from the slope of the linear plot of $\ln(A_t/A_0)$ versus time.

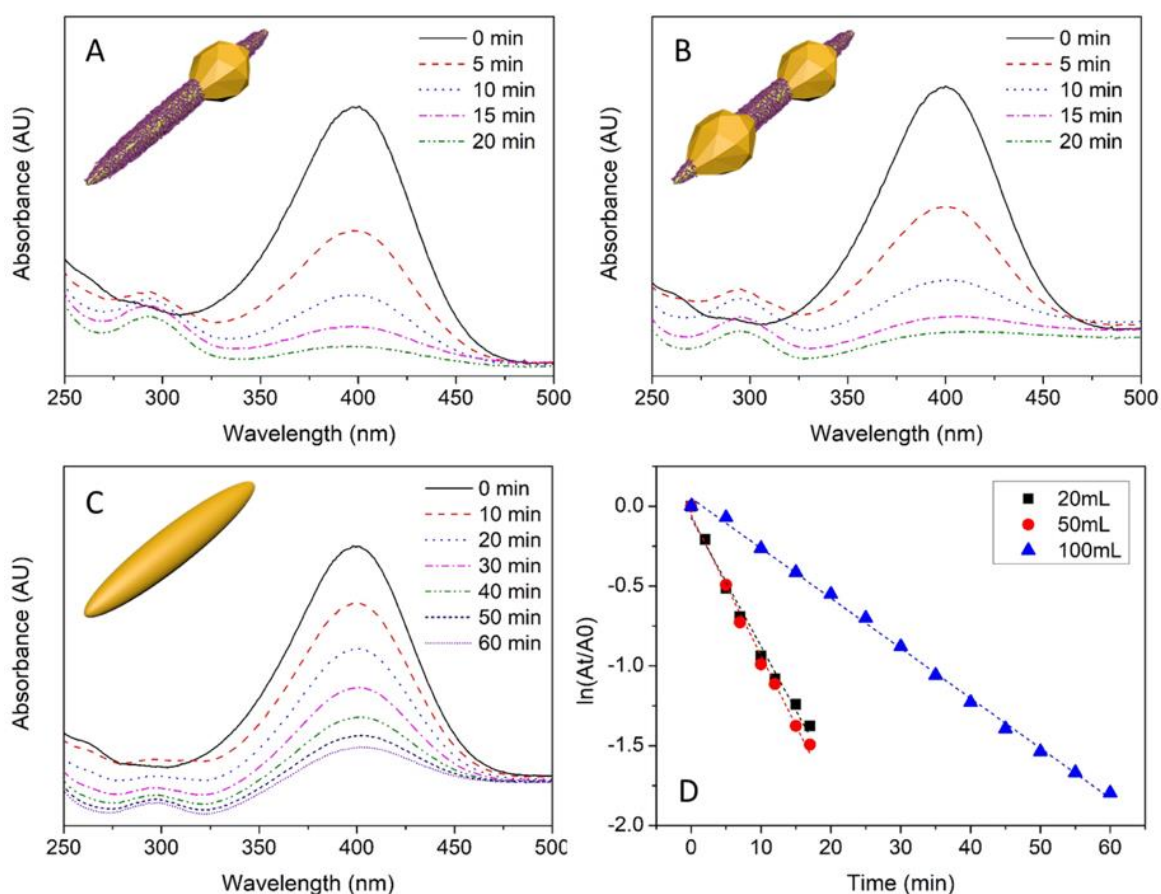


Figure 3.14 Time-dependent UV-vis spectrums of the 4-nitrophenol reduction catalyzed by different CNC-gold nanostructures prepared by the *in-situ* method after adding 20 mL (A), 50 mL (B), and 100 mL (C) of CTAB plating solution. (D) $\ln(A_t/A_0)$ versus reaction time t at 400 nm.

Table 3-2 Apparent rate constant k_{app} , and turnover frequency (TOF) of CNC-gold nanostructures prepared by the *in-situ* method after adding different amounts of CTAB plating solution and comparison of their catalytic performances with some other catalytic systems based on gold reported in the literature.

Catalyst stabilizer	Catalyst	k_{app} (s^{-1})	TOF (hr^{-1})	Reference
CNC-PDADMAC	Au (20 mL CTAB plating solution)	1.3×10^{-3}	263	This work
CNC-PDADMAC	Au (50 mL CTAB plating solution)	1.5×10^{-3}	274	This work
CNC-PDADMAC	Au (100 mL CTAB plating solution)	0.5×10^{-3}	85	This work
Fe ₃ O ₄	Au	-	269.5	308
SiO ₂	Au	-	240	309
CNC	Au	-	109	310
poly(4-vinylpyridine) grafted CNC	Au	-	5533	306

The turnover frequency (TOF, defines as the number of moles of 4-NP reduced per mole of catalyst per hour) was then estimated to compare the catalytic activity of different CNC-gold nanostructures (Table 3-2). The catalytic activity of CNC-gold nanostructures prepared by the *in-situ* method after the addition of 20 mL and 50 mL of CTAB plating solution were similar (263 hr^{-1} and 274 hr^{-1} , respectively) suggesting that the available surface of gold nanoparticles formed on CNC-PDADMAC after the addition 20 mL and 50 mL of plating

solution were comparable. The amounts of gold in each CNC-gold nanostructure were calculated assuming that the ratio between gold and CNC-PDADMAC remained the same and no change occurred during the centrifugation step. This assumption may introduce some error in the data. By forming the complete shell, the catalytic activity decreased dramatically to 85 hr⁻¹ due to the reduction of available surface. The catalytic performances of nanostructures prepared by the *in-situ* method for the reduction of 4-NP were compared with other catalytic system based on gold are included in Table 3-2. Nanostructures prepared by the *in-situ* method showed comparable catalytic performance to other catalytic systems except for poly(4-vinylpyridine) grafted CNC, where the decoration of CNCs with small size gold nanoparticles (about 3 nm) provided a very large available surface.

3.4 Conclusions

In summary, this study describes a convenient and successful fabrication of CNC gold nanoshells. First, a polymer wrapping strategy was developed to avoid the complicated surface functionalization steps to condition the CNC surfaces for AuNP attachment. Two sizes of AuNPs capped by TSC (2-10 nm) and THPC (1-3 nm) were employed for investigating the effect of AuNP size on the gold nanoshell quality. Gold nanoshells prepared by TSC capped AuNPs were more uniform and had a complete coverage of the CNC surface. A one-pot water-based shell growth method was then utilized to prepare CNC-gold nanoshells. Ascorbic acid was adsorbed on the CNC-PADADMAC surface acting as the reducing agent to suppress the undesired nucleation of gold in the bulk solution. CTAB was used as the capping and directing agent in the gold plating solution, and different extents of coverage were achieved by adding

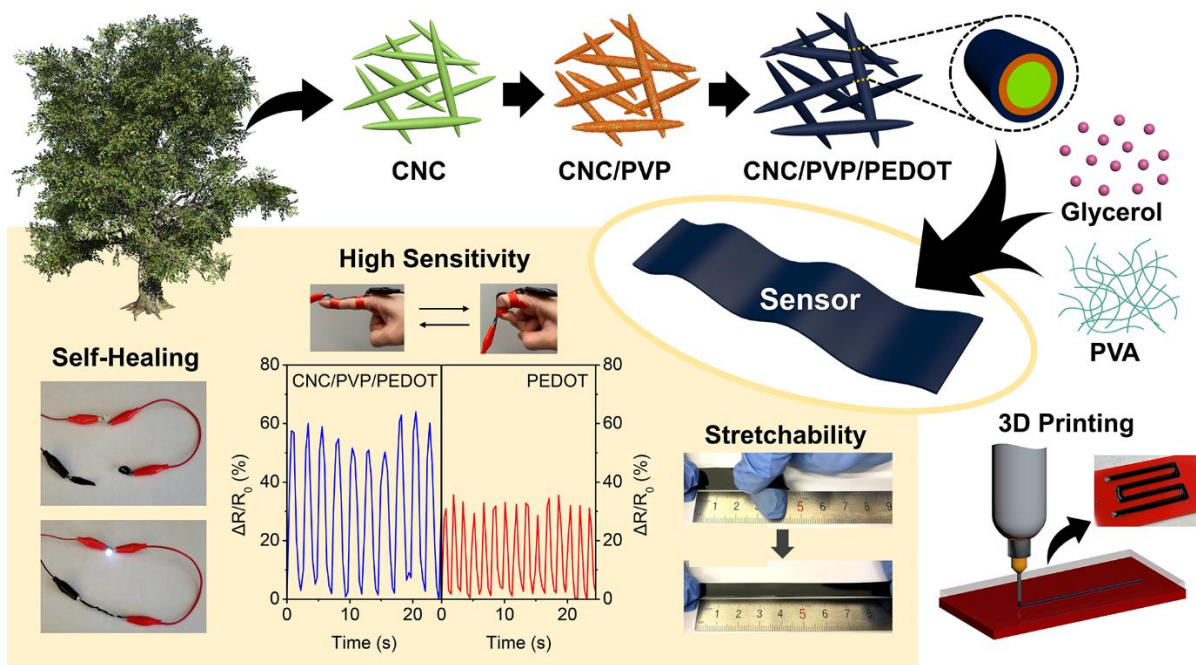
the different volumes of CTAB plating solution. Complete coverage of the CNC-PDADMAC surface and formation of continuous gold nanoshell was observed after the addition of 100 mL of CTAB plating solution. Finally, the catalytic activity of the resulting CNC-gold nanostructures was evaluated using a model reducing reaction of 4-NP to 4-AP by NaBH_4 . No significant difference was observed in the catalytic activity of partially covered CNC-gold nanostructures (20 mL and 50 mL CTAB plating solution). However, after the formation of the complete shell, the catalytic activity decreased dramatically due to the reduction of available catalytic surface.

Chapter 4^{††}

Sensitive, Stretchable, and Sustainable Conductive Cellulose Nanocrystal Composite for Human Motion Detection

Sensitive strain sensors (an important component of soft robotics, wearable devices, and biomedical electronics) with high sensitivity, stretchability, and long-term stability are still challenging. A sensitive, stretchable, and sustainable sensor using poly(3,4-ethylenedioxythiophene) (PEDOT) coated cellulose nanocrystals (CNC) with poly(vinyl alcohol)/glycerol (PVA/ Gly) composite is proposed. The low cost and sustainable PEDOT coated CNC with high aspect ratio lowered the electrical percolation threshold that significantly improved the electrical conductivity leading to better sensitivity (gauge factor = 21.25) compared to the PEDOT applied film without CNC (gauge factor = 9.35). The exceptional stretchability of up to 500% and a low Young's modulus with long-term stability exceeding 3 months are due to the glycerol plasticizer. The fabricated sensors possessed outstanding real-time strain sensing capability for a series of human motions, including complex joint bending motions, subtle muscle motions, wrist pulse, and excellent self-healing ability. This effective green strategy for preparing a highly stretchable conductive composite addresses current limitations in strain sensor preparation and offers a sustainable approach to sensor design and development.

^{††} This chapter is adapted from a paper “Lee, Y., Choi, H., Zhang, H., Wu, Y., Lee, D., Wong, W. S., ... & Tam, K. C. (2021). Sensitive, Stretchable, and Sustainable Conductive Cellulose Nanocrystal Composite for Human Motion Detection. *ACS Sustainable Chemistry & Engineering*” with permission from American Chemical Society.



4.1 Introduction

Stretchable strain sensors have been extensively investigated as an essential subcomponent of various applications, such as wearable devices,^{311, 312} electronic skins,^{313, 314} soft robotics,^{315, 316} and biomedical electronics³¹⁷⁻³¹⁹ to detect external deformation and convert to electronic signals. It is well-known that outstanding stretchability, high conductivity, excellent sensitivity, biocompatibility, long-term durability, and facile processing are essential requirements for these sensors. Various materials, such as elastic polymer composites and hydrogels, have been extensively explored to meet the increasing demand for strain sensors. Natural rubber, polyethyleneimine (PEI), polyvinyl alcohol (PVA), polydimethylsiloxane (PDMS), and polyurethane (PU) based flexible nanocomposites are very promising. These

nanocomposites have great mechanical strength, durability, and it is facile to impart electrical conductivity by adding conductive fillers, such as metal nanomaterials, carbon nanotubes, graphene, and conductive polymers.^{65, 320-326} However, the rigid nature of these conductive fillers and the aggregation of fillers negatively impact the stretchability and mechanical properties of the composites.^{65, 322-324}

Hydrogels (ionic hydrogel or hydrogel composites with secondary conductive fillers) with high stretchability have emerged as attractive solutions to prepare strain sensors. The low Young's moduli of hydrogels representing skin-like mechanical properties have opened the possibility for effective and sensitive detection of human motion and skin deformation. However, inevitable water evaporation from hydrogel degrades the hydrogel's performance over time and often requires additional encapsulation protection.^{318, 327}

Previous attempts to fabricate nanocomposites for strain sensors with high stretchability, conductivity, and long-term stability would incorporate plasticizers, such as non-volatile surfactants and polyols.^{320, 321, 323, 328} For example, Triton X-100 shows a significant plasticizing effect on PEDOT: PSS-PDMS composite by increasing the free volume and weakening the intermolecular interaction between polymer chains, leading to a dramatic reduction in the modulus and improved elongation at break.³²⁰ Polyols, such as polyethylene glycol and glycerol are effective plasticizers for PVA film. The mechanical properties of semi-crystalline PVA polymer with excellent processability, low cost, and high biocompatibility, can be adjusted by adding polyol plasticizers. Therefore, increased research efforts have been

devoted to studying the mechanical and electrical properties of PVA composites as candidates for strain sensors.^{323, 328}

Another strategy to address the trade-off between mechanical and electrical properties is to apply conductive fillers with high aspect ratio to generate an electrical percolation network at a lower amount of functional material.^{66, 329, 330} One-dimensional cellulose nanocrystals (CNC) are ideal nanofiller templates to reduce the percolation threshold and improve the dispersity of conductive materials within the composite matrix.^{66, 67, 330} Abundant surface functional moieties, such as hydroxyl groups, sulfate ester groups, and carboxylic groups on the CNC surface allow the conductive materials to be chemically and physically attached to its surface. The amphiphilic surface of CNC significantly enhances the dispersity of various conductive materials including graphene, CNT, and conductive polymers. Additionally, sustainable CNC allows for simple and environmentally friendly aqueous-based fabrication.^{65, 142, 331, 332}

In this chapter, we prepared a highly stretchable, sensitive, and self-healing strain sensor using a simple solvent casting and direct ink writing (DIW) with a 3D printer. The rod-shaped poly(3,4-ethylenedioxythiophene) (PEDOT) coated CNC was prepared and adapted as a conductive nanofiller that enhanced the dispersity of PEDOT within the hydrophilic PVA matrix. This PEDOT coated CNC also significantly lowered the electrical percolation onset of the composite and enabled it to achieve better strain sensitivity (Gauge factor = 21.25) compared to pure PEDOT polymer film (Gauge factor = 9.35). We also found that glycerol is

an ideal plasticizer for PVA composite to enhance the stretchability ($\sim 500\%$) and lower Young's modulus. The glycerol added conductive PVA composite (PVA/Gly-CNC/PVP/PEDOT) was fabricated through a facile solvent casting process and the mechanical and electronic properties of the strip-type sensor was studied. Also, the DIW technique allowed for scalable, fast, precise, and flexible customization and on-demand fabrication with low waste. Consequently, the as-prepared sensors exhibited excellent sensitivity to external strain and they could successfully detect various human activities. The sensor also shows excellent self-healing capability with only a trace amount of water, and its excellent strain sensing properties was maintained after 3 months, confirming its potential use in applications, such as wearable devices, soft robotics, and biomedical devices.

4.2 Experimental

4.2.1 Materials

Cellulose nanocrystal (CNC) was provided by CelluForce Inc. Polyvinylpyrrolidone (PVP, MW = 10,000), 3,4-Ethylenedioxythiophene (EDOT, 97%), and Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98.0-102%) were purchased from Sigma Aldrich. Polyvinyl alcohol (PVA, 86-89% hydrolyzed, medium molecular weight) was purchased from Fisher Scientific. Glycerol (Gly) was purchased from EMD Chemicals. All the chemicals were analytical grade and used as received if not specified. Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was utilized for preparing all aqueous solutions.

4.2.2 Synthesis of the CNC/PVP/PEDOT Hybrid Nanoconductor

The PVP-coated CNC (CNC/PVP) was prepared by dissolving 0.04 g of PVP in 100 ml water. It was then added to CNC dispersion at a CNC/PVP mass ratio of 9:1 and the mixture was stirred for 24 hours. The oxidative polymerization of EDOT monomers on the CNC/PVP template was conducted by mixing 0.9 g of EDOT with 75 mL of CNC/PVP dispersion (0.2 wt %) followed by the addition of FeCl₃ solution (50 mmol) under vigorously stirring for 3 hours at 70 °C. The dispersion was cooled and washed with water to remove unreacted chemicals, and the CNC/PVP/PEDOT dispersion was concentrated to 50 mL. CNC/PEDOT and PEDOT were also prepared as control samples under the same reaction conditions.

4.2.3 Preparation of PVA/Gly-CNC/PVP/PEDOT Nanocomposite films

PVA (1.25 g) and glycerol (1.25 g) were added to 31.06 mL of water and stirred at 90 °C for 2 hours to prepare a homogeneous PVA/Gly solution. After that, 18.94 mL of CNC/PVP/PEDOT dispersion was added to the PVA/Gly solution, and the mixture was stirred overnight at room temperature. The predetermined concentration of PVA/Gly in the mixture was 5 wt% after mixing. The prepared PVA/Gly-CNC/PVP/PEDOT solution was transferred to a Petri dish and dried in an oven at 60 °C under –10 in Hg vacuum condition for 6 hours. After the water evaporated, the film was separated from the Petri dish and stored in ambient conditions.

4.2.4 Fabrication of a 3D Printed PVA/Gly-CNC/PVP/PEDOT Nanocomposite

A concentrated PVA/Gly-CNC/PVP/PEDOT ink of viscosity suitable for 3D printing was prepared for improved printability. To prepare a highly concentrated solution, 18.94 mL of CNC/PVP/PEDOT dispersion was freeze dried, and the dried CNC/PVP/PEDOT powder was added to 7 mL of water and ultrasonically homogenized to yield a CNC/PVP/PEDOT suspension. Then, PVA (1.25 g) and glycerol (1.25 g) were added to the prepared suspension and stirred at 80 °C for 2 hours to produce viscous PVA/Gly-CNC/PVP/PEDOT ink. The predetermined concentration of PVA/Gly in the ink was 25 wt%. The 3D printing process was performed by a micro-extrusion printer, FlashForge Creator Pro (FlashForge, China), and a custom-made syringe holder. An Ultimus V high-precision dispenser (Nordson EFD, USA) was connected to a syringe containing PVA/Gly-CNC/PVP/PEDOT ink. The ink was extruded through a syringe needle (0.337 mm inner diameter) onto a 3M VHB 4905 double-sided tape as a stretchable substrate. The printed ink patterns were dried in an oven at 60 °C under –10 inHg vacuum for 2 hours.

4.2.5 Characterization

The hydrodynamic size and ζ -potential measurements were conducted in a Zeta-Sizer (Malvern, Nano ZS90) at 25 °C. The samples were dispersed in Milli-Q water and sonicated

in a bath sonicator for 10 min prior to measurements. The average values of at least three measurements were reported, and the range represents the standard error.

The water contact angles of CNC and CNC/PVP compressed pellets are tested by a contact angle measuring system (Dataphysics, Germany). The contact angles were determined within 3 seconds after placing 3 μ L of water drop onto the surface of samples.

The electrical conductivity of CNC/PVP/PEDOT and PVA/Gly-CNC/PVP/PEDOT was measured using a four-point probe system (Keithley 2400). The freeze-dried CNC/PVP/PEDOT powder was pressed into thin rectangular pellets, and the dried PVA/Gly-CNC/PVP/PEDOT film was cut into a rectangular shape. The conductivity was calculated from the measured sheet resistance values and the thickness of the pellets.

