FUNCTIONALIZATION AND CARBONIZATION OF CELLULOSE NANOFIBRILS
AS HIGH-PERFORMANCE FIBER MATERIALS AND THEIR APPLICATIONS

A Dissertation
Presented to
The Academic Faculty

by

Arie Mulyadi

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of the Requirements for the Degree
Doctor of Philosophy

School of Chemical and Biomolecular Engineering
Georgia Institute of Technology
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FUNCTIONALIZATION AND CARBONIZATION OF CELLULOSE NANOFIBRILS
AS HIGH-PERFORMANCE FIBER MATERIALS AND THEIR APPLICATIONS

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<th>Symbol</th>
<th>Abbreviation</th>
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<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
<td></td>
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<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance-Fourier transform infrared spectroscopy</td>
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<tr>
<td>BA</td>
<td>n-butyl acrylate</td>
<td></td>
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<tr>
<td>BET</td>
<td>Braunauer, Emmett, and Teller</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
<td></td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Electrochemical capacitive double layer</td>
<td></td>
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<tr>
<td>CNFs</td>
<td>Cellulose nanofibrils</td>
<td></td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
<td></td>
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<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
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</tr>
<tr>
<td>DTGA</td>
<td>First derivative thermogravimetric analysis</td>
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<tr>
<td>EDMA</td>
<td>Ethylene dimethacrylate</td>
<td></td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
<td></td>
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<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
<td></td>
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<tr>
<td>H$_2$</td>
<td>Hydrogen gas</td>
<td></td>
</tr>
<tr>
<td>$J_0$</td>
<td>Exchange current density</td>
<td></td>
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<tr>
<td>KPS</td>
<td>Potassium persulfate</td>
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<tr>
<td>L/D</td>
<td>Length over diameter</td>
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<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
<td></td>
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<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>MA-SEBS</td>
<td>Maleic anhydride-styrene ethylene butyl styrene coupling agent</td>
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<td>MPA</td>
<td>Melamine-phytic acid complex particles</td>
<td></td>
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<tr>
<td>N</td>
<td>Nitrogen atom</td>
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<tr>
<td>nm</td>
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<tr>
<td>NMP</td>
<td>Nitroxide mediated polymerization</td>
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<td>NSC</td>
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<td>N₂</td>
<td>Nitrogen gas</td>
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<tr>
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<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>RAFT</td>
<td>Reversible addition-fragmentation chain transfer</td>
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<td>RH</td>
<td>Relative humidity</td>
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<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
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<td>S</td>
<td>Sulfur atom</td>
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<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
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<td>T</td>
<td>Temperature</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>Tetrahydrofuran</td>
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<tr>
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<td>weight</td>
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<tr>
<td>3D</td>
<td>3 dimensional</td>
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<td>μm</td>
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SUMMARY

Cellulose is a structural component of plant cell walls that serve as most abundant organic polymer on Earth. The latest study indicated that cellulose as renewable and sustainable resources is produced $1.5 \times 10^{12}$ tons annually and could be considered an almost inexhaustible source of raw material. With the primary occurrence in the form of lignocellulosic material in forests, commercialization of cellulose has been utilized for extensive applications in various industries, primarily as paper and cardboard. In the past decade, a new field of nanoscale cellulose fibers (nanocellulose) has garnered increasing attentions as promising bio-based fibers that can deliver environmentally friendly, high-performance material with additional unique properties. Many scientists believe that nanocellulose can be developed as the next generation of materials. Nanocellulose has the potential to be the basis platform of sustainable building blocks that can compete and substitute some of the markets dominated by petroleum-based feedstock.

Cellulose nanofibrils (CNFs) as nanocelluloses with typical fiber dimension of 5-100 nm in diameter and up to several microns in length give the smallest structural fiber of cellulose with high aspect ratios (L/D). The material can be prepared by breaking down the hierarchical structure of the cellulose fiber from the wood pulp using mechanical disintegration. The wood pulp could be obtained either with or without chemical/enzymatic pretreatment. Owing to the individualized fibrous form, CNFs yield materials with a high surface area, crystallinity, and aspect-ratio-fiber. These properties would potentially allow CNFs as suitable material for various applications such as bio-filler reinforcement, bioabsorbent, and “green” electrocatalyst.
Although the nanosize dimensions of CNFs possess unique properties to expand their functionality toward new application platform, the inherent chemical structure of cellulose would still limit its functionality. CNFs, as straight chain polymers consisted of D-glucose units, have strong hydrophilic tendency due to the present of polar hydroxyl groups and weak hydrophobic nature due to less exposed surface of hydrophobic –CH moieties. In addition, CNFs are intrinsically electric insulators without catalytic property. Therefore, the focus of this dissertation is to promote CNFs functionalities by studying modification approaches aimed to fabricate hydrophobic/oleophilic surface and electrocatalytically-active nanofibers via thermochemical treatment of cellulose. There are three major components of this dissertation:

(1) Water-free grafting of hydrophobic polymer via coupling agent

In the first part, surface hydrophobization of CNFs using coupling agent consisting of the well-defined hydrophobic polymer backbone and reactive anhydride group was applied. The impact of surface hydrophobization treatment via coupling agents on CNFs properties were evaluated. The effect of the modified CNFs as reinforcing filler on the mechanical properties of polystyrene (PS) composite films was tested and compared to that of neat CNFs. The results ascertained the enhancement in mechanical properties of hard, brittle thermoplastic polymer by utilizing CNFs as fillers and the role of surface hydrophobization to optimize the mechanical performance of polymer composites.

(2) In-situ hydrophobic polymer grafting in aqueous medium

In the second part of this study, an approach to prepared surface hydrophobized CNFs in aqueous solution was achieved. The grafting of hydrophobic polymer on the surface of CNFs based on dropwise suspension polymerization was applied to the well-dispersed CNFs suspension in water. The properties of hydrophobic CNFs were confirmed, and the reaction
mechanism of polymer grafting was proposed. The hydrophobic CNFs was further utilized to form hydrophobic CNFs aerogels. The characteristics of the hydrophobic CNFs aerogels as effective oil absorbent materials was demonstrated.

(3) CNFs-derived carbocatalyst

The third part of this study focused on the transformation of CNFs as a precursor material for carbon electrode. The fabrication of metal-free carbon electrocatalyst toward oxygen reduction and hydrogen evolution reaction by a combination of heteroatoms-doping, complex particle recombination, and high-temperature annealing was adopted. Carbonization of CNFs easily yielded 3D interconnected carbon nanofibers with high mesopores and good conductivity. The inclusion of heteroatoms on the aromatic carbon structures induced good electrocatalytic activities toward oxygen reduction reaction. To further upgrade carbon nanofiber functionality toward hydrogen evolution reaction, recombination of N,P-doped carbon shell layer on the surface of the N,S-doped CNFs-derived carbon nanofibers was investigated. The results indicated that the hybrid carbon nanofibers obtained by a mixture of heteroatoms-doped CNFs-derived carbon and complex particles of melamine-phytic acid could enhance the electrocatalytic performance of the carbon electrocatalysts toward both oxygen reduction reaction and hydrogen evolution reaction.
CHAPTER I

INTRODUCTION

Cellulose as a naturally occurring polymer produced primarily by plants, algae, and some bacteria is one of the most important sustainable materials. For millennia, this organic polymer has been part of human civilization in the form of wood and plant fiber as an energy source, construction material, and textile. Today, the use of cellulose-based materials continues as raw materials for a broad spectrum of applications in various industries, primarily as paper and cardboard materials. As the most abundant natural polymer, cellulose is a linear homopolymer composed of D-gluco-pyranose units linked by \( \beta-1,4 \)-glycosidic bonds shown in Figure 1.1.\(^1\) The degree of polymerization of cellulose varies depending on its source with a range between few hundred and up to 20,000.\(^{1, 2}\)

The linear chain of the cellulose molecular structure along with the numerous surface hydroxyl groups and its tightly packed arrangement leads to the formation of semicrystalline fiber morphology. The cellulose fibril, which is originated from flat sheets being held together by van der Waals forces and strong intra- and intermolecular hydrogen bonding,\(^{3, 4}\) is the main cause of its outstanding physical properties, such as high tensile strength and elastic modulus, low density,
good thermal stability, and excellent solvent resistance. A recent study showed that the mechanical and thermal properties of the crystalline domain of cellulose are comparable or even better than some reinforcement materials.\cite{5} Table 1.1 presents the summary of physical properties of some reinforcement materials, including the crystalline domain of cellulose.