The real-time resistance response to strain was measured using an electrometer (Agilent, 34460A, USA) with a constant applied voltage of 0.5 V. The PVA/Gly composite was cut in a rectangular shape (4 cm $\times$ 1 cm $\times$ 0.1 mm) for strain sensor fabrication. The resistance change upon stretching was calculated by Ohm's law ($R = V/I$). The relative resistance change and gauge factor (GF) was obtained based on the following equations:

$$\frac{\Delta R}{R_0} = \frac{(R - R_0)}{R_0} \quad (4.1)$$

$$GF = \frac{\Delta R/R_0}{\varepsilon} \quad (4.2)$$

where R_0 represents the initial resistance, R is real-time resistance, and ε is the applied strain.

Fourier-transform infrared (FTIR) spectrometer (Thermo Scientific, Nicolet 6700) with an ATR accessory was used to characterize the chemical structures in the 650 – 4000 cm^{-1} wavelength range.

The samples for transmission electron microscopic (TEM, Philips, CM10) were prepared by placing 20 μL of suspension (< 0.01 wt %) on a copper grid followed by drying overnight at room temperature.

The field emission scanning electron microscope (FE-SEM, SIGMA, Carl Zeiss) was used to image the freeze-fractured surface morphology of the composites at an acceleration voltage of 5.0 kV. Each film was coated with platinum layers via ion sputter coating before the characterization (Hitachi, E-1010, Tokyo, Japan).

The mechanical properties of the composite samples cut into a rectangular shape (4 cm $\times$ 1cm $\times$ 0.1 mm) were analyzed using a universal material tester (UMT, CETR). The initial length of the sample between two clamps was fixed to 10 mm, and a stretching rate of 2 mm sec^{-1} was used. All measurements were taken at room temperature (25 $^{\circ}\text{C}$), and at least three samples were prepared and tested for each condition. The Young's modulus was determined from the slope of the linear region of the stress-strain curve.

Differential scanning calorimetry (DSC, Q2000, TA Instruments, USA) was performed to investigate the glass transition behavior of PVA-CNC/PVP/PEDOT and PVA/Gly-CNC/PVP/PEDOT. Each 10 – 13 mg sample was placed in an aluminum pan, and an empty

pan was used as a reference. The glass transition temperature was determined from the second heating scan with a heating rate of 3 °C min⁻¹.

The moisture content of the films was determined with a moisture analyzer (VWR) using standard mode, using temperatures up to 110°C.

A self-healing test for the strip-type sensor was conducted by placing one drop of water on the sensor followed by overlapping 1 cm of the two cut films with moderate pressure (by hand) and drying for 30 min in ambient conditions. 10 µL of water was dropped on the damaged site and dried for 30 min in ambient conditions to assess the self-healing characteristic of the printed pattern.

4.3 Results and Discussion

The preparation of CNC/PVP/PEDOT is schematically shown in Figure 4.1a. Pristine CNC before polymer coating has a one-dimensional structure with a length between 150 – 350 nm and 10 nm diameter, as shown in Figure 4.1b. After the PVP and PEDOT coating, the diameter of CNC/PVP/PEDOT increased in diameter to around 40 nm, with a much stronger contrast in the TEM picture confirming the successful coating of PEDOT on CNCs (Figure 4.1d). The PEDOT coating preserved the CNC rod-like structure, and the continuous and smooth PEDOT coating generated a conductive pathway at a low amount of functional material. However, the as-prepared PEDOT prepared using the same condition possessed a scrambled egg-like morphology with diameters larger than 500 nm (Figure 4.1 c).

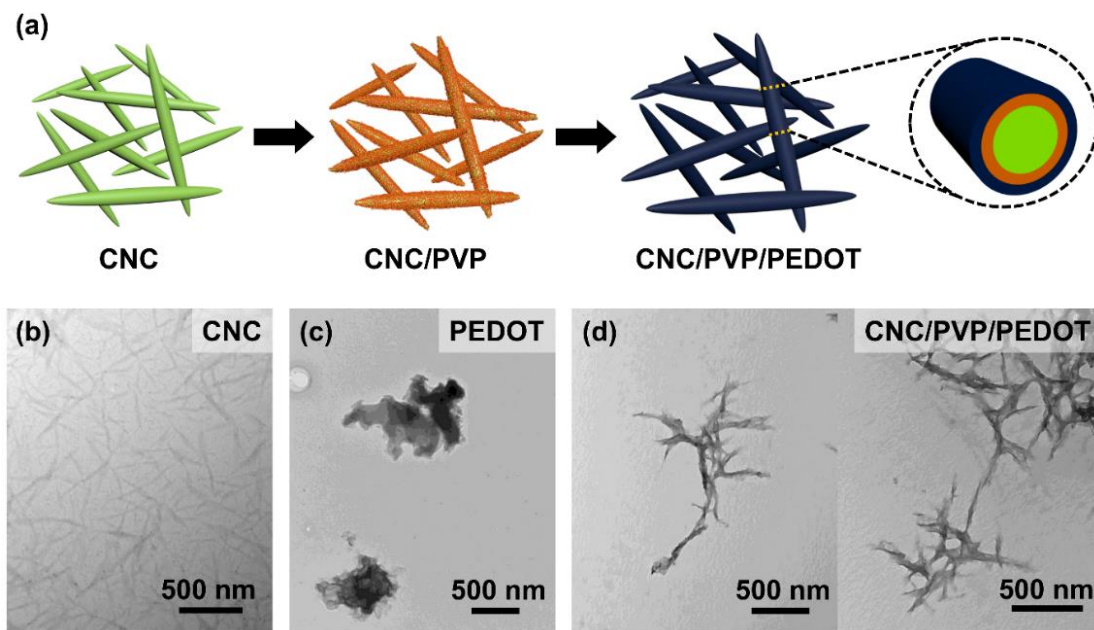


Figure 4.1 (a) Schematic illustration of the synthesis of CNC/PVP/PEDOT. TEM images of (b) pristine CNC, (c) PEDOT, and (d) CNC/PVP/PEDOT.

The PEDOT coating on pristine CNC surface without PVP was not successful; PEDOT was only partially coated with very weak contrast and mostly exists as a free PEDOT, as shown in Figure 4.2a. This result confirmed that amphiphilic PVP formed an inter-layer between CNCs and EDOT, yielding a smooth and uniform PEDOT layer. PVP has been used with CNCs to introduce hydrophobicity to the CNC surface and also shield the heterogeneous surface chemistry of CNCs.^{46, 47} The contact angle test also confirms the reduced hydrophilicity of CNC/PVP by the water contact angle of $34.0 \pm 3^\circ$ compared to the pristine CNC having $25.9 \pm 4.7^\circ$ contact angle. (Figure 4.2b)

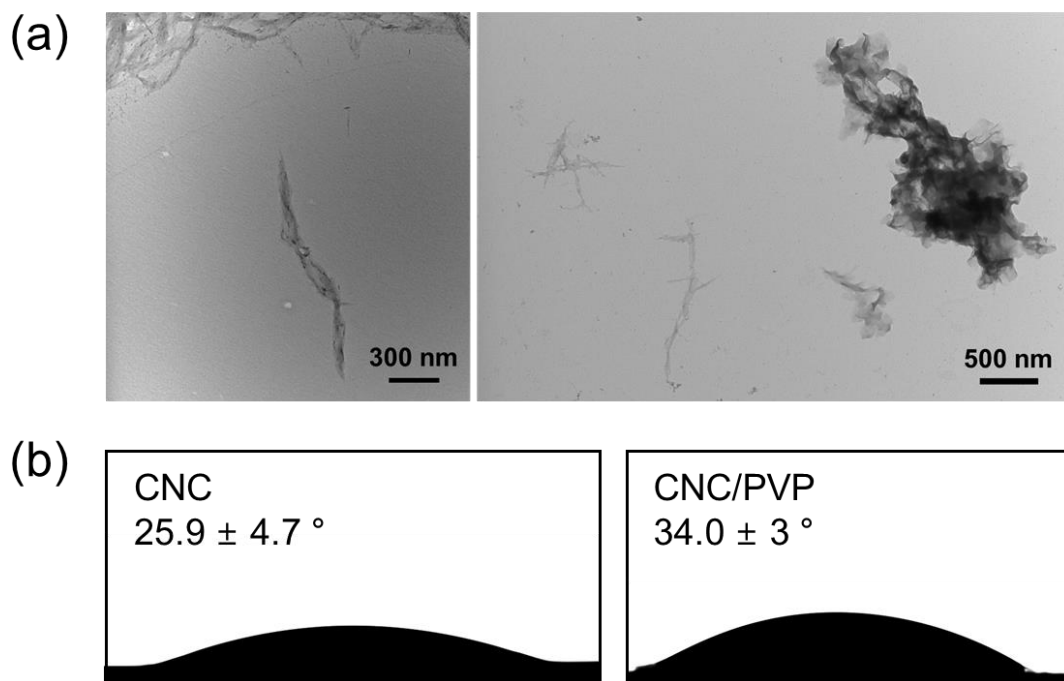


Figure 4.2 (a) TEM image of CNC/PEDOT without PVP layer, (b) water contact angles of CNC and CNC/PVP.

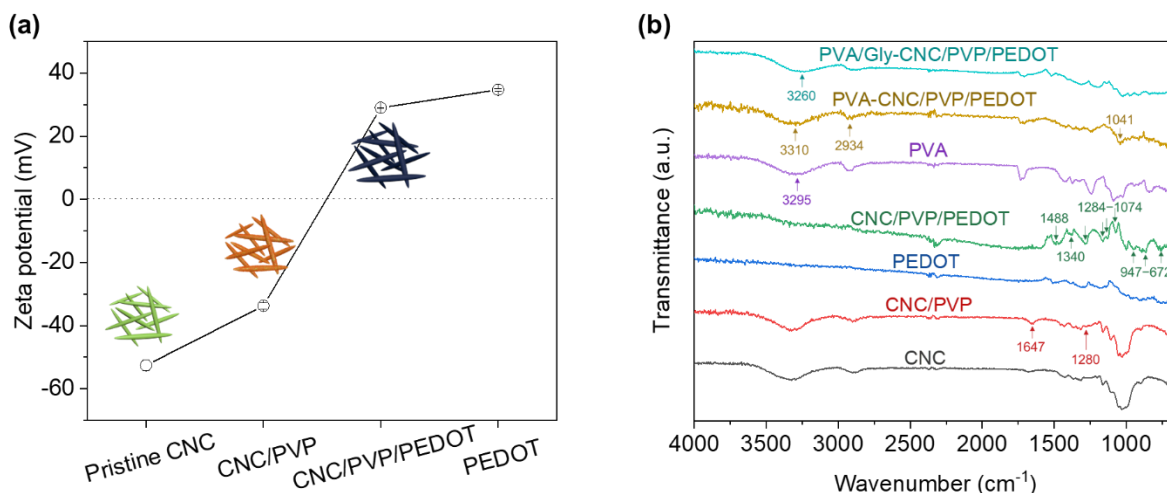


Figure 4.3 (a) Schematic illustration of the synthesis of CNC/PVP/PEDOT. TEM images of (b) pristine CNC, (c) PEDOT, (d) CNC/PVP/PEDOT, (e) Zeta potential of CNC, CNC/PVP, CNC/PVP/PEDOT, and PEDOT. (f) FTIR characterization for CNC, CNC/PVP, PEDOT, CNC/PVP/PEDOT, PVA, PVA-CNC/PVP/PEDOT, and PVA/Gly-CNC/PVP/PEDOT.

The zeta potential change in CNCs during the preparation process also confirmed the successful PEDOT coating on the CNCs. (Figure 4.3a) The CNCs without coating possessed a large negative zeta potential of -52.6 ± 1.7 mV. Once PVP was coated on the surface of CNC, this value became less negative (-33.7 ± 1 mV). After PEDOT coating, it increased to $+29 \pm 0.1$ mV due to the screening effect of positively charged PEDOT layer, indicating high coverage of PEDOT on the surface of the CNCs.^{64, 333}

Figure 4.3b shows the FTIR spectra of PEDOT coated CNC. CNC/PVP displayed new small absorption bands at 1280 and 1647 cm⁻¹ that were associated with C–N bending and C=O stretching respectively, confirming the presence of PVP coating.³³⁴ The FTIR spectra of CNC/PVP/PEDOT displayed bands at 1488 and 1340 cm⁻¹ that corresponded to C=C

asymmetric and C-C inter-ring stretching respectively. Also, the absorption bands around 1284, 1160, 1130, and 1074 cm^{-1} are considered C-O-C bending of the ethylenedioxy group. The peaks at 947, 863, 760, and 672 cm^{-1} are typical C-S-C absorption bands stretching in the thiophene ring.^{335, 336} These bands are similar to the major peaks of PEDOT, confirming the successful polymerization of PEDOT on the CNC surface.

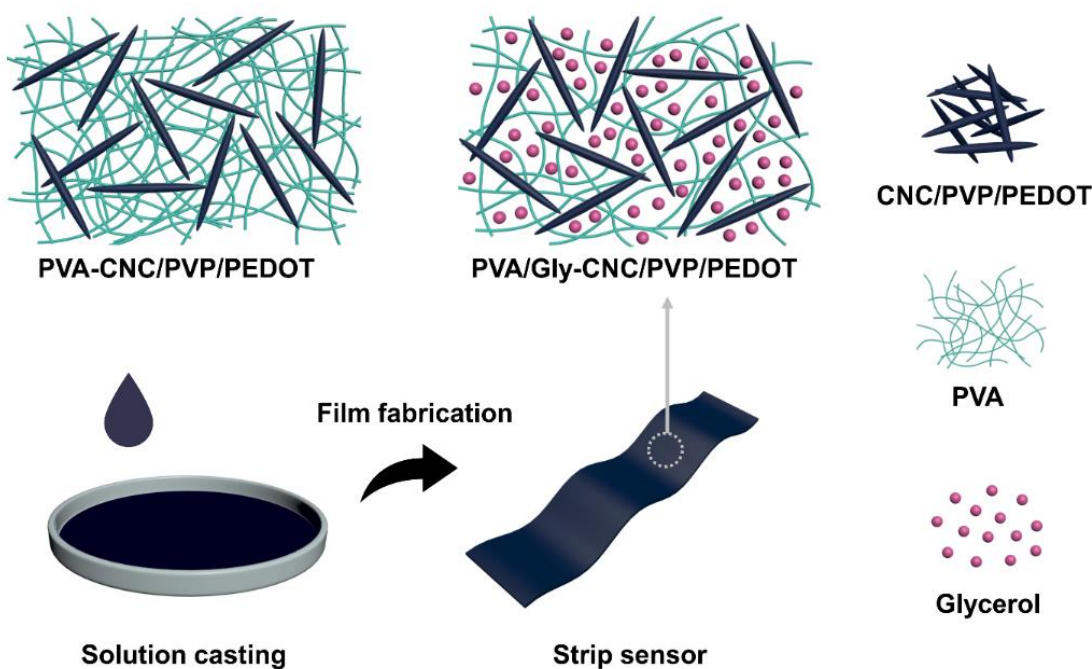


Figure 4.4 Schematic images of the PVA/Gly-CNC/PVP/PEDOT nanocomposites.

Figure 4.4 illustrates the proposed structure of a highly stretchable conductive CNC nanocomposite prepared with PVA matrix polymer and glycerol plasticizer. Neat PVA composite generally possesses limited elasticity and brittle mechanical properties due to the high crystallinity, which limits its use in stretchable electronics.^{323, 337} Furthermore, the addition of conductive nanofiller, such as conductive polymers with rigid conjugated

backbones increased the brittleness while reducing the stretchability of the composite. A plasticizer could be added to the matrix polymer to increase the mobility of the polymer chains that addressed these weakness; and glycerol was adopted as a plasticizer for PVA. Glycerol is non-toxic, and it has diverse applications not only as a plasticizer but in cosmetics, food, and pharmaceuticals. By replacing a certain amount of PVA polymer with glycerol, the stretchability of the composite was significantly enhanced due to the increased PVA inter-chain mobility and the disruption of the hydrogen bonds between the PVA chains.³²³

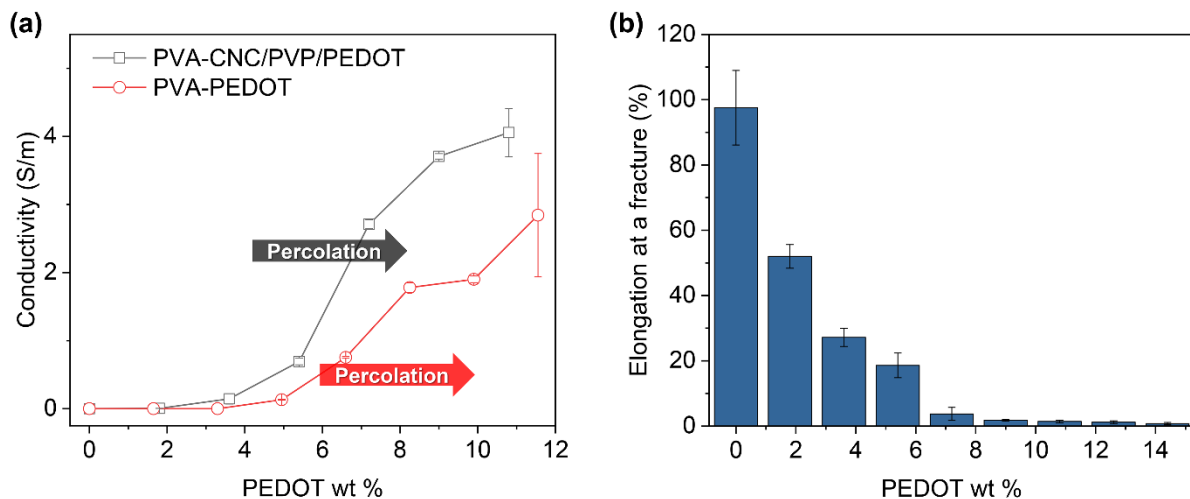


Figure 4.5 (a) Electrical conductivity of PVA-CNC/PVP/PEDOT and PVA-PEDOT composites as a function of PEDOT weight fraction. (b) Elongation at break of the PVA-CNC/PVP/PEDOT as a function of PEDOT weight fraction.

The changes in the electrical conductivity and stretchability of the prepared nanocomposites are shown in Figure 4.5. Unsurprisingly, the electrical conductivity of the composite increased with increasing content of PEDOT, but the degree of conductivity variation was entirely dissimilar between the two composites (Figure 4.5a). Since the high

aspect ratio of the CNC template lowered the onset of the electrical percolation of PEDOT, the PVA-CNC/PVP/PEDOT experienced a much earlier and faster conductivity rise than PVA-PEDOT.^{65, 66} This result confirmed the superiority of CNC template for preparing conductive materials with high electrical conductivity producing functional materials that were cheaper.

Figure 4.5b shows the elongation at break of PVA-CNC/PVP/PEDOT composite with different amounts of PEDOT coated on the CNC. The CNC/PVP/PEDOT fraction had a considerable influence on the failure strain of the PVA-CNC/PVP/PEDOT composites. The elongation at break (EAB) of neat PVA film was 97.6 %, and this value decreased with increasing amount of CNC/PVP/PEDOT, achieving an EAB of 1.5 % at PEDOT content of 9 wt%. The lower stretchability was caused by rigid conjugated backbone of PEDOT, making the composites very brittle, which is consistent with the literature.^{322, 324}

The 7.2 wt% PEDOT contained PVA-CNC/PVP/PEDOT sample was selected for further experiments to prepare a highly stretchable and sensitive strain sensor after considering the conductivity and the mechanical properties of the PVA composite. Since the PEDOT content was within the electrical percolation region, its electrical conductivity was expected to depend strongly with strain.^{338, 339} Also, at 9 wt% PEDOT content, the elongation at break plateau was very low, making the higher amount of PEDOT content unfavorable in terms of stretchability.

Strain sensors with high stretchability and low Young's modulus are advantageous for detecting human motion since the sensor can readily deform with the application of stress.^{318, 340-342} However, the PVA composites containing PEDOT were very brittle, which are not

desirable for stain sensors. The glycerol concentration in the PVA-CNC/PVP/PEDOT composite was varied to improve the tensile properties, including Young's modulus and elongation at break. The mechanical properties of the composite changed considerably with the addition of glycerol (Figure 4.6a).

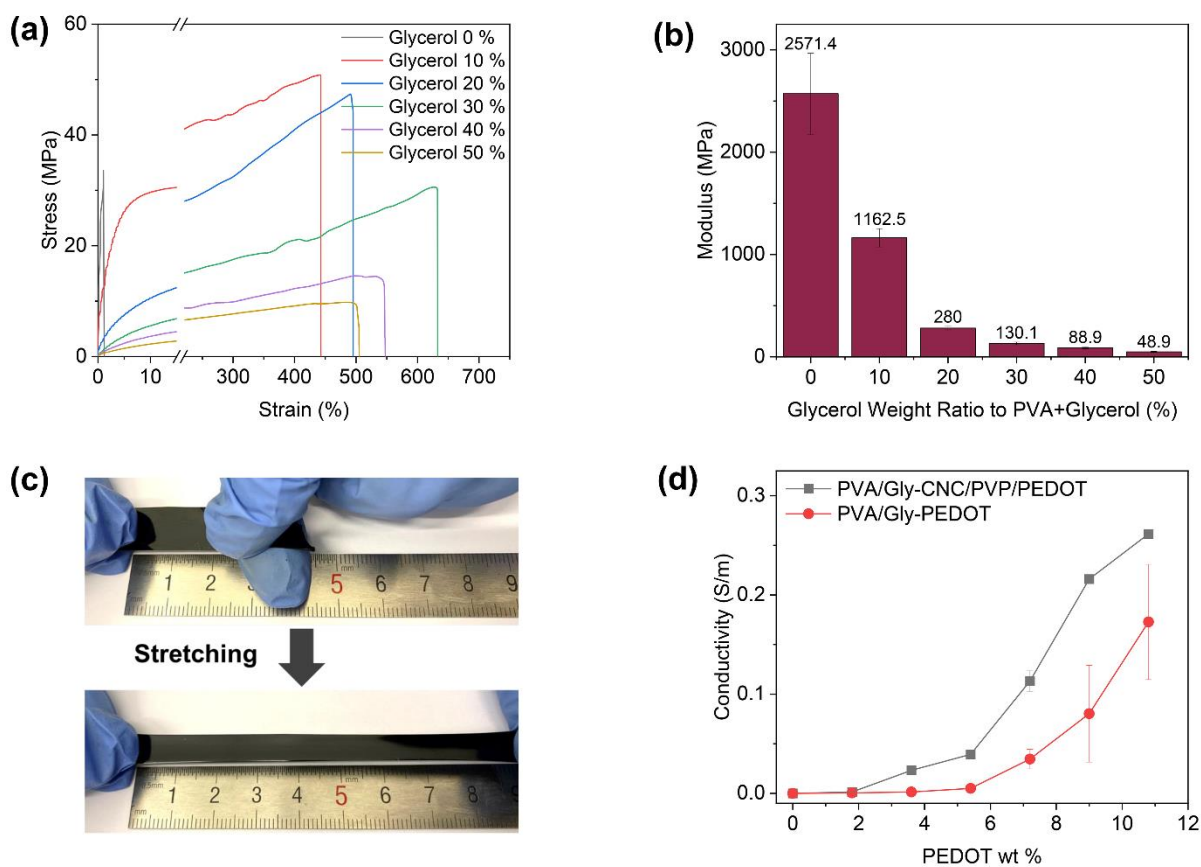


Figure 4.6 (a) Representative stress-strain curves of PVA/Gly-CNC/PVP/PEDOT with different glycerol concentrations. (b) Modulus of PVA/Gly-CNC/PVP/PEDOT with different glycerol concentrations. (c) Optical demonstration of excellent stretchability. (d) Electrical conductivity of PVA/Gly-CNC/PVP/PEDOT and PVA/Gly-PEDOT composites as a function of PEDOT weight fraction.

The PVA-CNC/PVP/PEDOT showed a very low failure strain of about 2 %, while all composite samples with 10 – 50 % glycerol content showed a dramatic improvement in tensile elongation. Additionally, with increasing glycerol content, the Young's moduli of the PVA/Gly-CNC/PVP/PEDOT composites decreased, as shown in Figure 4.6b. Young's modulus achieved 48.9 MPa at 50 % of glycerol content with a high stretchability of 508.6 ± 15.4 %, suitable for use as a strain sensor for human motion detection. The enhanced ductility originated from the plasticizing effect of glycerol, improving the internal mobility of the PVA chain.^{323, 337, 343} The plasticizer effect of glycerol for PVA/Gly-CNC/PVP/PEDOT was also demonstrated by the lowering of the glass transition temperature from 90 °C with no glycerol to 81 °C with 50 % glycerol (Figure 4.7a).

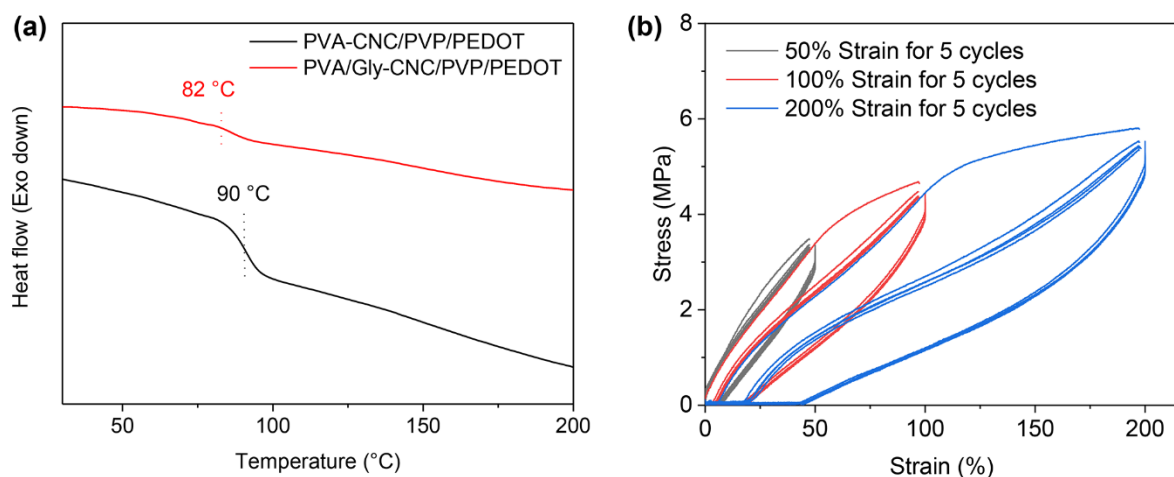


Figure 4.7 (a) DSC curves of PVA-CNC/PVP/PEDOT and PVA/Gly-CNC/PVP/PEDOT. (b) Stress-strain curves of PVA/Gly-CNC/PVP/PEDOT sensor during loading and unloading cycles (50 %, 100 %, and 200 % consecutively) with 2 mm sec^{-1} rate.

The outstanding stretchability of the 50 % glycerol sample is visually demonstrated in Figure 4.6c. The cyclic stress-strain responses of 50 % glycerol contained sensor show hysteresis curve with stress softening like common elastomers based sensor as shown in Figure 4.7b.³⁴⁴⁻³⁴⁶ The stress-strain curves overlapped and showed excellent reversibility after the first cycle during cyclic loading and unloading, and the most strain was recovered elastically. However, glycerol content above 50 % was not examined as the excessive (60 %) glycerol resulted in phase separation, and the glycerol escaped from the matrix, as shown in Figure 4.8. The composite containing 50 % glycerol was stable until 100 days without noticeable phase separation.

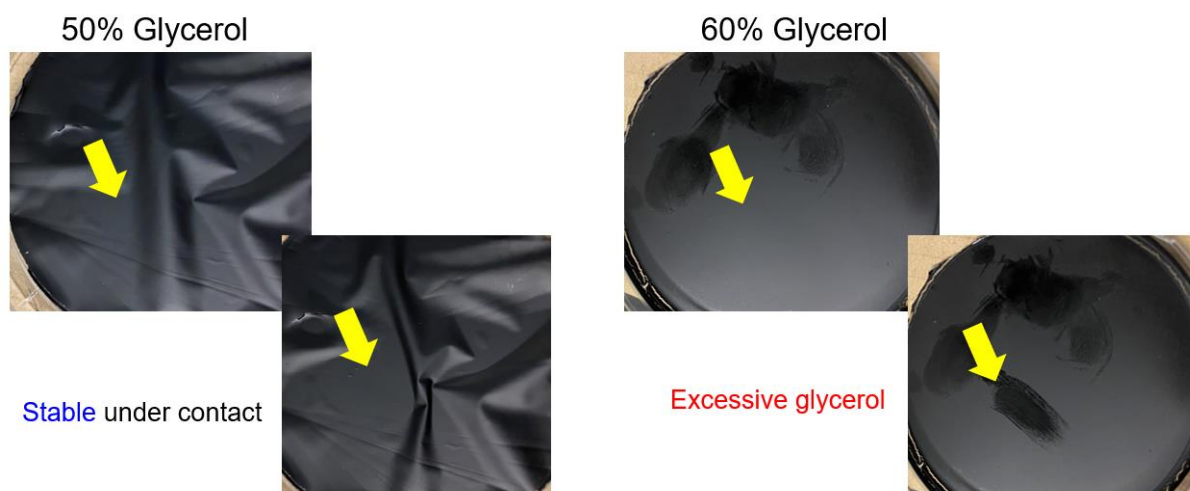


Figure 4.8 The photographs of PVA/Gly-CNC/PVP/PEDOT films after drying.

The electrical conductivity of composite with 50 % of glycerol was determined to identify the percolation onset (Figure 4.6d). Although the overall conductivity decreased compared to the PVA composite without glycerol, it showed similar trend in the change of the

conductivity. The reduction of conductivity could be caused by different densities of glycerol and PVA and the increased moisture content of the PVA/Gly film due to the hydrophilicity of the glycerol plasticizer.³⁴⁷ The moisture content analysis revealed that the water content of the PVA/Gly-CNC/PVP/PEDOT composite was $15.4 \pm 2.4 \%$ and $6.4 \pm 1.0 \%$ in the absence of glycerol. These factors could change the distance between the conductive fillers and led to conductivity reduction. The conductivity of PVA/Gly-CNC/PVP/PEDOT composite was increased to $1.73 \pm 0.99 \text{ S/m}$ after drying the composite at high vacuum and 60°C for 20 hours, lowering the water content ($7.6 \pm 2.6 \%$). Like the PVA composite, PVA/Gly-CNC/PVP/PEDOT also exhibited a higher conductivity than the PVA/Gly-PEDOT at all the PEDOT content tested. The conductivity of composite containing 7.2 wt% PEDOT was within the percolation region where the electrical conductivity changed dramatically.^{338, 339} Also, the video “Movie4-1. The luminance variation of an LED bulb by stretching and releasing the PVAGly-CNCPVPPEDOT.mp4” in Appendix A demonstrates the luminance variation of an LED bulb by stretching and releasing the 50% glycerol and 7.2 wt % PEDOT containing nanocomposite. The luminance change also confirmed the sensitivity of PVA/Gly-CNC/PVP/PEDOT to deformation. Therefore, the 50 % glycerol and 7.2 wt % PEDOT content conditions were selected for fabricating the highly sensitive and stretchable strain sensor, and “PVA/Gly-CNC/PVP/PEDOT” represents the composite at this condition unless otherwise stated.

SEM images were taken to examine the cross-sectional morphology of the nanocomposites. The neat PVA film shows a very smooth fractured surface (Figure 4.9a), and

the PVA/Gly film exhibited only marginally increased roughness due to the addition of glycerol (Figure 4.9d). The excellent miscibility of PVA and glycerol is shown in Figure 4.9d, demonstrating a homogeneous film with no phase separation. Figures 4.9b and 4.9e display the homogeneous dispersion of CNC/PVP/PEDOT within the PVA and PVA/Gly matrix, respectively. In contrast, films with PEDOT displayed increased surface roughness suggesting the uneven distribution and aggregation of PEDOT. This different distribution behavior of CNC/PVP/PEDOT and PEDOT was also observed from the photographs of a film prepared by solution-casting (Figure 4.10). This is because of the insoluble character of PEDOT in most solvents, leading to aggregation and non-homogeneous distribution in the aqueous PVA solution, whereas the amphiphilic CNC/PVP template allows PEDOT to be well dispersed in the PVA solution.⁴⁷

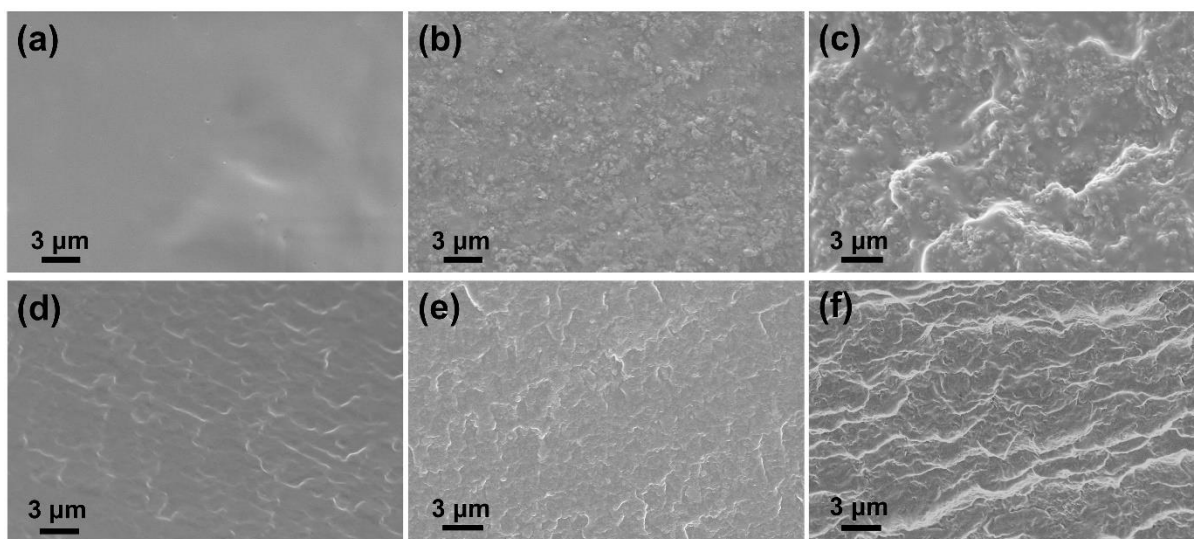


Figure 4.9 SEM images of fractured surfaces of (a) PVA, (b) PVA-CNC/PVP/PEDOT, (c) PVA-PEDOT, (d) PVA/Gly, (e) PVA/Gly-CNC/PVP/PEDOT, and (f) PVA/Gly-PEDOT

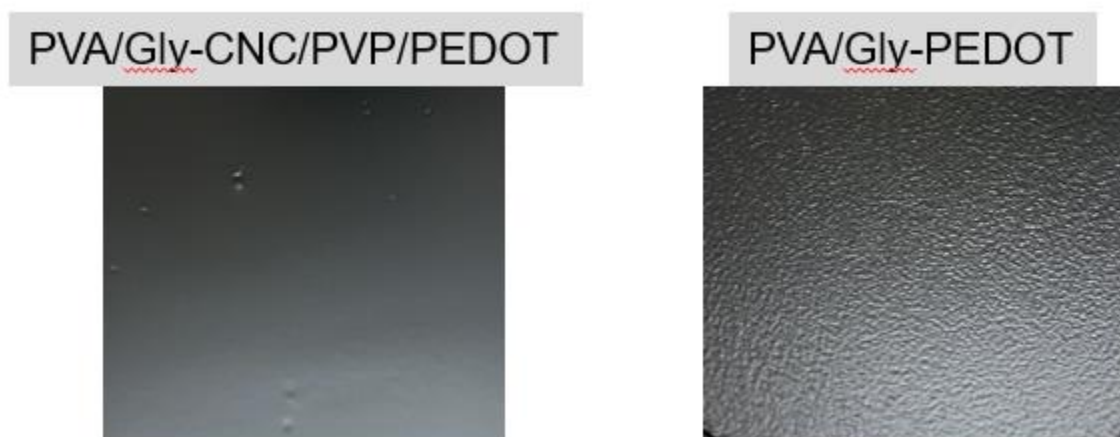


Figure 4.10 The photographs of PVA/Gly-CNC/PVP/PEDOT film (left) and PVA/Gly-PEDOT film (right).

The FT-IR spectra of the PVA composites are shown in Figure 4.3b. The major peaks originated primarily from the PVA structure because the CNC/PVP/PEDOT in the composite was relatively minimal. The broad band at 3310 cm^{-1} was ascribed to O–H groups, which was shifted from 3295 cm^{-1} in pure PVA, suggesting hydrogen bonds formation between PVA and CNC/PVP/PEDOT. The peak around 2934 cm^{-1} was attributed to C–H stretching, and the peaks around 1237 cm^{-1} , and the band at 1041 cm^{-1} were considered to be C–O stretching.³⁴⁸ The introduction of glycerol into the composite led to a slight shift of the stretching vibration to 3260 cm^{-1} of the hydroxyl groups, corresponding to the hydrogen bond formation between PVA and glycerol.^{343, 349}

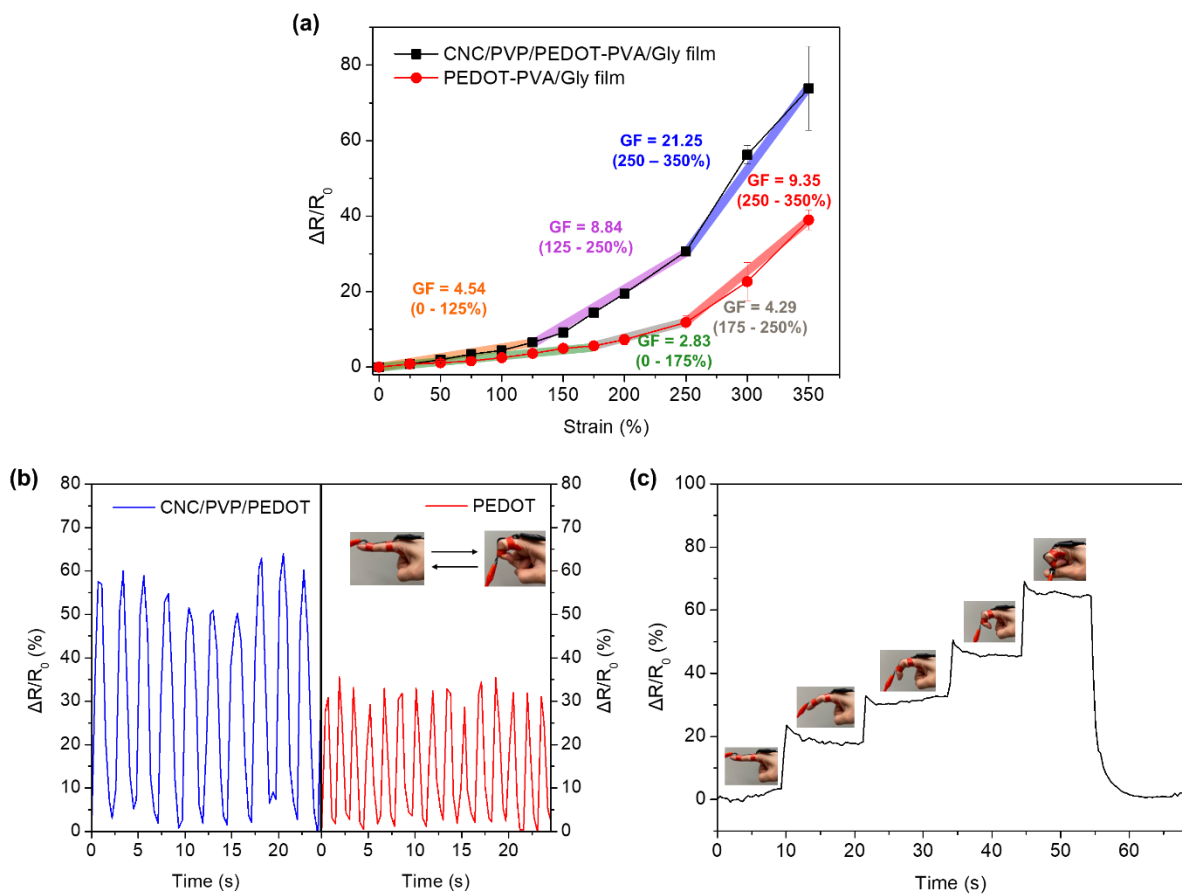


Figure 4.11 Relative resistance responses of PVA/Gly-CNC/PVP/PEDOT: (a) Comparison of the CNC/PVP/PEDOT and PEDOT containing sensors as a function of applied strain from 0 % to 350 %, and real-time recording of (b) finger motion and (c) step-by-step finger bending motion.