**Table 1.1** Physical properties of some reinforcement materials. Adapted from Moon et al.\cite{5} with permission of The Royal Society of Chemistry

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g·cm(^{-3}))</th>
<th>Tensile Strength (GPa)</th>
<th>Axial Elastic Modulus (GPa)</th>
<th>Coefficient of Thermal Expansion (ppm·K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar-49 fiber</td>
<td>1.4</td>
<td>3.5</td>
<td>124-130</td>
<td>-2.7</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>1.8</td>
<td>1.5-5.5</td>
<td>150-500</td>
<td>-0.1</td>
</tr>
<tr>
<td>Steel Wire</td>
<td>7.8</td>
<td>4.1</td>
<td>210</td>
<td>11.1</td>
</tr>
<tr>
<td>Carbon Nanotubes</td>
<td>-</td>
<td>11-63</td>
<td>270-950</td>
<td>-</td>
</tr>
<tr>
<td>Boron Nanowhiskers</td>
<td>-</td>
<td>2.8</td>
<td>250-360</td>
<td>-</td>
</tr>
<tr>
<td>Crystalline Cellulose</td>
<td>1.6</td>
<td>7.5-7.7</td>
<td>110-220</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Given its abundance availability and outstanding inherent properties, cellulose-based materials have been continuously developed in various forms, including cellulose esters, cellulose ethers, and regenerated cellulose, to provide new functionalities and extend its application range. Recently, the development of cellulose based materials focuses mainly toward a novel form of cellulose called nanocellulose. Nanocellulose is a nanosize dimension of cellulose that can be produced by either top-down approach via delamination of the hierarchical structure of plants or bottom-up approach via cellulose growth from glucose by the assistance of a bacteria. In essence, nanocellulose combines the intrinsic characteristics of cellulose with unique features of a significantly higher surface area, less defect, and higher crystallinity compared to those of traditional wood cellulose fibers. This next generation of cellulose-based materials has the ability to impart diverse functionalities that are suitable as a building block for high-performance engineering applications.
The isolation of microfibrillated cellulose as nanocellulose was first published in 1983.\textsuperscript{[6]} However, the interest toward nanocellulose technology has only been established in the last decade as illustrated in Figure 1.2. With the high expectation of commercial nanocellulose products in the near future, the current stage of research and development on nanocellulose technology is still relatively immature, and there is a numerous opportunity available for scientists to explore. While there has been an extensive on-going research related to the nanocellulose processing method and the fundamental properties of nanocellulose, the designing of nanocellulose-based material for high-performance applications remains uncovered adequately. Therefore, in this dissertation, we focus on not only the technological possibilities in nanocellulose modification approaches but also the development of nanocellulose-based material as a sustainable platform for diverse engineering applications.
The outline of this work is organized as the following: Chapter II provides a brief review of the state-of-the-art of nanocellulose modification approaches and applications, focusing primarily on cellulose nanofibrils (CNFs). Chapter III describes the specific objectives of this research. The approaches to achieve these specific objectives are determined, and some crucial issues are listed. Chapter IV contains the study of surface modification via coupling agent polymer to introduce hydrophobic surface. It focuses on the characteristics of the modified CNFs and its influence on mechanical properties of polystyrene (PS) composite. In Chapter V, the surface hydrophobization approach is extended toward aqueous solution modification, in which in-situ grafting polymerization is introduced. The creation of hydrophobic CNFs is further employed to form aerogels, which have the capabilities as an effective oil bio-absorbent for oil–water separation. In Chapter VI, a study on the versatility of CNFs as carbon precursors for electrocatalyst application is explored. The feasibility of doping heteroatoms to CNFs-derived carbon toward oxygen reduction reaction is demonstrated. Furthermore, the benefits of CNFs structural morphology and porosity as a template is utilized via recombination with different carbon catalyst to exhibit superior hydrogen evolution reaction. Finally, Chapter VII gives the overall conclusion and the possible future works of this research.
CHAPTER II

LITERATURE REVIEW

2.1 Nanocellulose

In general, nanocellulose can be classified into two different kinds based on their dimension and composition, cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). CNCs, also previously known as cellulose whiskers, are generated by removal of the amorphous domain of cellulose microfibrils by acid hydrolysis and have the rod-like shape. The geometrical dimension of CNCs varies with their cellulose source and isolation method, but typically they display a diameter ranging from 5 to 10 nm and length of 50-300 nm.\(^5,7,8\) On the other hand, CNFs are long and fibrous cellulose fibrils composed of both amorphous and crystalline domains with a typical dimension of 5-100 nm in width and up to several micrometers in length.\(^7-10\) The geometrical dimension of CNFs leads to nanofiber with high aspect ratio (L/D) and highly entangled network that exhibits gel-like characteristics in water suspension. CNFs can be produced by either biosynthetic extrusion from bacteria yielding pure native cellulose with high crystallinity\(^11-13\) or defibrillation of wood pulp with the aid of chemical\(^14-18\) or enzymatic treatment\(^19,20\) and/or mechanical disintegration\(^21,22\). However, given the accessibility of wood cellulose as raw material provided by forest product industry, bleached kraft pulp and sulfite pulp are often used as the starting material for CNFs production. The delamination process of the hierarchical structure of wood cellulose and their respective CNCs and CNFs products are illustrated in Figure 2.1. In this dissertation, the focus of the work will only cover CNFs material obtained primarily from wood pulp defibrillation.
2.2 Modification of cellulose nanofibrils