The outstanding strain sensitivity with excellent stretchability of the fabricated sensor was shown by measuring the relative resistance changes depending on deformation. Figure 4.11a shows the relative resistance responses and calculated GF values of the PVA/Gly-CNC/PVP/PEDOT sensor and PVA/Gly-PEDOT at a strains range of 0 – 350%. The relative resistance was increased with increasing applied strain leading to an expanded distance between the conductive fillers that controlled the number of tunneling junctions and the

number of noncurrent flowing CNC/PVP/PEDOT and PEDOT conductors.^{144, 338} Also, the relative changes in resistance occurred exponentially rather than linearly, and this trend agreed with the results from other literature using CNC-based conductive fillers^{142, 330, 332, 350}, including carbon blacks,³³⁹ carbon nanotubes,^{339, 351} and silver nanowire³³⁸, dispersed in a polymer matrix with concentration below the percolation thresholds. Regarding the effect of the CNC template, the CNC/PVP/PEDOT containing sensors presented a much higher gauge factor of 4.54 (0 – 125 %), 8.84 (125 % – 200 %), and 21.25 (200 % – 300%) than the PVA/Gly-PEDOT sensor as shown in Figure 4.11a. This result is attributed to the higher electrical conductivity of the PVA/Gly-CNC/PVP/PEDOT film within the percolation network formation.^{351, 352} The role of the CNC template to prepare strain sensors for human motion monitoring was even more apparent by comparing the relative resistance change during real-time finger bending motion (Figure 4.11b). Strip-type strain sensors were attached to fingers to monitor the changes in the real-time resistance during finger bending. The degree of relative resistance change showed a significant difference with and without CNC, and the CNC/PVP/PEDOT sensor presented a much higher value, about 55%, compared to 30 % for the PEDOT sensor. These results demonstrated that the addition of a cheap and sustainable CNC template enabled the fabrication of a highly sensitive strain sensor.

The PVA/Gly-CNC/PVP/PEDOT sensor also detected the step-by-step finger joint motion presented in Figure 4.11c. The resistance value of the sensor exhibited a gradual increase while bending the finger at a step-by-step angle, and the resistance value was constant without any change when the finger was maintained at a certain angle. In addition, subtle

human motion were also monitored by the sensor due to its high sensitivity and low modulus, which favored the detection of small skin deformations (Figure 4.12a–f). Depending on where the sensor was attached, it showed the effective real-time resistance change signals from face and body movements.

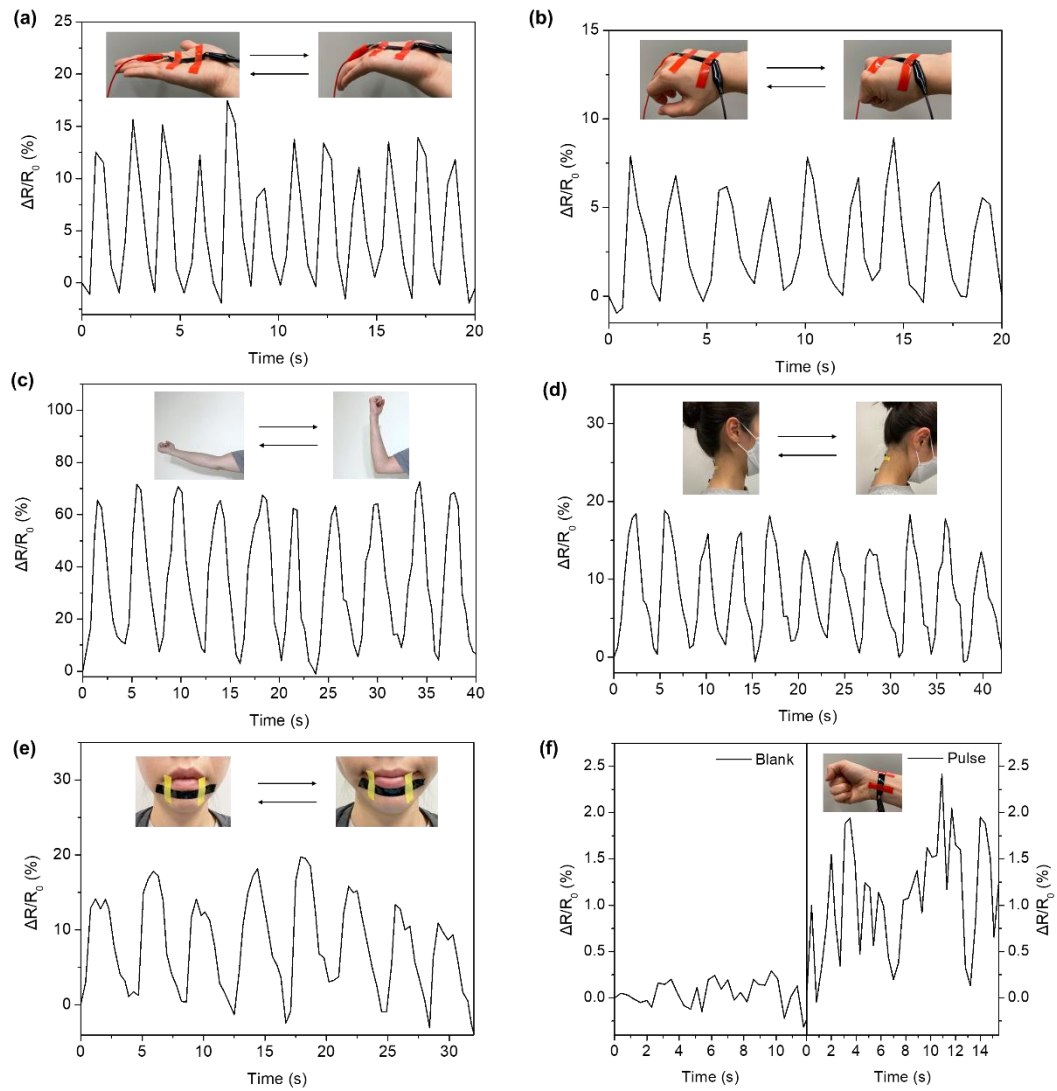


Figure 4.12 Real-time recording for (a) palm movement, (b) fist movement, (c) elbow, (d) neck, (e) smile, and (f) pulse beating.

The excellent sensitivity and stretchability were maintained after 3 months of film fabrication due to the remarkably stable glycerol plasticizer having extremely low vapor pressure compared to water (Figure 4.13a). Figure 4.13b summarizes the comparison of the gauge factor of PVA-based nanocomposite sensors. The graph shows that PVA/Gly-CNC/PVP/PEDOT has excellent stretchability with outstanding gauge factors even without using expensive conductive materials, such as graphene, carbon nanotubes, or silver.

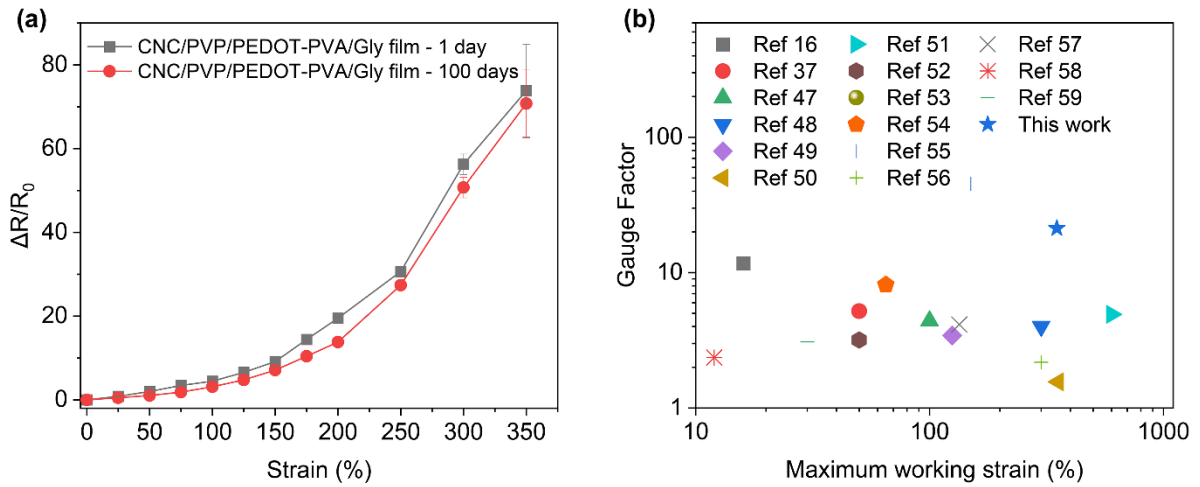


Figure 4.13 (a) The relative resistance responses of PVA/Gly-CNC/PVP/PEDOT after fabricating 100 days. (b) Comparison of reported maximum gauge factor of PVA-based nanocomposites as a function of applied strain. ^{325, 340, 352-364}

Noticeably, the stretchability of our sensor is just slightly below the values of hydrogels, but it shows significant durability during 200 cycles (Figure 4.14) and long-term sensitivity over several months, making it comparable or better than the hydrogel-based sensors.

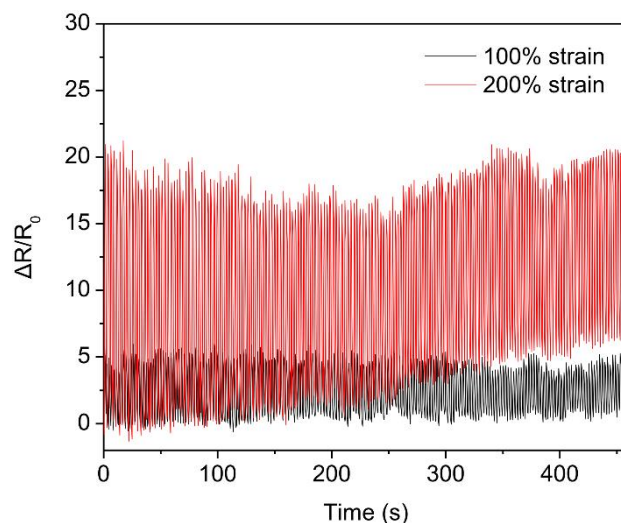


Figure 4.14 The relative resistance changes of PVA/Gly-CNC/PVPV/PEDOT sensor during 200 cycles of 100% and 200% strain.

The PVA/Gly-CNC/PVP/PEDOT also demonstrates an outstanding self-healing capability. Figure 4.15a illustrates the self-healing behavior of the sensor through the illuminance variation before and after healing. After cutting the sensor film, an LED bulb was turned off due to the open circuit. However, the sensor recovered its electrical performance within 30 min of the simple water-induced self-healing process, and the LED showed a bright light, proving the self-healing capability of PVA/Gly-CNC/PVP/PEDOT, which is attributed to the synergistic effect of abundant hydrogen bonding within PVA, glycerol, and CNC.^{142, 144, 332, 343, 350} The self-healed film slightly decreased but it still possessed excellent stretchability of about 400% (Figure 4.15b). It also exhibited stable and high sensitivity corresponding to around 80 % of its original relative resistance change during finger bending detection (Figure 4.15c). The slightly decreased relative resistance change could be originated from the higher

moisture content of the healed sensor after water-induced self-healing, and another possibility is some damaged conductive paths that could not be fully restored.

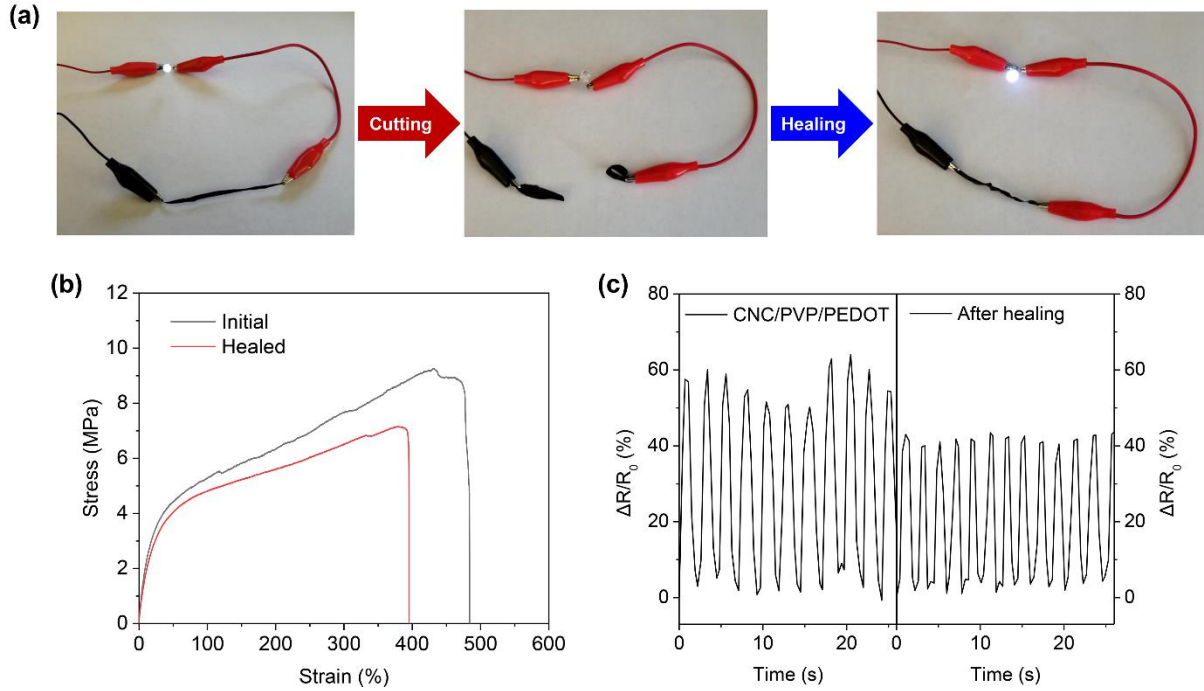


Figure 4.15 (a) Illuminance change of a LED bulb over the cutting/healing process. (b) Representative stress-strain curves of the sensor before/after self-healing. (c) Real-time response of relative resistance changes of the sensor for finger bending detection before/after self-healing.

The PVA/Gly-CNC/PVP/PEDOT aqueous solution with 5 wt% of PVA/Gly allows for facile processing; designed patterns could be made with a fountain pen, as shown in Figure 4.16. The patterns were easily written due to the moderate viscosity of the ink and dried within 30 min in ambient conditions, without the need for toxic solvents or chemicals.



Figure 4.16 The patterned PVA/Gly-CNC/PVPV/PEDOT through a fountain pen.

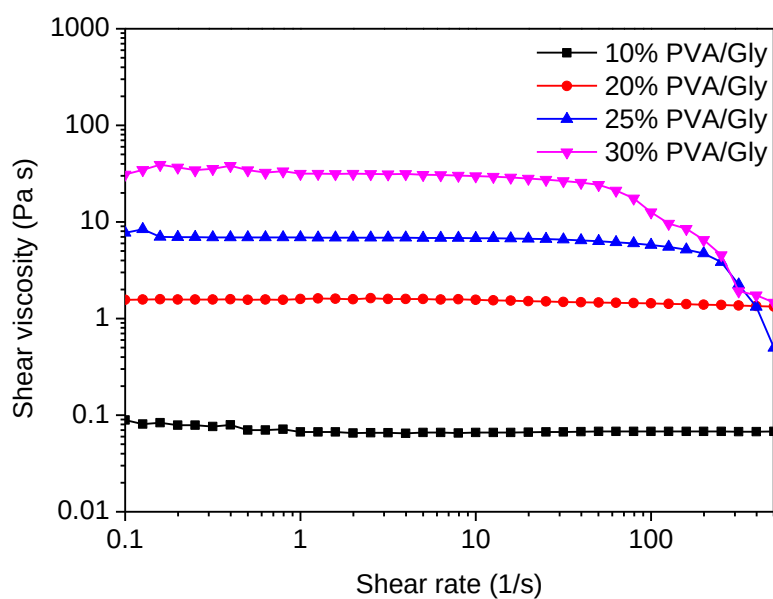


Figure 4.17 Shear viscosity of PVA solutions with the concentration of 10, 20, 25, 30 wt % of PVA as a function of shear rate.

An extrusion 3D printing technique was employed to fabricate more accurate and reproducible sensors. The ink for 3D printing required high viscosity, so the extruded ink maintained continuous ink extrusion and retained its shape after printing. Therefore, the rheological behavior of the PVA/Gly solution was first examined to determine the printable

ink condition for 3D printing. Figure 4.17 demonstrates the shear viscosity of the PVA solution of different PVA concentrations as a function of shear rates. The PVA solutions displayed a gradual increasing shear viscosity and shear-thinning behaviors at the high shear rate region with increasing PVA concentrations.

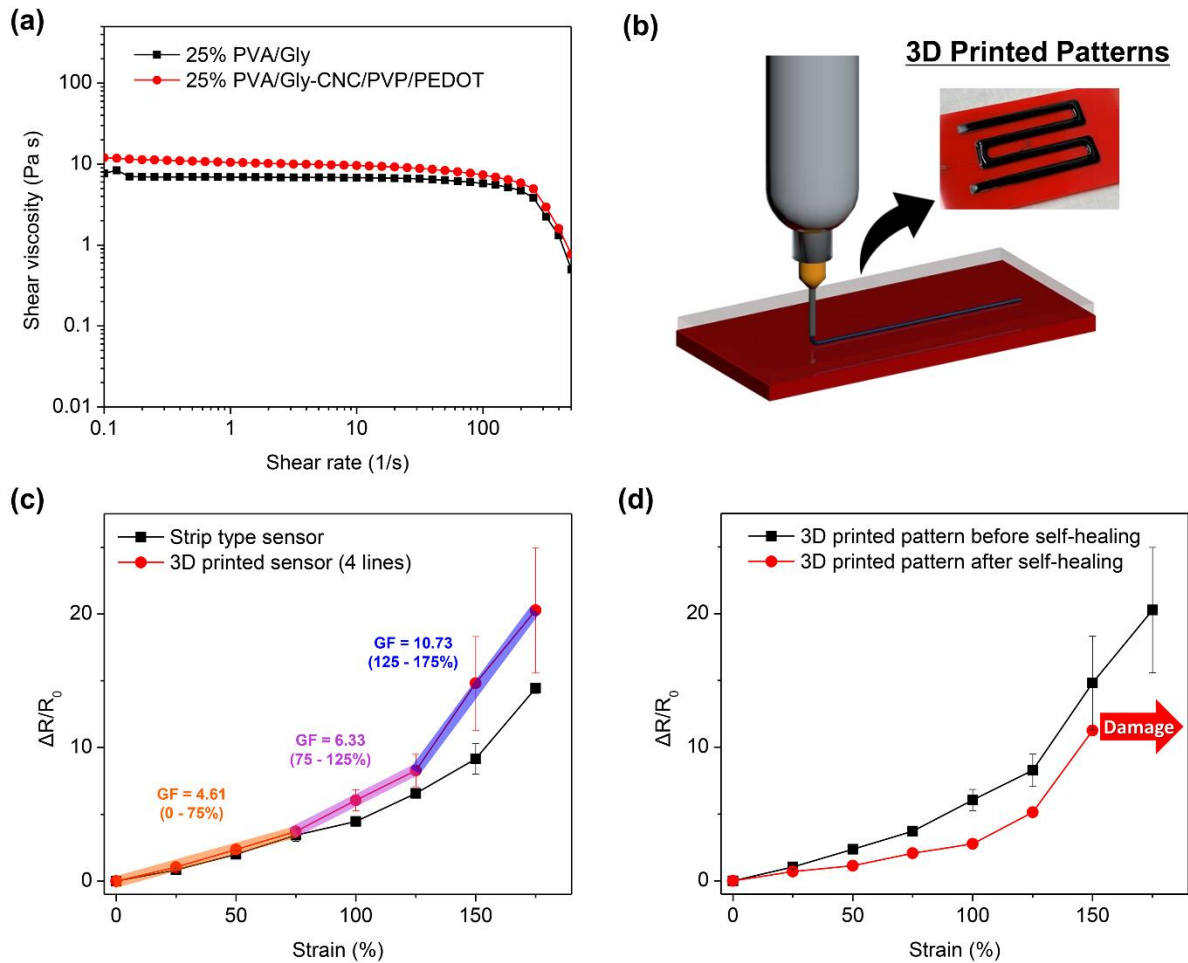


Figure 4.18 (a) Shear viscosity of PVA/Gly-CNC/PVP/PEDOT with 25 wt % of PVA/Gly as a function of shear rate. (b) Schematic illustration of a 3D printing process for 1 line and 4 line gauge sensor patterns. (c) Relative resistance responses of 3D printed PVA/Gly-CNC/PVP/PEDOT sensors. (d) Relative resistance responses of self-healed 3D printed PVA/Gly-CNC/PVP/PEDOT sensors.

The 25 wt% PVA/Gly concentration was chosen for 3D ink formulation due to its moderate viscosity leading to stable and continuous ink extrusion and high printing accuracy (Figure 4.18a). Below this concentration, the extruded ink from the nozzle formed droplets, and printed patterns showed poorly defined structure. The ink above this concentration was hardly extruded because of its high viscosity. The 25 wt % PVA/Gly containing PVA/Gly-CNC/PVP/PEDOT solution was prepared as a 3D ink solution for sensor fabrication, and it had similar shear viscosity to the 25% PVA/Gly solution but slightly increased shear-thinning behavior due to the high aspect ratio of CNC.^{365, 366} Figure 4.18b shows the fabrication process of typical strain gauge patterns on the stretchable substrate using the extrusion of 3D printing technique and printed sensors. 3M VHB 4905 double-sided tape was used as a substrate for the patterned sensors due to its high stretchability and good adhesion with the printed patterns (Figure 4.19). The PVA/Gly-CNC/PVP/PEDOT pattern shows a precisely printed structure with uniform width (2 mm) and height because concentrated PVA/Gly-CNC/PVP/PEDOT solution maintained a well-defined structure, and there was no bump or break of the line observed. The strain sensing capability of printed patterns was evaluated after the oven drying process.

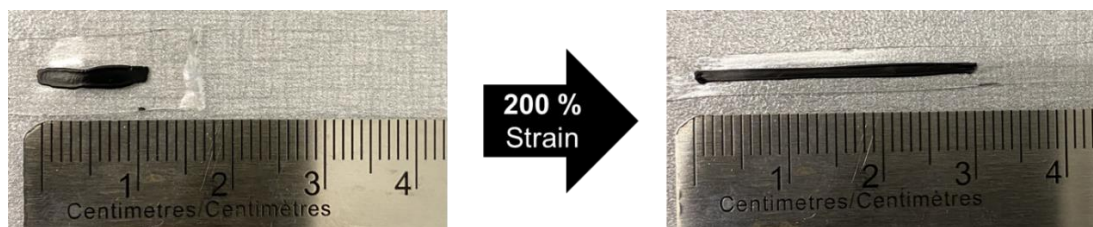


Figure 4.19 The picture of 3m VHB 4905 double side tape after removing protection film before/after 200 % strain with PVA/Gly-CNC/PVPV/PEDOT hand-written pattern.

Figure 4.18c shows the relative resistance change of printed sensors in the strain range between 0 % and 175 % because the substrate was damaged over this strain range. The four-lined printed pattern exhibited somewhat higher relative resistance change with a 10.73 (125 – 175 %) gauge factor compared to 8.84 (125 – 250 %) for the strip-type sensor. The improved sensitivity could be due to two reasons.

The first possible mechanism is that many grids for printed sensors experienced longer total strain under the same substrate strain than the simple strip-type sensor.³⁶⁷ The slightly lower relative resistance change of the single line pattern might imply this mechanism, as shown in Figure 4.20.

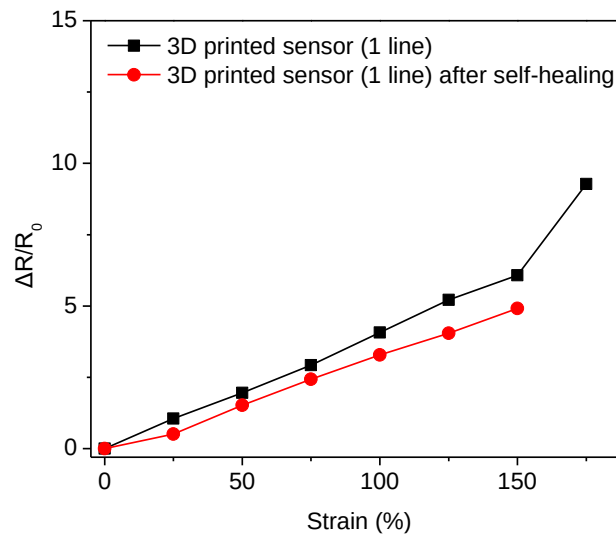


Figure 4.20 Relative resistance responses of 3D printed single-line patterned sensors.

Second, the induced alignment of the CNC/PVP/PEDOT conductive fillers within the printed matrix can affect the sensitivity change. When the ink was extruded through the nozzle during the printing process, the high aspect ratio of CNC/PVP/PEDOT results in the shear-thinning

behavior of ink originating from the CNC alignment under the shear stress.^{365, 368} The alignment of the anisotropic conductive filler within the matrix could significantly impact the sensitivity of the sensors depending on the direction of applied stress and strain.³⁶⁹⁻³⁷¹ Therefore, compared to the randomly oriented CNC/PVP/PEDOT in the solution casted strip sensor, the CNC/PVP/PEDOT within the printed pattern has a certain degree of orientation resulting in the changes in the sensitivity of the strain sensor.

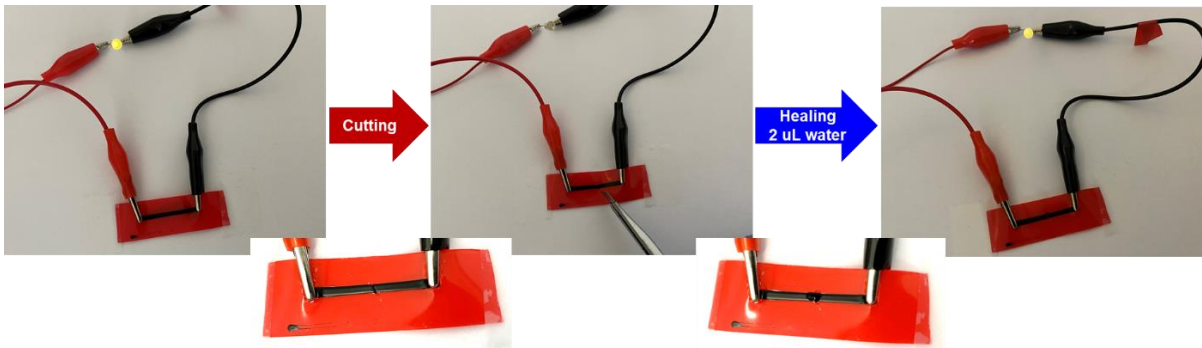


Figure 4.21 The illuminance changes of an LED bulb over cutting/healing process of printed pattern.

The printed CNC/PVP/PEDOT pattern displayed outstanding self-healing capability. Intentional damage was applied to the printed pattern using a knife, and the extinguishing of the light confirmed the short circuit (Figure 4.21). However, the sensor was easily self-healed by dropping 2 μ L of water onto the damaged region and waiting several minutes for it to dry. After the self-healing, the relative resistance changes of the sensor were decreased, but it still could effectively detect the deformation of the sensor until 150 % strain, as shown in Figure 4.18d. This outstanding printability and performance of the printed PVA/Gly-CNC/PVP/PEDOT sensor suggested its potentials for accurate, customized production and

mass production using a low amount of materials and zero waste. Also, the 3D printed sensors were thin enough to transfer the deformation of human skin to electrical signals without being cumbersome to the wearer.

4.4 Conclusions

In this study, we prepared a highly sensitive and stretchable strain sensor using CNC and glycerol plasticizer. PEDOT coated CNC was prepared via *in-situ* oxidative polymerization with a PVP interlayer to obtain conductive filler with a high aspect ratio. The prepared CNC/PVP/PEDOT was added to the PVA and glycerol mixture, and the strip-type sensor film was fabricated through facile solution casting. The PVA/Gly-CNC/PVP/PEDOT sensor film showed significantly high elongation up to 500 % at the fracture point, a low Young's modulus to 48.9 MPa, and a higher sensitivity of $GF = 21.25$ compared to the PVA/Gly-PEDOT ($GF = 9.35$). Thanks to its outstanding electrical and mechanical properties, the fabricated sensor monitored various human activities, such as finger bending and subtle muscle movement. Furthermore, the sensor composite exhibited excellent self-healing capability and maintained outstanding stretchability with sensitivity 3 months after fabrication. The observed superiorities of PVA/Gly-CNC/PVP/PEDOT are primarily attributed to (i) the 1-dimensional structure of the CNC template allowing composites to achieve high conductivity and excellent sensitivity with a lower amount of PEDOT (ii) the glycerol plasticizer increasing the PVA chain mobility rendering excellent stretchability of the sensor film (iii) the low vapor pressure of glycerol enabling the composite to maintain long-term outstanding performance.

Additionally, the sensor was also prepared by 3D printing after optimizing the ink viscosity to offer PVA/Gly-CNC/PVP/PEDOT facile production, suggesting that this unique material could be adapted to various fabrication methods. We believe this environmental-friendly and low-cost CNC and PVA/Gly derived sensor design strategy paving an effective pathway to the facile fabrication of highly stretchable conductive composite. The PVA/Gly-CNC/PVP/PEDOT sensor could be used in a wide range of applications, such as wearable devices, medical electronics, and soft robotics.

Chapter 5

Antimicrobial Copper Oxide Nanoparticle Coated Cellulose Nanocrystal for the Fabrication of Rapid Bacteria-killing Fabrics

Antibiotic resistance and pandemics that are confronting humanity pose a serious global health threat. Consequently, there is growing interest in developing novel antimicrobial systems that can be used to manage the health challenges brought about by bacteria and fungal infection. In this study, cuprous oxide (Cu_2O) nanoparticle-deposited cellulose nanocrystal (CNC) was synthesized for use as a highly effective, inexpensive, sustainable antimicrobial agent compared to the expensive conventional counterparts. The polyethylenimine was coated onto CNC, enabling the direct deposition of ultrafine copper (Cu) and Cu_2O nanoparticles and promoting its attachment to bacteria cells. The CNC/PEI/Cu and CNC/PEI/ Cu_2O were synthesized respectively by controlling the pH of the reaction, and CNC/PEI/ Cu_2O displayed better antimicrobial properties than CNC/PEI/Cu. The superior antibacterial CNC/PEI/ Cu_2O was successfully used to fabricate antibacterial fabrics through spray coating, with negligible loss of filtration or breathability performance. The prepared antibacterial fabric killed *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) within 3 and 10 min of treatment, respectively. This remarkable antibacterial performance of the modified fabric was maintained even after long-term storage under ambient conditions and repeated washing.

5.1 Introduction

The persistent effort of humanity to eradicate infectious diseases via the development of antibiotics, vaccination, and improvement in sanitation and hygiene has led to reduced morbidity and mortality. However, the recent COVID-19 pandemic was a painful reminder that infectious diseases are still posing a severe menace to global public health and the economy.

Since the discovery of penicillin, the first antibiotic in 1928, the standard approach to treat bacterial infections is antibiotics. However, the mutation of bacteria into more resistant strains has produced a host of drug-resistant bacterial infections that are becoming a global health threat.³⁷²⁻³⁷⁴ Antibiotic resistance-related infections cause severe illnesses worldwide, with over 14,000 deaths in Canada in 2018 alone that are linked to these infections.³⁷⁵ Furthermore, if the current rates of resistance are maintained, infections are expected to reach alarming proportions on a global scale by 2050, resulting in 10 million deaths every year—a higher mortality rate than cancer and diabetes.²⁰⁸ In this context, there is an urgent need to develop novel, alternative solutions to address the impending antibiotic resistance crisis.

Antimicrobial metal nanoparticles are emerging as attractive systems to address the drug-resistance problem. Human has used metals as antimicrobial agents throughout history.^{376, 377} The combination of the antimicrobial activity of metals and emerging nanotechnology enables metal nanoparticles as promising candidates to replace conventional antibiotics. Metal nanoparticles produce reactive oxygen species (ROS) and provide the specific localization of high metal ion concentration by continuously releasing its ions.^{219, 220,}

³⁷⁸ These ROS and released metal ions from the metal nanoparticles lead to damage of the bacterial cell membrane and the inactivation of essential biomolecules.^{219, 220, 379}

Copper (Cu) is a particularly promising metal due to its low cost, abundance, and extensive antimicrobial properties versus the more expensive noble metals. However, there is limited research on the antibacterial Cu nanoparticles compared to other metals as its lower standard redox potential complicates the synthesis of Cu nanoparticles.^{378, 380} Furthermore, even after synthesizing Cu nanoparticles, they could be readily oxidized to form undesirable oxidation states that reduce their antimicrobial activity.^{381, 382} Therefore, the synthesis and handling of Cu nanoparticles require more care and effort than synthesizing other metallic systems.

The antimicrobial activity of Cu is governed predominantly by its oxidation state. Although all forms of Cu and copper oxide nanoparticles are widely known to possess outstanding antimicrobial agents, the antimicrobial activity of Cu and cuprous oxide (Cu₂O) usually exceed that of cupric oxide (CuO) since CuO is fully oxidized and is thermodynamically stable under ambient conditions.³⁸¹⁻³⁸⁵ Regarding the antimicrobial activity of Cu and Cu₂O, some studies have demonstrated that the Cu₂O possessed comparable or better antimicrobial activity than pure Cu, and also silver, which is a well-known antimicrobial compound.^{381, 383, 386} The superior antimicrobial performance of Cu₂O could be due to the release of Cu⁺ exhibiting higher toxicity than Cu²⁺.³⁸⁶⁻³⁸⁸

Besides the oxidation state of Cu nanoparticles and their size are critical parameters governing their antimicrobial performance. The smaller metal nanoparticle has more potent antimicrobial effects due to the larger surface area to volume ratio.^{219, 389, 390} However, in terms of the inherent tendency of metal nanoparticles toward aggregation and agglomeration, smaller nanoparticles are more prone to aggregate to reduce the surface energy, resulting in a significant reduction in antimicrobial activity.^{172, 391-394} Therefore, the control of metal nanoparticle size and prevention of aggregation are critical strategies to prepare efficient antimicrobial metal nanoparticles.

Standard metal nanoparticle synthesis involves using large amount of capping agents to control the dispersity, size, and shape of metal nanoparticles. Although typical capping agents, such as cetyltrimethylammonium bromide (CTAB), citrates, polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG) commonly used to prepare stable and reproducible metal nanoparticle, are potentially toxic, non-biodegradable, and they reduce the anti-microbial performance due to the shielding effect. To address this challenge, natural biopolymers are being exploited as sustainable stabilizers to support the synthesis of stable metal nanoparticles.^{395, 396} Cellulose nanocrystal (CNC) is particularly promising among various biomass-derived materials because of its biodegradable and biocompatible nature and its earth abundance, industrial-scale production, large specific surface area, water-dispersibility, surface functional groups for versatile chemical modification.^{1, 7, 39}

In this study, we develop an efficient strategy to synthesize ultrafine Cu and Cu₂O nanoparticle-coated CNC with remarkable antimicrobial properties. The sustainable CNC

template surface was first coated with branched polyethylenimine (PEI) and the abundant amino groups could chelate with Cu ions and nanoparticles and promote the adhesion to the bacteria cell wall. Cu and Cu₂O nanoparticles were then deposited onto PEI-coated CNC (CNC/PEI) using a hydrazine reducing agent. The excellent antimicrobial activity of prepared Cu and Cu₂O nanoparticle-coated CNC was investigated on yeast cells, gram-positive and gram-negative bacteria. The prepared antibacterial agents were then coated onto fabrics using a simple spray coating process to fabricate antibacterial fabrics with rapid and durable bactericidal activity. The remarkable antibacterial performance of modified fabrics was evaluated in terms of time-dependent bactericidal effect, washing durability, and stability toward long-term storage under ambient conditions.

5.2 Experiments

5.2.1 Materials

Cellulose nanocrystal (CNC) was provided by CelluForce Inc. Branched polyethylenimine (PEI, average $M_w \sim 25,000$), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), and hydrazine hydrate (N_2H_4 50–60%) were purchased from Sigma-Aldrich and used as received. Cotton fabric ($104 \times 53 = 157$ Threads per inch) and polycotton fabric ($77 \times 59 = 136$ Threads per inch) were purchased from a retail store. Milli-Q grade ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) purified water was used to prepare all aqueous solutions.

5.2.2 Preparation of PEI-coated CNC (CNC/PEI)

The PEI coating procedure was conducted based on the protocol proposed by Lin *et al.*³⁹⁷ with minor modifications. A PEI aqueous solution (0.4 wt%, 100 mL) was slowly added to the CNC dispersion (0.2 wt%, 100 mL) under continuous stirred overnight to produce a homogeneous dispersion. To enhance electrostatic adsorption of PEI on the CNC surface, the pH of the mixture was adjusted with 1 M HCl solution to ~ 1.5 . The suspension was then purified by repeated ultrafiltration and dialysis.

5.2.3 Synthesis of Copper-Coated CNC (CNC/PEI/Cu)

In the typical synthesis process, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 mg) was dissolved in water (100 mL) to prepare the Cu solution. The NaOH solution (1 mM, 100 mL) was then slowly added

to the Cu solution, followed by the drop-wise addition of CNC/PEI dispersion (0.018%, 20 mL). Finally, the N_2H_4 solution was added rapidly to the mixture under vigorous stirring. The color of the resulting solution changed from light blue to reddish-brown, indicating the formation of Cu nanoparticles over time. The synthesized Cu nanoparticle-coated CNC (CNC/PEI/Cu) was concentrated via centrifugation. CNC/Cu and PEI/Cu were prepared using the same conditions in the absence of PEI and CNC, respectively.

5.2.4 Synthesis of Cuprous Oxide-Coated CNC (CNC/PEI/Cu₂O)

CNC/PEI/Cu₂O was synthesized under identical conditions in the absence of NaOH. The concentrated solution was stored at room temperature overnight, oxidizing and forming Cu₂O with a dark green color.

5.2.5 Fabrication of CNC/PEI/Cu₂O-Coated Fabrics

The CNC/PEI/Cu and CNC/PEI/Cu₂O dispersions were centrifuged to remove water and washed with ethanol. The washed products were then re-dispersed in ethanol with 0.5 wt% (w/v) concentration to prepare the ink for fabric modification. The fabrics for the pressure drop test (8 × 8 cm square), the modified zone inhibition test (5/8" diameter circle), and the time-kill test (1 × 1 cm square) were washed repeatedly with ethanol and dried overnight in a vacuum oven at room temperature. The prepared CNC/PEI/Cu and CNC/PEI/Cu₂O inks were evenly sprayed on each side of the cleaned fabrics and dried under ambient conditions. The dried modified fabrics were thoroughly rinsed with running water and dried in a vacuum oven overnight.

5.2.6 Characterization

The zeta potential was measured at 25 °C using a Zeta-Sizer (Malvern, Nano ZS90). Each sample was prepared as an aqueous dispersion via 10 minutes of sonication before the measurement. At least three measurements were conducted, and an average value with the standard error was reported.

The morphology of CNC, CNC/PEI, CNC/PEI/Cu, and CNC/PEI/Cu₂O were examined using a transmission electron microscope (TEM, CM10, Philips). The samples were prepared by placing 25 µL of suspension on a carbon-coated Cu grid and dried in a vacuum oven. Energy-dispersive X-ray spectroscopy (EDS) line scans information was collected in the TEM (JEOL JEM-F200) in order to examine and elucidate the CNC/PEI/Cu and CNC/PEI/Cu₂O, respectively.

X-ray diffraction (XRD) patterns were recorded using an X-ray diffraction instrument (D8-Advance, Bruker-AXS) with Cu K α radiation at a scan speed of 4° min⁻¹. The particle sizes of Cu and Cu₂O nanoparticles were calculated according to the Scherrer equation:^{398, 399}

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (5.1)$$

where D is the average width of the crystal size, K is the shape factor of 0.9, λ is the X-ray wavelength used for the measurement, β is the full width at half maximum (FWHM) of the peak, and θ is the Bragg angle.

A field emission scanning electron microscope (FE-SEM, SIGMA 300, Carl Zeiss) was used to examine the morphology of the fabrics and bacterial cells at an acceleration voltage of 5.0 kV. The bacterial cells were initially fixed using a glutaraldehyde solution, followed by dehydration in ethanol. Each sample was then coated with layers of platinum via the ion sputter coating prior to characterization (Sputter Coater 108auto, Cressington).