As CNFs are essentially designed to have nanoparticle morphology and structure while maintaining their cellulose molecular structures, modification of CNFs is one of the important steps to further tailor the properties of this material to meet the specific demand in their utilization for high-performance applications. Furthermore, due to their large specific surface area, it is expected that the modification of CNFs not only provides more challenges during its preparation but also produces more significant impact than that of traditional wood cellulose fiber. In general, there are two common CNFs modification approaches (Figure 2.2): surface functionalization and chemical/physical transformation.
2.2.1 Surface functionalization

Surface functionalization is targeted to modify the surface of either individual CNFs in their dispersed state or bulk material of aggregated CNFs (i.e. film or aerogel) and can be performed through chemical and physical treatment. The surface of the nanofibrils is composed of a periodical distribution of surface hydroxyl groups. These high number of hydroxyl groups lead to two effects that may not be desirable: strong hydrogen interactions between two nanofibrils and highly polar nanomaterial. Some chemical and physical treatments involving lower hydroxyl groups have been reported. Physical treatment is performed with the aid of electric discharge such as cold plasma\textsuperscript{32, 33} and laser\textsuperscript{34}. In this study, no physical treatment was applied, and only topochemical surface
functionalization is covered. Moreover, direct surface chemistry of CNFs such as TEMPO-oxidation, sulfonation, etc. is not included as part of surface functionalization step.

There are two main strategies for chemical surface functionalization of CNFs: physical adsorption and covalent bonding. In the physical adsorption method, weak chemical bonds are employed through hydrogen or ionic bonds. The adsorption phenomena of xyloglucan onto cellulose via hydrogen bonding has been successfully studied.\textsuperscript{[25, 35]} Meanwhile, surfactants and polyelectrolytes are utilized to facilitate ionic interaction.\textsuperscript{[36-41]} The negative surface charge of cellulose (arising from either oxidative bleaching of cellulose during pulping process or additional oxidative pretreatment process) could provide electrostatic adsorption with the positive ammonium of cationic surfactants/polycations as the counterions. Different types of polymer chains in the cationic surfactants and polyelectrolytes have been successfully deposited to render different functionality, i.e. lower surface adhesion\textsuperscript{[39]}, multilayer polyelectrolyte deposition\textsuperscript{[17]}, and nanoparticle binder\textsuperscript{[42]}. However, it is expected that migration of the adsorbed moieties can occur easily through extensive mixing. Furthermore, the presence of excess surfactants or polyelectrolytes may also induce undesirable property such as lower mechanical performance for nanocomposite.\textsuperscript{[43]}

In comparison to the physical adsorption, covalent bonding method creates a chemical interaction that results in a more stable form. A wide range of these methods has been demonstrated. In most cases, the reaction involves a heterogeneous system, in which CNFs would be insoluble nanoparticles and the reacting agent would be soluble in the reaction medium. Generally, there are two types of covalent bonding approach depending on the size of attached molecules: molecule chemical grafting and polymer grafting. Some notable molecule chemical grafting of cellulose involve silylation\textsuperscript{[44-47]}, esterification via carboxylic acid\textsuperscript{[48]}, anhydride\textsuperscript{[49-52]},
or acyl chloride\textsuperscript{[53]}, isocyanate\textsuperscript{[54-56]}, and ring opening reaction of epoxide group\textsuperscript{[57-59]}. In the silylation approach, chlorosilane is often used as the reacting agent and the silyl group (R\textsubscript{3}-Si) replaces the hydroxyl group of the cellulose structure. Esterification is another common reaction, in which an ester functional group is introduced onto the surface hydroxyl group of the cellulose structure by condensation mechanism. Carboxylic acid, anhydride, and acyl chloride as reacting agents to induce esterification for nanocellulose have been reported in the literature. Depending on the reaction conditions, it has been found that esterification could proceed effectively not just on the surface of nanofibers but also inside the core of the crystalline region of nanofibers\textsuperscript{[53, 60]}. Both silylation and esterification approach often result in the generation of acid by-products. Carbanilation using isocyanate as reaction agents serve as the alternative approach that eliminates this issue. The isocyanate acts as the electrophile that can easily react with the hydroxyl group of cellulose to form a urethane linkage. Nevertheless, all the reported approaches based on silylation, esterification, and carbanilation require water-free condition, which often makes the preparation step for CNFs more complex. In this regards, the ring opening reaction of epoxide group onto cellulose has been performed to graft molecules in the aqueous medium. In this reaction, the hydroxyl group of cellulose is alkali activated by adding sufficient amount of base solution.