The amine content of the CNC/PEI was determined using the conductometric-potentiometric titration (Metrohm 809 Titrando auto-titrator, Switzerland). The pH of the CNC/PEI dispersion (0.1%, 40 mL) was adjusted to 3 and titrated with a 0.02 M NaOH solution (100 uL/min). The amine content was calculated according to Equation (5.2):

$$\text{Amine content (mmol/g)} = \frac{C(\text{NaOH}) \times V(\text{NaOH})}{m} \quad (5.2)$$

where C is the concentration of NaOH (mol/L), V is the volume of NaOH (L), and m is the weight of CNC/PEI (g) in the solution.

The copper(II) ion adsorption of CNC/PEI was determined using a Copper Ion Selective Electrode (Cu-ISE, Cole-Parmer). The concentrations of Cu^{2+} in the mixture solution of Cu^{2+} (16.66 ppm, 90 mL) and CNC/PEI (0.018%, 10mL) and control solution of Cu^{2+} (16.66 ppm, 90 mL) and Milli-Q water (10 mL) were measured, and the amount of adsorbed Cu was calculated based on the Equations (5.3):

$$\text{Copper(II) ion adsorption} = \frac{C(\text{Control}) - C(\text{Cu}^{2+} + \text{CNC/PEI})}{m} \quad (5.3)$$

where C is the copper(II) ion concentration of each solution (mmol/L) and m is the weight of CNC/PEI (g) in the solution.

The particle filtration efficiency and flow resistance of the fabrics were determined using a fractional efficiency filter tester (Automated Filter Tester 3160, TSI). For the test, neutralized NaCl particles of a known size were generated, and their penetrations across the test area of 25 cm² were measured at a preset face velocity (flow velocity). Particles with size 100, 300, and 700 nm were introduced at two different face velocities of 5 and 20 cm s⁻¹. Three replicate measurements were conducted, and the average values and standard error were reported.

5.2.7 Antimicrobial Test

The antifungal activities of CNC/PEI/Cu and CNC/PEI/Cu₂O were tested against yeast cells. Dry yeast (50 mg) and glucose (50 mg) were added to water (5 mL, pH 7.5) at 40 °C and stirred for 5 min to initiate the activation and respiration. The prepared CNC/PEI/Cu or CNC/PEI/Cu₂O dispersion was added to the yeast solution, and the extent of yeast respiration was measured from the volume of carbon dioxide generated over a 30 min period.

The antibacterial study was conducted against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria. Both bacteria were cultivated in Lysogeny broth (LB) nutritional broth at 37 °C for 20 h, then diluted with LB broth to a cell density of 10⁸ CFU mL⁻¹.

The broth dilution method was used to determine the minimum inhibitory concentration (MIC)—the lowest concentration at which the antibacterial agents prevent the visible growth of the bacterium. The prepared bacteria broths were treated with CNC/PEI/Cu and CNC/PEI/Cu₂O, respectively, in concentrations ranging from 5 to 160 ppm. The control sample was produced using the same methodology but with only pure bacteria broth. The solution mixture was incubated at 37 °C for 24 h under continuous shaking. The treated solutions were then serially diluted with phosphate-buffered saline (PBS) buffer and spread on the agar plates. The prepared plates were incubated for colony growth for 24 h at 37 °C, and the quantity of CFUs was manually counted.

A zone inhibition test was conducted to examine the antibacterial activity of modified fabrics. The bacteria broths (10^7 CFU mL⁻¹) were evenly spread on the agar plates, and the pristine fabrics and modified fabrics were placed on the prepared plates. These plates were incubated for 12 h at 37 °C to determine the bacteria growth-inhibition zone.

The time-dependent antibacterial activity of modified fabric was investigated using a time-kill test. The 30 µL bacteria solution (10^8 CFU mL⁻¹) was dropped and spread on the modified and pristine fabrics. The bacteria-treated fabrics were incubated in the 15 mL tube at 37 °C for different time intervals and then washed with 5 mL of PBS buffer with vigorous agitations via vortexing to detach the bacteria cells from the fabrics. The PBS washing solutions containing the bacteria cells were serially diluted and then transferred and spread on the agar plates, followed by 12 h of incubation at 37 °C. Two or three replicate experiments were conducted, where the error bars indicate standard deviations.

A washing durability test of modified fabric was conducted after 1, 5, 10, and 10 washing cycles. The prepared CNC/PEI/Cu₂O-coated polycottons were washed repeatedly using a detergent solution on a plate shaker (Titer Plate Shaker, Barnstead International, Lab-Line Instruments, Inc.) for 10 min, followed by rinsing with deionized (DI) water and drying.

5.3 Results and Discussion

Figure 5.1a illustrates the preparation process and synthesis of CNC/PEI/Cu and CNC/PEI/Cu₂O. Before the Cu reduction, CNC was initially coated with a biocompatible PEI polymer with abundant amine groups. PEI serves multiple functions in the synthesis of the antibacterial system. First, it provides the anchor sites for Cu ions and enables the deposition of small-sized Cu nanoparticles on the CNC surface and minimizes aggregation.^{380, 400, 401} Second, the positively charged PEI can promote the binding to bacteria cells that enhance the antibacterial activities since both the gram-positive and gram-negative bacterial membranes bear overall negative charges.^{219, 402-405} Another vital role of PEI is its excellent adhesive property enabling CNC/PEI/Cu and CNC/PEI/Cu₂O to be coated on the targeted surface, including fabrics.⁴⁰⁶⁻⁴⁰⁸ The PEI was electrostatically coated onto individual CNC surfaces to exploit its superior, versatile properties, and excess PEI in the bulk solution was removed by repeated purification. The successful PEI coating on CNC was confirmed from the zeta potential analysis and TEM micrographs.

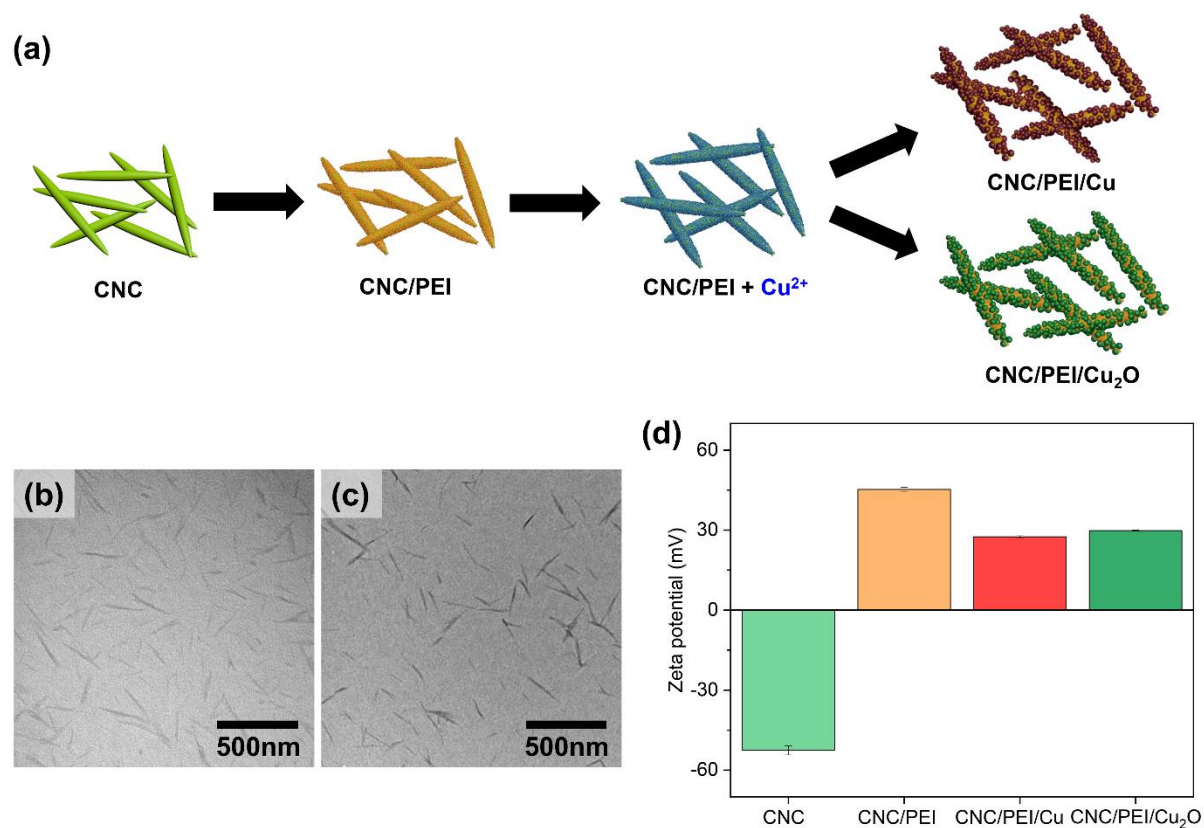


Figure 5.1 (a) Schematic of CNC/PEI/Cu and CNC/PEI/Cu₂O preparation process. TEM images of (b) pristine CNC, (c) CNC/PEI. (d) Zeta potential of CNC, CNC/PEI, CNC/PEI/Cu, and CNC/PEI/Cu₂O.

The TEM image of CNC/PEI revealed typical rod-shaped CNC particles, with slightly darker contrast than pristine CNC in the absence of staining. This confirmed the successful PEI adsorption, as depicted in Figures 5.1b–c. The zeta potential measurements provided further evidence of PEI coating on CNC. After the adsorption of PEI on the CNC surface, the zeta potential increased significantly, from -52.6 ± 1.7 mV to $+45.3 \pm 0.7$ mV, due to the abundant amine groups on the PEI chains (Figure 5.1d).

Chelation of Cu ions with CNC/PEI is crucial for the synthesis of Cu nanoparticle-coated CNC because the amine groups on the PEI chains could capture the Cu ions and the Cu nanoparticles could be selectively deposited onto the CNC surface rather than the bulk solution. The chelation capability of CNC/PEI was examined using the conductometric-potentiometric titration and copper(II) ion concentration measurements.

Figure 5.2a shows the titration results of CNC/PEI, where the quantity of amine groups of CNC/PEI was determined to be 5.85 mmol/g with a primary:secondary:tertiary amine groups molar ratio of 1:2:1. When the CNC/PEI with abundant amine groups was added to the Cu solution, 0.104 mmol Cu ions were adsorbed by 3.37 mg CNC/PEI (Figure 5.2b). The change in the copper(II) ion concentration before and after the addition of CNC/PEI revealed that almost half of the copper(II) ion in the Cu solution was bound to CNC/PEI, indicating the strong chelation capability of CNC/PEI toward Cu ions.

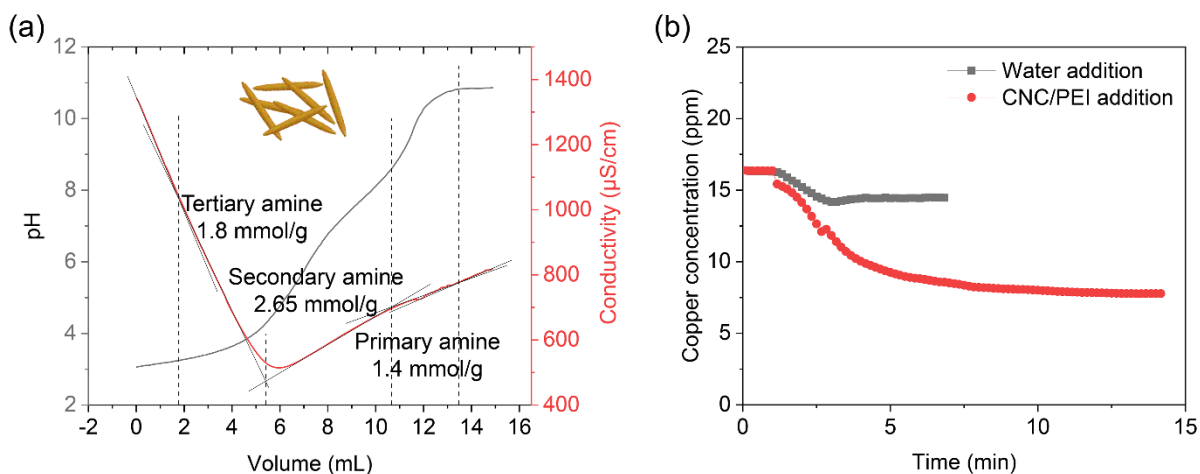


Figure 5.2 (a) Conductometric-potentiometric titration curve of CNC/PEI, and (b) concentration of Cu (II) ions after water or CNC/PEI solution addition at 1 min.

After the Cu ion adsorption to CNC/PEI, the N_2H_4 reducing agent was added to synthesize Cu nanoparticles coated onto the CNC/PEI surface. Figures 5.3a and 5.3b illustrate the morphology of the resultant CNC/PEI/Cu and CNC/PEI/Cu₂O, respectively. The TEM images revealed that Cu nanoparticles under 10 nm were well-deposited onto the CNC/PEI surface in both CNC/PEI/Cu and CNC/PEI/Cu₂O systems. However, the Cu nanoparticles synthesized under the same condition in the absence of CNC or PEI possessed a non-uniform and larger particle size of up to 200 nm (Figure 5.4). These results suggested that the prepared CNC/PEI template controlled the nucleation and growth of Cu nanoparticles and reduced the aggregation, resulting in well-controlled Cu nanoparticle deposition onto the CNC/PEI surface, which would be advantageous for antimicrobial applications. Based on these results, CNC/PEI/Cu and CNC/PEI/Cu₂O were selected for further experiments since the antimicrobial activity of metal nanoparticles relies on size, and a smaller size renders higher antimicrobial performance.

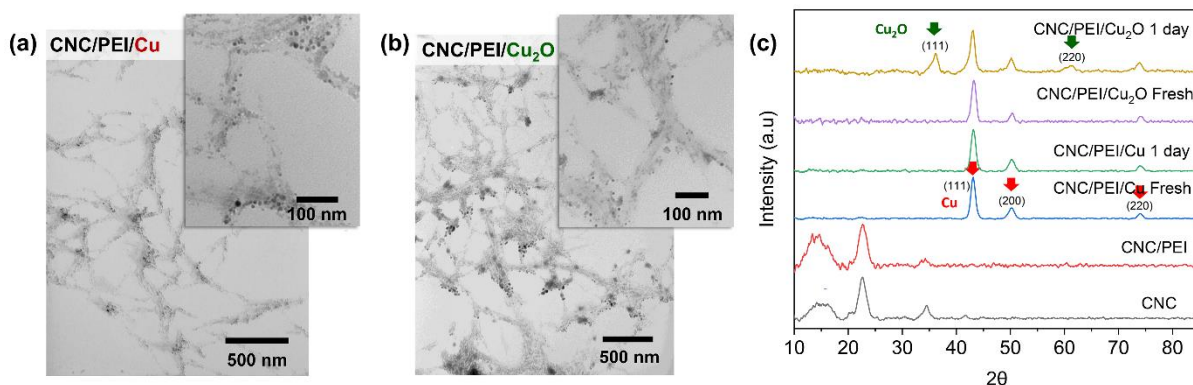


Figure 5.3 TEM images of (a) CNC/PEI/Cu and (b) CNC/PEI/Cu₂O. (c) XRD pattern of pristine CNC, CNC/PEI, CNC/PEI/Cu, and CNC/PEI/Cu₂O before/after aging.

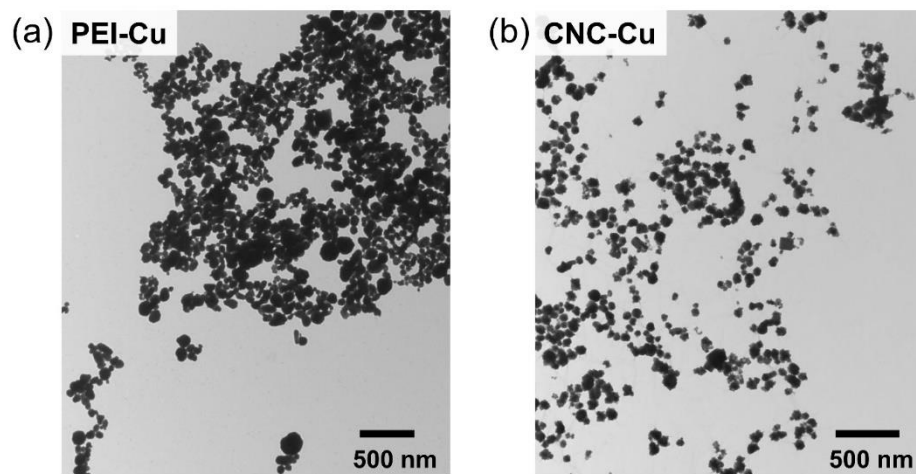


Figure 5.4 TEM images of synthesized copper nanoparticles in the absence of (a) CNC and (b) PEI.

The oxidation states of Cu nanoparticles were controlled by NaOH addition to the reaction solution. It is known that the resulting oxidation state of metal nanoparticles could be governed by the pH of the reaction condition.^{409, 410} When the Cu nanoparticle was synthesized with NaOH at pH 7.1, no further oxidation occurred; it maintained its reddish-brown color for several days. However, the Cu nanoparticle synthesized without NaOH at lower pH conditions (pH 4.6) changed color noticeably from reddish-brown to reddish-green during centrifugation; it gradually became dark green after 1 day of aging at room temperature. This color change represents a clear evidence of the oxidation of the outer layer of Cu nanoparticle when exposed to air; this dark green color is consistent with the intrinsic color of a Cu/Cu₂O core/shell particle.^{384, 411, 412} The dark green color of the resultant CNC/PEI/Cu₂O solution persisted for more than one week under ambient conditions and a month in the fridge as the surface oxide layer prevented further oxidation.⁴¹²

The oxidation states of prepared CNC/PEI/Cu and CNC/PEI/Cu₂O were further confirmed by an EDS line scan and XRD analysis. Figures 5.5a and 5.5d illustrate the STEM images of CNC/PEI/Cu and CNC/PEI/Cu₂O, with the scanning path represented as a yellow line. From the EDS line scanning spectra of Cu and O, as depicted in Figures 5.5b–c and 5.5e–f, strong O signals appeared only for the CNC/PEI/Cu₂O, indicating the presence of Cu₂O rather than pure Cu.

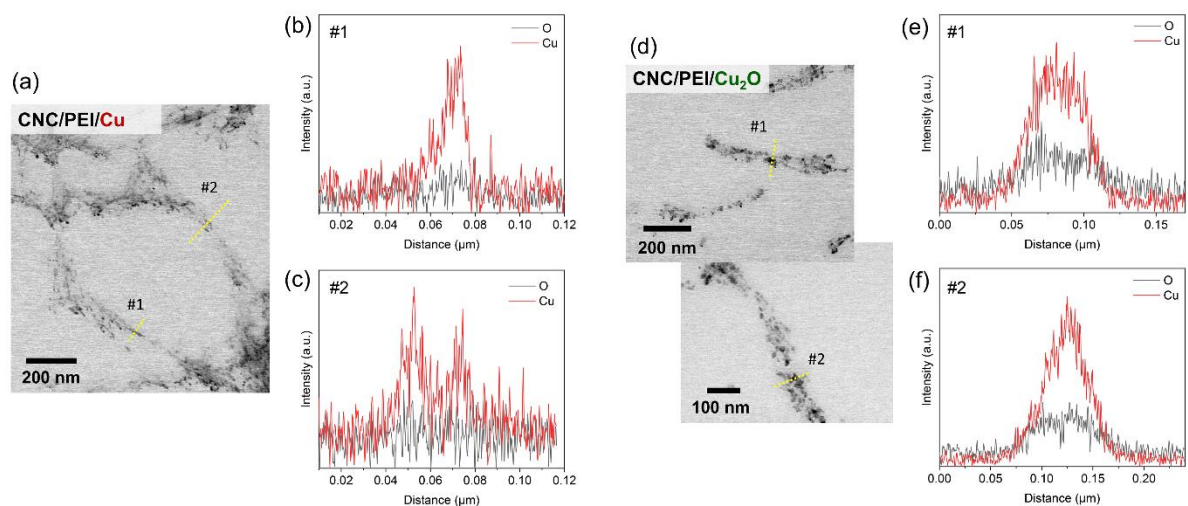


Figure 5.5 STEM images and EDS line scanning spectra of (a - c) CNC/PEI/Cu and (d - f) CNC/PEI/Cu₂O.