Given the limited amount of substituted molecules could have on the CNFs surface, the changes on surface properties of nanofibrils may not be apparent. In this regards, polymer grafting is often desired in order to integrate new surface functionality more sufficiently. Depending on the formation of the polymer chain, general route of polymer grafting involves either “grafting from” or “grafting to” approach. “Grafting to” approach considers attaching pre-formed polymer chains onto cellulose backbone, while “grafting from” approach proceeds by growing polymer chains from the active sites of cellulose backbone.
There are only a few methods regarding “grafting to” approach. Polymers consisting of a functional species that are capable of esterification\(^{[61, 62]}\), forming carbodiimides coupling\(^{[63]}\), terminating living polymer cation\(^{[64]}\), inducing “click chemistry”\(^{[65-68]}\), are typically required to mediate a linkage to attach the high molecular weight polymer. Although the attached polymer has a well-defined characteristic, the grafting density for this approach is often low due to the steric hindrance of the long polymer chain.\(^{[69]}\) Thus, the “grafting to” approach may not be the effective strategy to ensure good grafting coverage.

In comparison to “grafting to” approach, “grafting from” approach can achieve relatively high grafting density with varying degree of control on polydispersity. Various methods have been reported as representation of this approach, such as conventional free-radical polymerization\(^{[70-73]}\), direct oxidation on cellulose backbone\(^{[74-76]}\), ionic graft polymerization\(^{[77-79]}\), ring opening polymerization\(^{[80-84]}\), atom transfer radical polymerization (ATRP)\(^{[27, 67, 85-87]}\), nitroxide mediated polymerization (NMP)\(^{[88]}\), and reversible addition-fragmentation chain transfer (RAFT)\(^{[89, 90]}\).

Among all the polymerization methods, polymer grafting on cellulose via free-radical initiation is the most popular choice. The attractiveness of this method originates from the diverse
monomers applicability, the unlimited copolymer formation, the high tolerance of reaction condition, and the technological feasibility in terms of a large-scale process.\textsuperscript{[91]} Grafting via conventional free-radical polymerization method can be performed using typical free-radical initiators such as dibenzoyl peroxide (BPO), Azobis(isobutyronitrile) (AIBN), potassium persulfate (KPS), potassium permanganate, and Fenton’s reagent. In this method, free-radical could initiate on either cellulose structure or monomer. Thus, the generation of ungrafted polymer (homopolymer) would be unavoidable. In this regards, grafting via free-radical exclusively on cellulose structure or direct oxidation on cellulose is found as an alternative solution. However, relatively expensive transition metal ions such as ceric ammonium nitrate are required as the initiator. Moreover, the ceric ammonium nitrate is known to be active only in a very acidic condition (i.e. pH of the medium is 1), in which a severe damage on the nanofibers could be expected for this reaction medium. Nonetheless, the two methods would still have an issue with regards to controlling the polydispersity of grafted polymer.

Ionic graft polymerization and ring-opening polymerization serve as the alternative methods to use a different mechanism other than free-radical. There are, however, only limited amount of studies performed. It has been noted that ionic graft polymerization will be difficult to implement given the high-demanding reaction conditions (anhydrous and high purity reagents).\textsuperscript{[91]} On the other hand, ring-opening polymerization is only limited to certain monomers, such as ε-caprolactone and L-lactic acid.

In the recent advance of polymerization techniques, living polymerizations have been explored as grafting method. Szwarc first defined “living polymerization” in 1956 as chain polymerization growth in the absence of chain breaking reaction (i.e. chain transfer or irreversible termination steps).\textsuperscript{[92]} Such mechanism would generate the polymers with controlled composition,
molecular weight distribution, and architecture. In combination with a radical process, the concept of living radical polymerization (LRP) was introduced as a versatile approach that gives precisely controlled polymers for a wide range of monomers and reaction conditions.[93] Moreover, in grafting process, the large amount of homopolymer formation could be easily avoided. Atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT) are the three major methods representing LRP mechanism. Nevertheless, these methods are still not widely used for industrial-scale, and their applicability would strongly depend on the practical application of the end-products.