The XRD patterns in Figure 5.3c revealed the peaks for CNC and CNC/PEI corresponding to the typical crystallographic planes of cellulose I at $2\theta = 14.2^\circ$, 16.2° , 22.5° , and 34.6° .^{413, 414} Just after the Cu nanoparticle deposition onto CNC/PEI, both CNC/PEI/Cu and CNC/PEI/Cu₂O displayed peaks at 43.0° , 50.4° , and 74.1° , which are assigned to the (111), (200), and (220) crystal planes of Cu nanoparticles respectively. In terms of CNC/PEI/Cu₂O, it exhibited new distinct peaks at 36.2° and 61.0° , corresponding to the diffractions from the

(111) and (220) Cu_2O planes due to the oxidization of pure Cu to Cu_2O nanoparticles after 1-day aging. In contrast, no further oxidation occurred for CNC/PEI/Cu. The XRD patterns of both Cu and Cu_2O nanoparticles displayed broad Bragg peaks due to their small size, and the average Cu and Cu_2O crystallite sizes calculated using the Scherrer equation were 7.2 ± 0.3 nm and 7.5 ± 0.5 nm, respectively. These results closely matched those obtained from the TEM images.

The prepared CNC/PEI/Cu and CNC/PEI/ Cu_2O exhibited adequate positive zeta-potentials of $+27.5 \pm 0.4$ mV and $+29.8 \pm 0.2$ mV (Figure 5.1d) and excellent dispersity of more than 5 h, as depicted in Figure 5.6. Given that the positively charged antibacterial metal nanoparticles are advantageous in disrupting the bacteria membrane, the surface charges of CNC/PEI/Cu and CNC/PEI/ Cu_2O with ultrafine Cu and Cu_2O nanoparticles are expected to enhance antimicrobial activity and ensure these systems are promising antimicrobial agents.^{202,}

220



Figure 5.6 Aqueous suspension stability of (left) CNC/PEI/Cu and (right) CNC/PEI/ Cu_2O over 5 h.

The antimicrobial activity of CNC/PEI/Cu and CNC/PEI/ Cu_2O was initially tested against *Saccharomyces cerevisiae* (*S. cerevisiae*) yeast, a single-celled fungus microorganism.

The amount of CO₂ produced during the respiration of yeast was measured and used as the criteria to assess the viability of the yeast cell. Figure 5.7a illustrates the reduction in the rate of CO₂ generation with increasing amounts of CNC/PEI/Cu, where there was a 99.3% reduction in respiration when the yeast was treated with 200 ppm of CNC/PEI/Cu. Interestingly, the inhibition activity of CNC/PEI/Cu₂O in yeast cell respiration was more effective than CNC/PEI/Cu. Exposure of only 100 ppm of CNC/PEI/Cu₂O to yeast cells led to 100% respiratory inhibition (Figure 5.7b). This superior antimicrobial performance of CNC/PEI/Cu₂O was further observed in comparing the CO₂ generation rate as depicted in Figure 5.8 and Video “Movie5-1. The CO₂ generation rate during the respiration of yeast treated with CNC/PEI/Cu₂O.mp4” in Appendix B. In contrast, the CNC/PEI template did not impact the normal respiration of yeast cells.

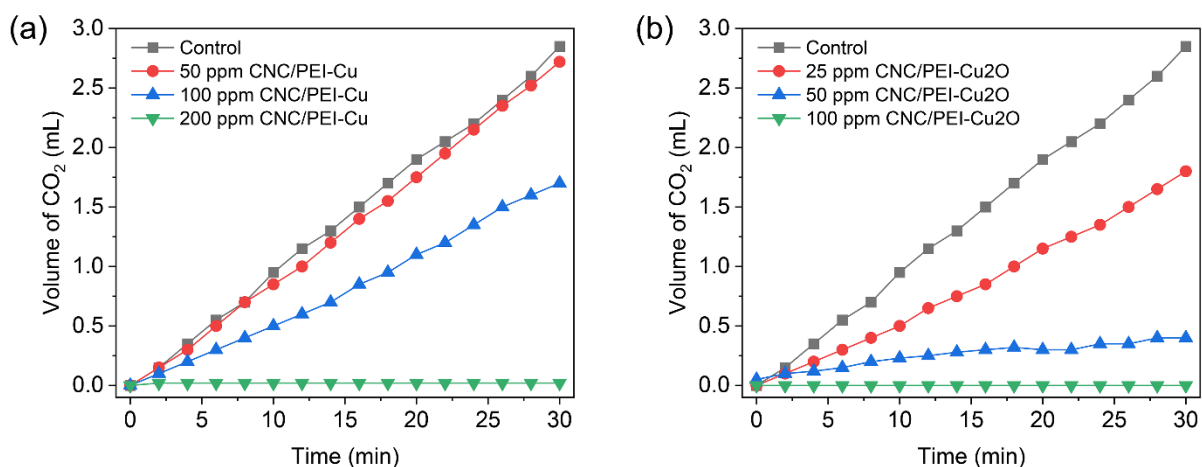


Figure 5.7 Antimicrobial activity of CNC/PEI/Cu and CNC/PEI/Cu₂O based on the rate of CO₂ production as a byproduct of yeast respiration.

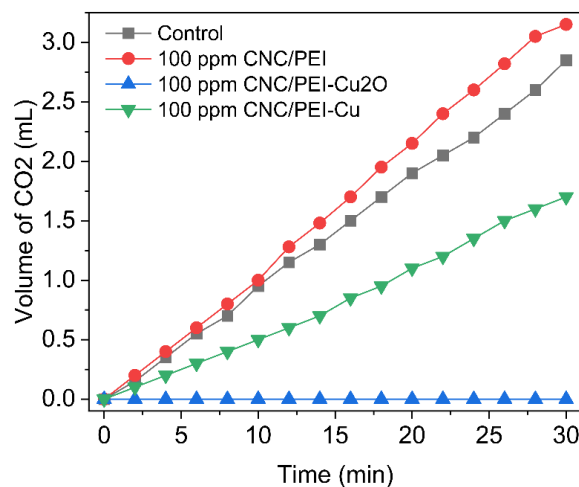


Figure 5.8 Antimicrobial activity of CNC/PEI, CNC/PEI/Cu, and CNC/PEI/Cu₂O 100 ppm evaluated by measuring the rate of CO₂ production as a byproduct of yeast respiration.

The antibacterial test of CNC/PEI/Cu and CNC/PEI/Cu₂O against gram-negative *E. coli* and gram-positive *S. aureus* bacterial cells demonstrated similar results. Figure 5.9 illustrates the comparative percentages of survival of bacterial cultures after incubating with CNC/PEI/Cu and CNC/PEI/Cu₂O. For both bacteria, the bacterial viability decreased with the increase in CNC/PEI/Cu and CNC/PEI/Cu₂O concentration, and CNC/PEI/Cu₂O displayed higher bactericidal efficiency than CNC/PEI/Cu. Although the bacteria colony was not entirely eliminated within the concentration range of CNC/PEI/Cu, the CNC/PEI/Cu₂O treated bacteria exhibited 0% bacterial viability with an MIC of 40–80 ppm against *E. coli* and 80–160 ppm toward *S. aureus*. This result could be explained by the higher toxicity of Cu⁺, which is the primary ion released from Cu₂O. Cu⁺ could penetrate more readily into the cytoplasmic membrane due to its higher avidity for sulfhydryls in proteins compared to Cu²⁺.^{195, 381, 386-388,}

⁴¹⁵ The antibacterial performance of CNC/PEI/Cu₂O was especially remarkable toward the *E.*

coli, with 93.7% of cells killed in the presence of trace amounts of CNC/PEI/Cu₂O (5 ppm). This was attributed to the structural differences between gram-negative and gram-positive bacterial cells, and gram-negative bacteria are usually less resistant to metal nanoparticles than gram-positive bacteria.^{219, 220}

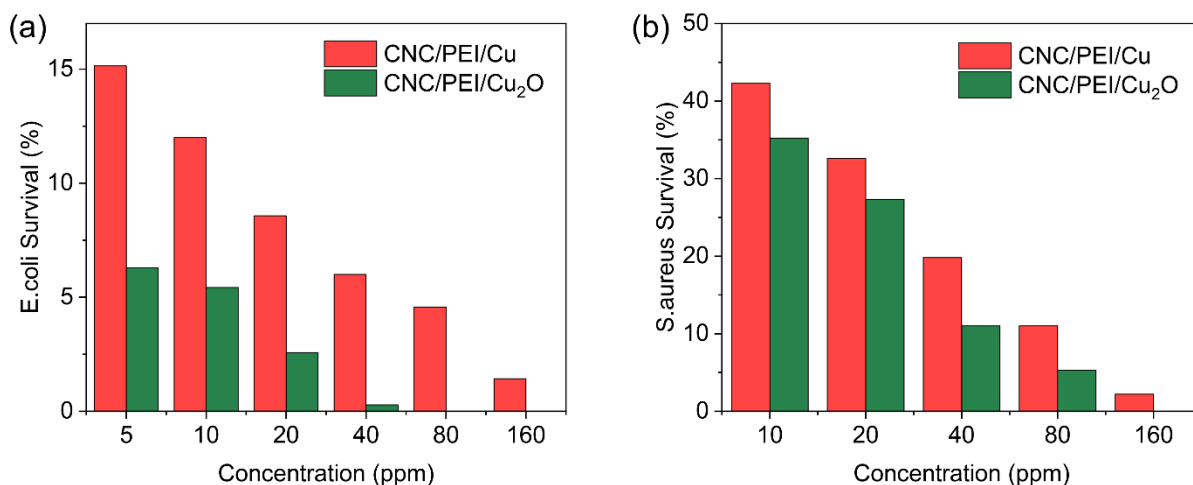


Figure 5.9 Antibacterial effects of CNC/PEI/Cu and CNC/PEI/Cu₂O after 24 h treatment against (a) *E. coli* and (b) *S. aureus*.

The CNC/PEI template was also tested to confirm that the extraordinary bactericidal activities were caused primarily by the Cu and Cu₂O nanoparticles, not CNC/PEI template. As depicted in Figure 5.10, even at the very high concentration of CNC/PEI (160 ppm), it exhibited poor antibacterial performance toward either *E. coli* or *S. aureus*, with 76.6% and 80.6% survival percentages, respectively. Due to its superior antimicrobial performance, CNC/PEI/Cu₂O was selected for the fabrication of antibacterial fabrics.

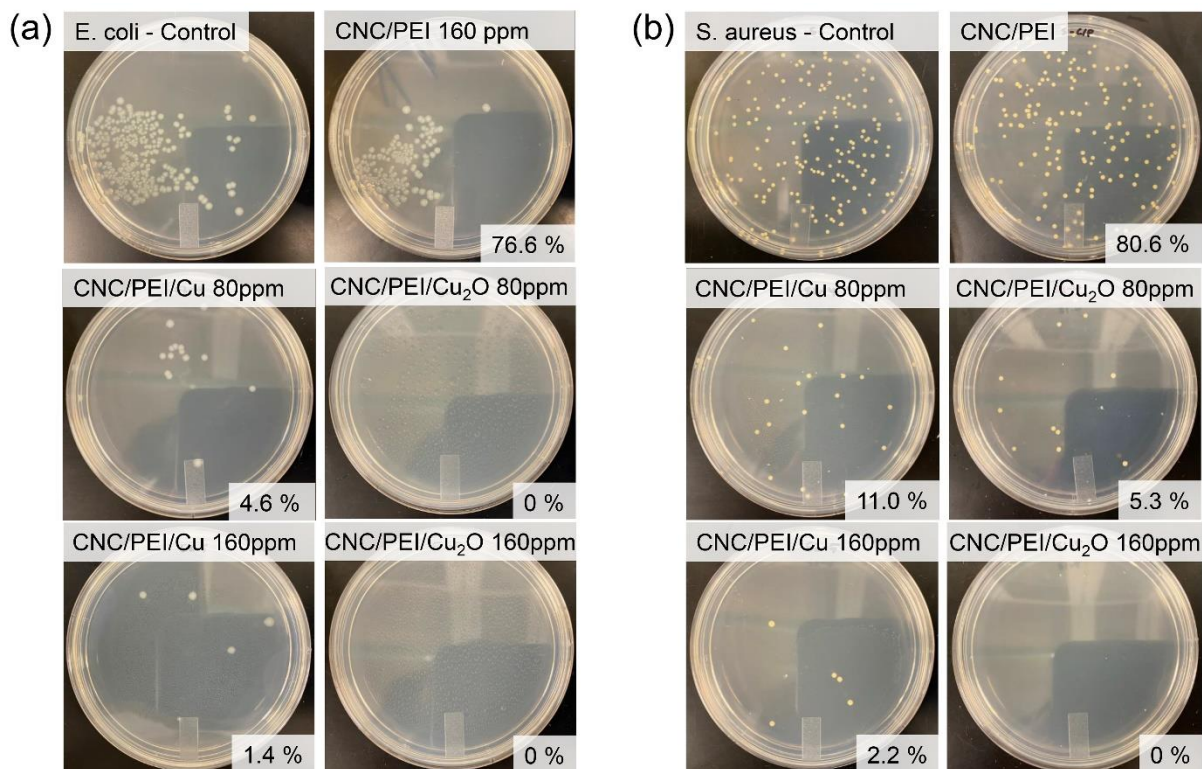


Figure 5.10 Digital photographs of (a) *E. coli* and (b) *S. aureus*. colonies grown on agar plates after treated with CNC/PEI, CNC/PEI/Cu, and CNC/PEI/Cu₂O.

A simple spray coating method was used to fabricate CNC/PEI/Cu₂O modified fabrics. A CNC/PEI/Cu₂O ethanol dispersion of 0.5 wt% (w/v) was sprayed onto polycotton and cotton fabrics, followed by drying under ambient conditions. Distinct visible color changes in the polycotton and cotton fabrics were observed in the digital photographs. Figures 5.11a and 4.11h show that the pristine fabrics were in white color, and they became dark green after modification with CNC/PEI/Cu₂O (Figure 5.11d and 5.11k).

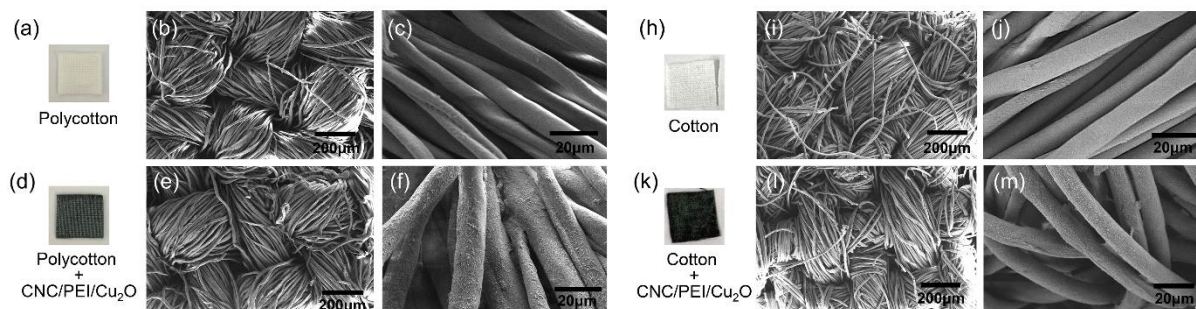


Figure 5.11 Digital photographs of (a) pristine polycotton, (d) CNC/PEI/Cu₂O-modified polycotton, (h) pristine cotton, and (k) CNC/PEI/Cu₂O-modified cotton. SEM images of (b, c) pristine polycotton, (e, f) CNC/PEI/Cu₂O-modified polycotton, (i, j) pristine cotton, and (l, m) CNC/PEI/Cu₂O-modified cotton.

The SEM analysis also revealed the successful deposition of CNC/PEI/Cu₂O onto fabric based on the surface morphology analysis. Both pristine polycotton and cotton revealed the assembly of threads woven into the fabric, as presented in Figures 5.11b-c and 5.11i-j. The high magnification images of individual threads (Figures 5.11e-f and 5.11l-m) confirmed the successful deposition of CNC/PEI/Cu₂O as revealed by the increased surface roughness after the modification maintaining its original structure without blocking of the pores (Figures 5.11e and 5.11l). It is worth noting that once the CNC/PEI/Cu₂O was coated onto the fabrics, they bound strongly to both fabrics, which remained stable on the threads even after rinsing with water to wash away the CNC/PEI/Cu₂O that were not bound to the fabric. The stable CNC/PEI/Cu₂O deposition could stem from the PEI acting as an adhesive and the electrostatic interaction between the positively charged CNC/PEI/Cu₂O and negatively charged polycotton and cotton fibers.^{406, 408, 416-418}

The change in the particle filtration efficiency and flow resistance of fabrics were examined to ensure it did not compromise the properties of the fabric after the coating with CNC/PEI/Cu₂O, confirming that we could extend its potential application to fabricating a personal protective mask. The filtration efficiency is the most critical feature describing the percentage of particles that would be filtered by the fabric, where it was evaluated using a specific particle size impacting on the fabric at a preset flow velocity. The mask's flow resistance is also a critical characteristic since it represents how the breathing air passes through the mask. The filtration efficiency and flow resistance are based on different mechanisms, where in most cases, a trade-off is required. Therefore, it is desirable that the CNC/PEI/Cu₂O coating only imparts an antibacterial role to the existing mask without affecting its physical properties.

The test was conducted using neutralized NaCl particles of three sizes (100, 300, and 700 nm) subjected to face velocities ranging from 5 and 20 cm s⁻¹. As presented in Table 4-1, there was no significant difference before and after the CNC/PEI/Cu₂O modification in terms of filtration efficiency and flow resistance of both polycotton and cotton fabric. This result implied that the CNC/PEI/Cu₂O coating could be effectively applied to the fabrication of antibacterial masks without losing the original performance of pristine filter fabrics.

Table 4-1 Filtration efficiency and flow resistance of fabrics under face velocities of 5 and 20 cm s⁻¹ Error bars represent standard error.

Particle size	Face velocity 5 cm s ⁻¹			
	Filtration Efficiency (%)			Resistance (mm H ₂ O)
	100 nm	300 nm	700 nm	
Polycotton	9.45 ± 0.12	3.17 ± 0.67	2.52 ± 0.44	1.07 ± 0.03
Modified polycotton	9.25 ± 0.18	3.74 ± 0.63	2.51 ± 0.54	1.11 ± 0.04
Cotton	13.33 ± 0.64	5.90 ± 1.35	6.61 ± 1.00	2.30 ± 0.04
Modified cotton	13.40 ± 0.92	6.24 ± 1.13	7.25 ± 1.11	2.28 ± 0.03
Particle size	Face velocity 20 cm s ⁻¹			
	Filtration Efficiency (%)			Resistance (mm H ₂ O)
	100 nm	300 nm	700 nm	
Polycotton	2.29 ± 0.50	3.53 ± 1.00	2.99 ± 0.22	4.85 ± 0.16
Modified polycotton	2.61 ± 0.62	4.62 ± 1.30	3.61 ± 0.45	4.92 ± 0.17
Cotton	6.98 ± 0.24	3.33 ± 0.83	14.15 ± 0.75	10.50 ± 0.12
Modified cotton	6.95 ± 0.70	4.88 ± 1.41	14.82 ± 0.49	10.46 ± 0.13

The antibacterial activity of CNC/PEI/Cu₂O-modified fabric was first tested using a zone of inhibition test against *E. coli* and *S. aureus*. As depicted in Figures 5.12a and 5.12b, the modified fabrics produced bacteria growth inhibition rings around the fabrics, indicating an excellent antibacterial performance. The distinct inhibition area, contacting with the modified fabrics, suggested that bacteria growth was effectively suppressed by contacts between the bacteria cells and Cu₂O nanoparticles. The bacteria growth near the modified fabric was also effectively inhibited due to the fast Cu ion released from the nanoparticle to the surroundings.³⁷⁸

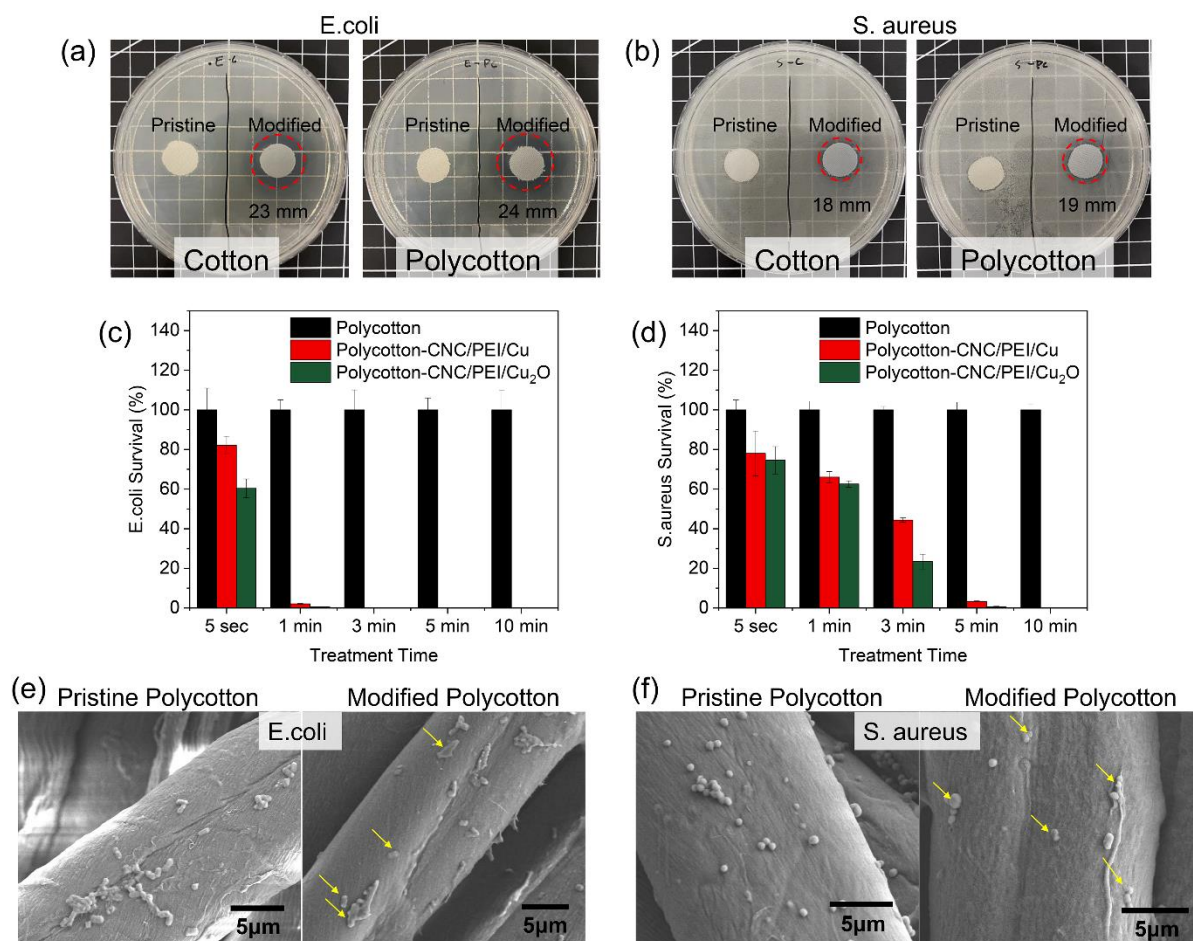


Figure 5.12 Antibacterial activity of fabrics. Inhibition zones against (a) *E. coli* and (b) *S. aureus*. Survival of (c) *E. coli* and (d) *S. aureus* was quantitatively determined by counting colonies. SEM images of (e) *E. coli* and (f) *S. aureus* treated with pristine and modified fabrics, respectively.

Time-kill test was conducted against *E. coli* and *S. aureus* to study the kinetics of antibacterial activities of the modified fabrics. In realistic situations, common infections occurred when viruses or bacteria were spread by droplets transmission. Therefore, an antimicrobial fabric must have fast inhibitory and bactericidal performance at the early stage of droplet contact with its surface to effectively prevent the transmission of infectious diseases.

Modified polycotton was selected as an antibacterial fabric to test the kinetics of bactericidal activities because polycotton is one of the representative fabrics for personal protective equipment (PPE) fabrication. The CNC/PEI/Cu modified fabric was also prepared using the same ink preparation and spraying method, and its antibacterial properties were tested simultaneously with the CNC/PEI/Cu₂O modified fabric to compare their antibacterial performance under practical conditions.

Figures 5.12c and 5.12d show the time-dependent antibacterial activity of modified fabrics against *E. coli* and *S. aureus*. Although the pristine polycotton did not reveal any reduction in the bacteria survival rate over a 10 min period, CNC/PEI/Cu and CNC/PEI/Cu₂O rapidly eliminated the *E. coli* within 3 min and *S. aureus* within 10 min. This fast and superior antibacterial activity of the modified fabrics was comparable to or outperformed the expensive silver nanoparticle modified fabrics, despite our system using a low-cost CNC and Cu nanoparticles with simple fabrication methods.^{419, 420} The higher bacterial reduction rate of CNC/PEI/Cu₂O agreed with the previous antimicrobial test results using the yeast and broth dilution method and further confirmed its excellent antibacterial activity.

The morphology of bacterial cells was analyzed using SEM to investigate the antibacterial activity of the CNC/PEI/Cu₂O modified fabric (Figures 5.12e and 5.12f). Both *E. coli* and *S. aureus* cells on pristine polycotton remained plump, smooth, and intact shape, similar to the regular and healthy bacteria membrane. However, after being treated with CNC/PEI/Cu₂O-coated fabric, clear evidence of bacterial membrane deformation and disruption were observed as observed from the flattened and distorted bacteria cell surface.

These morphological features of the damaged bacteria membrane confirmed the outstanding antibacterial activity of CNC/PEI/Cu₂O, causing a loss of cellular integrity and leakage.

For practical applications, the stability and durability of antibacterial fabrics for long-term storage and repeated washing are essential aspects to consider in fabricating reusable products. Therefore, the stability and durability of CNC/PEI/Cu₂O-coated polycotton's antibacterial properties were evaluated by monitoring the bacteria reduction rate. Figure 5.13a shows the antibacterial activity of CNC/PEI/Cu₂O-coated polycotton before and after storage for 30 days under ambient conditions. The previously tested rapid and remarkable antibacterial activity of modified fabric was maintained even after the 30 days of storage, with no bacterial colony after treatment for 3 min for *E. coli* and 10 min for *S. aureus*.

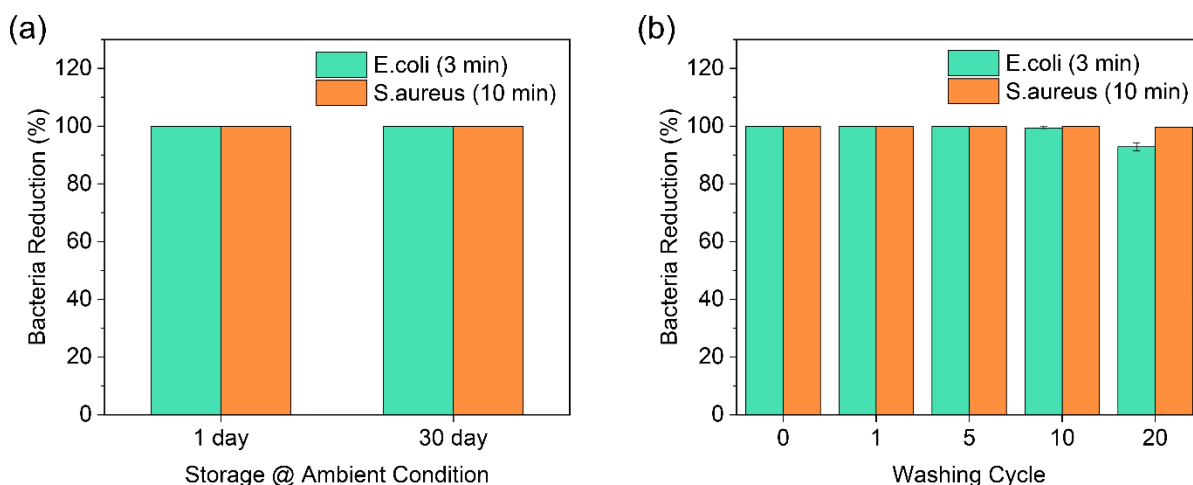


Figure 5.13 Antibacterial performance of CNC/PEI/Cu₂O modified polycotton (a) after one-month storage under ambient conditions and (b) after repeated washing.

The excellent washing durability of the prepared CNC/PEI/Cu₂O-coated polycotton is shown in Figure 5.13b. There was no observed deterioration in the antibacterial rate until after

five washing cycles, with high inactivation efficiencies of 92.9% and 99.6% within only 3 min and 10 min against *E. coli* and *S. aureus*, respectively, even after washing 20 times. This excellent durability after washing could be explained by the strong adsorption of CNC/PEI/Cu₂O onto the polycotton surface, with a negligible loss of some bound CNC/PEI/Cu₂O during the washing cycle, as depicted in Figure 5.14. These remarkable stability and durability results confirmed that fabricated antibacterial fabric is practically reusable with long-term storage and repetitive washings.

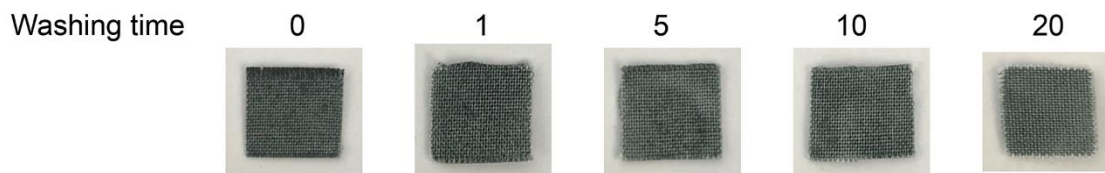


Figure 5.14 Digital photographs of CNC/PEI/Cu₂O modified polycotton after washing.

5.4 Conclusions

We developed a rapid and effective antibacterial system using inexpensive and sustainable Cu₂O nanoparticle-coated CNC. Due to the CNC/PEI template, the ultrafine, approximately 7-nm Cu and Cu₂O nanoparticles were well-deposited onto the CNC surface without aggregation. The oxidation states of copper nanoparticles were controlled by the pH of reactant solutions to further enhance the antimicrobial activity. The prepared CNC/PEI/Cu and CNC/PEI/Cu₂O exhibited excellent dispersity in water and the positive surface charges promoted bacteria killing. Consequently, both CNC/PEI/Cu and CNC/PEI/Cu₂O demonstrated outstanding antimicrobial performance against *S. cerevisiae*, *E. coli*, and *S. aureus*, and the

antimicrobial activities of CNC/PEI/Cu₂O exceeded that of CNC/PEI/Cu due to the high toxicity of Cu⁺ ions. The prepared CNC/PEI/Cu₂O was coated onto cotton and polycotton fabrics using a simple spray coating method, which did not affect the fabric filtration efficiency or breathability. The time-kill test confirmed the exceptional antibacterial property of the modified fabric. The CNC/PEI/Cu₂O-coated fabric rapidly killed bacteria in less than 3 min for *E. coli* and 10 min for *S. aureus*. This rapid bactericidal activity was comparable to or even faster than expensive noble metal-based systems. The excellent stability of modified fabric over long-term storage and washing durability suggest its enormous potential for antimicrobial applications, including PPE fabrication. An overview of the system being developed and evaluated as a sustainable anti-microbial compounds is shown in Figure 5.15.

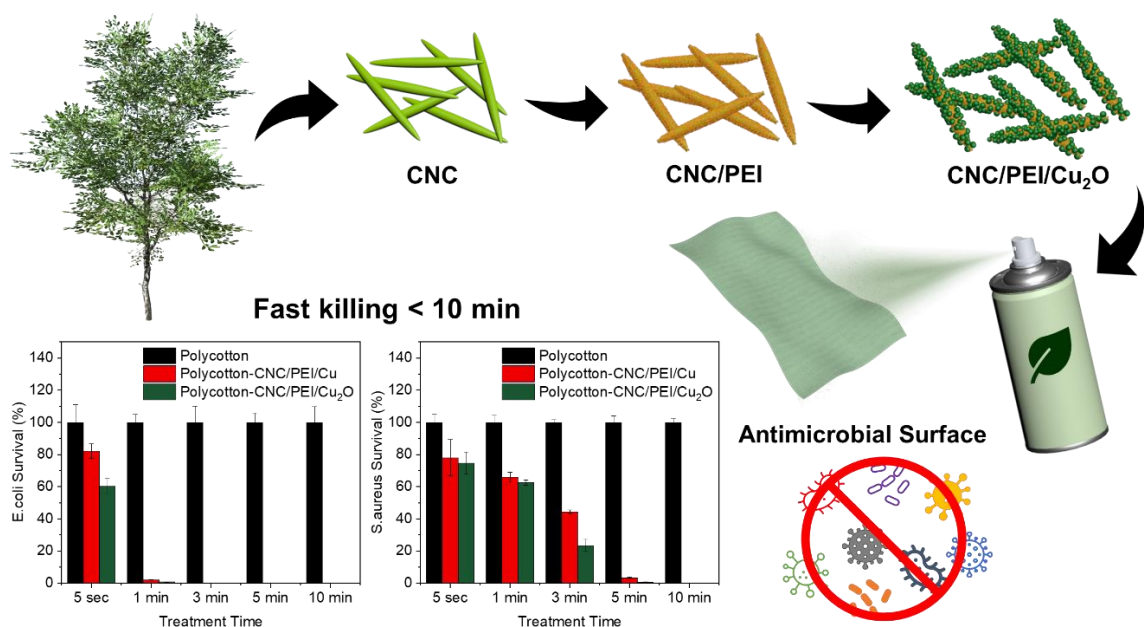


Figure 5.15 Overview of the development of anti-microbial compounds on fabrics.

Chapter 6

Conclusions and Recommendations

6.1 Conclusion and contributions

With the growing concern on the depletion of petroleum resources and their effect on our ecosystems, increased attention has been paid to the use of renewable resources. In this context, sustainable and earth-abundant CNC has been emerging as attractive solutions to surmount the current sustainability issue as well as a range of technological challenges. This thesis is devoted to converting CNC into advanced engineered materials using simple synthetic processes. To achieve this goal, we successfully developed and prepared various functional coatings on the CNC surface, depending on the target applications. Facile physical adsorption and/or hydrogen bonding were used to develop the coating layers in consideration of the practical utility of the methodology. The following sections summarize the major contributions and findings of this doctoral research.

6.1.1 Interfacial Control of the Synthesis of Cellulose Nanocrystal Gold Nanoshells

This study focuses on comparing and developing different strategies for gold nanoshell synthesis, namely the *ex-situ* seed-mediated method and the *in-situ* one-pot method. In both methods, cationic PDADMAC was coated on the CNC surface via electrostatic interaction, facilitating the attachment of gold precursors. In the *ex-situ* seed-mediated method, the effect of two different gold seeds on shell growth was investigated by applying TSC and THPC

capping agents, respectively. It was demonstrated that TSC capped gold nanoparticles were favorable in preparing a more continuous gold shell on CNC due to their larger size and strong surface charge compared to those of THPC capped seeds. Furthermore, we first developed the novel one-pot gold nanoshell synthesis to simplify the traditional complicated synthetic steps. Careful control of physical interaction between CNC and chemical species resulted in a uniform gold shell coating on individual CNC, which displayed superior shell quality compared to the *ex-situ* method in terms of smoothness, evenness, and continuity. This study demonstrated the sustainable and efficient strategies for synthesizing anisotropic gold shell structure, which can be applied to a range of applications, such as photothermal cancer therapy, drug delivery, surface-enhanced spectroscopies (Raman and infrared), and biosensing.

6.1.2 Sensitive, Stretchable, and Sustainable Conductive Cellulose Nanocrystal Composite for Human Motion Detection

In this study, the rod-liked conductive polymer was prepared by coating PEDOT on the surface of CNC. PVP inter-layer was firstly adsorbed onto CNC to render the hydrophobicity that shield the heterogeneous surface chemistry for further PEDOT coating. Uniform PEDOT coating was successfully prepared via an *in-situ* oxidative polymerization on the CNC surface (CNC/PVP/PEDOT). The prepared CNC/PVP/PEDOT demonstrated enhanced dispersity in water and hydrophilic PVA matrix compared to the pure PEDOT. Importantly, the high aspect ratio of CNC/PVP/PEDOT lowered the electrical percolation onset of composites and achieved higher conductivity with less PEDOT. The fabricated PVA/Gly-CNC/PVP/PEDOT composite

exhibited a long-term outstanding human motion-detecting performance due to the glycerol plasticizer having extremely low vapor pressure. This study clearly showed that the addition of a low-cost CNC template could significantly improve the electrical properties of composites.

6.1.3 Antimicrobial Copper Oxide Nanoparticle Coated Cellulose Nanocrystal for the Fabrication of Rapid Bacteria-killing Fabrics

In this study, ultrafine copper and cuprous oxide nanoparticle coated CNC were successfully prepared for use as antimicrobial agents. PEI with abundant amine groups was initially coated onto CNC to chelate the copper ions and enhanced the attachment to bacteria cells. The CNC/PEI template led to the synthesis of the stable and smaller size of copper nanoparticles deposited on the CNC surface. The pH of the reaction mixture played a key role in the determination of the oxidation state of the copper nanoparticle. The cuprous oxide nanoparticle coated CNC (CNC/PEI/Cu₂O), synthesized at a lower pH condition, demonstrated better antimicrobial activity than copper nanoparticle coated CNC (CNC/PEI/Cu). The antimicrobial fabric was then prepared by spray coating CNC/PEI/Cu₂O onto the fabric. The CNC/PEI/Cu₂O modified fabric exhibited outstanding and fast bacteria-killing performance compared to the expensive silver-modified fabrics. Furthermore, the superior antibacterial activity of modified fabric was maintained after the storage under ambient conditions for more than 1 month and subjected to repeated washing cycles. These results demonstrated a simple process to fabricate practical antimicrobial fabrics.

6.2 Recommendations for future studies

According to the results of this doctoral research, the following recommendations on the functionalized CNC may be considered for future studies.

The novel gold shell synthesis strategy in Chapter 3 can be applied to other metal coatings such as silver, copper, and platinum. Considering the distinct characteristics of each metal precursors, suitable reducing and capping agents can be selected to promote the electrostatic interaction between the CNC and the metallic ions. In addition, the gold nanoshell and gold nanorod are well-known candidates for biomedical imaging, surface-enhanced Raman spectroscopy, and surface-enhanced infrared absorption spectroscopy due to their unique optical, chemical, and physical properties. Therefore, it will be interesting to apply the gold nanoshell coated CNC to those practical applications because its synthesis method is more sustainable and efficient compared to conventional metal nanomaterial synthesis.

The strategy for fabricating PEDOT coated CNC in Chapter 4 can be applied to a cellulose nanofiber (CNF), which possesses a much higher aspect ratio. The CNF template is expected to impart a higher conductivity and the formation of a free-standing object without a polymer matrix; therefore, it would find other applications in addition to sensors. Also, the prepared PEDOT coated CNC can be a promising scaffold in muscle tissue engineering due to its conductivity and biocompatibility. Therefore, CNC/PVP/PEDOT offers a more sustainable and low-cost tissue engineering system compared to the traditional and expensive materials-based system being used.

The application of copper oxide nanoparticle coated CNC in Chapter 5 can be further extended. Firstly, the incorporation of CNC/PEI/Cu₂O into polymer matrices can facilitate the antimicrobial packaging system, which provides a prolonged shelf life, quality, and safety of fresh products such as fruits, vegetables, and meat. In terms of the fabrication of antimicrobial fabrics, a more precise and controlled coating method, such as spray coating using a 3D printer, could be applied for to optimize the processing of such materials and systems. Furthermore, copper ions are well-known to have a stimulation effect on wound healing with significant antimicrobial activity and low toxicity; therefore, CNC/PEI/Cu₂O nanocomposites can be used for wound healing applications as well.

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Appendices

Appendix A

Multimedia Appendix

This appendix is a video file of the luminance variation of an LED bulb by stretching and releasing the PVA/Gly-CNC/PVP/PEDOT.

The file name of this sound file is “Movie4-1. The luminance variation of an LED bulb by stretching and releasing the PVAGly-CNCPVPPEDOT.mp4”.

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Appendix B

Multimedia Appendix

This appendix is a video file of the CO₂ generation rate during the respiration of yeast treated with CNC/PEI/Cu₂O.

The file name of this sound file is “Movie5-1. The CO₂ generation rate during the respiration of yeast treated with CNCPEICu₂O.mp4”.

If you accessed this thesis from a source other than the University of Waterloo, you may not have access to this file. You may access it by searching for this thesis on <https://uwspace.uwaterloo.ca/UWSpace>.