2.2.2 Surface hydrophobization

Among various properties that are desired to obtain, tuning the surface wetting properties of CNFs is one of the most common objectives for surface functionalization. Neat CNFs are amphiphilic materials that are composed of hydrophilic and hydrophobic sites.[94, 95] Although the inherent amphiphilicity of CNFs has been taken advantages as dispersant agent,[94] surface hydrophobization of CNFs is often desired and has been proven to contribute significantly to various aspect of field, such as to maintain barrier and mechanical properties of CNFs films in the environment with high relative humidity,[96] to produce a stable colloidal suspension in various organic solvents,[26, 83], to be utilized as stabilizer for formation of water-in-oil (w/o) Pickering emulsion,[97, 98], to improve surface compatibility with hydrophobic polymer matrices,[47, 81, 99], and to induce oil/water separation property.[100, 101].
Figure 2.4  (a) 3D molecular structure of cellulose. (b) Schematic model of cellulose crystal in the elementary fibrils with the representation of both hydrophobic and hydrophilic face \(^{[94, 102]}\)

Various attempts have been reported in either introducing hydrophobic compound or lowering accessible hydroxyl groups. Using fluorosurfactant, Aulin et al. could reduce the high dispersive surface energy of cellulose at 54.5 mN/m to ~12 mN/m.\(^{[41]}\) Rodionova et al. performed gas-phase esterification of nanocellulose films using trifluoroacetic acid anhydride and acetic acid to render esterified film with a contact angle of \(79.2^\circ\).\(^{[48]}\) The same group also used acetylation reaction to obtain acetylated films with a contact angle of \(82.7^\circ\).\(^{[96]}\) Using the similar acetylation reaction, Jonoobi et al. were able to achieve higher contact angle of \(115^\circ\).\(^{[60]}\) Yoshida et al.\(^{[52]}\) and Missoum et al.\(^{[103]}\) utilized AKD as a sizing agent using solvent-free condition and nanoemulsion, respectively. In both methods, contact angle value around 100\(^\circ\) was observed. Tome et al. tested surface hydrophobization of bacterial cellulose using several anhydrides (acetic, butyric, hexanoic, and alkenyl succinic anhydride) and hexanoyl chloride in an ionic liquid. Contact angle values in
the range of 80-104° were obtained. Surface silylation of nanocellulose using chlorodimethylisopropylsilane was able to generate modified nanocellulose with water contact angle between 111-146°.[104] Lu et al. could attain hydrophobic microfibrillated cellulose that gave a water contact angle value of 110° using a titanate coupling agent (Lica 38).[47] Recently, a commercial-scale hydrophobic nanocellulose with contact angle around 90° was available developed by American Process Inc. through the American Value Added Pulping (AVAP)® technology.[105]

2.2.3 Carbonization and its surface functionalization

Aside from surface functionalization, in which the molecular structure and physical properties of CNFs backbone remain unaltered, chemical/physical transformation of CNFs is another type of modification approach. The transformation of CNFs is aimed to convert either the molecular structure or physical morphology of CNFs. Some examples of cellulose transformation are dissolving pulp and carbonization. In this thesis work, only carbonization of CNFs is considered.

In general, the term “carbonization” refers to the thermal transformation of organic molecules into inorganic solid carbon. During the carbonization, thermochemical process causes the organic molecules of material to be broken down into volatile matter, non-volatile matter, and ash.[106, 107] The volatile matter can be categorized into two products: the condensed liquid fraction called bio-oil and the non-condensable gas called syngas. The volatile matter is often the major products of carbonization process. The non-volatile matter of carbonized cellulose is a carbon-rich material composed of a complex mixture of polycyclic aromatic carbon sheets.[108, 109] When obtaining the carbonaceous material, a small amount of inorganic residue may present. The term used for this inorganic residue is called ash.
Common methods of preparing carbonized cellulosic materials are pyrolysis (slow, fast, or flash), flash carbonization, gasification, hydrothermal treatment, or a combination thereof.\textsuperscript{106, 107, 110-113} Depending on the carbonization method, the yield of carbonaceous material may vary. In the slow pyrolysis process, slow heating rate (5-7 °C/min), relatively long vapor residence time (>1 h), and a wide temperature range (300-800 °C) was executed. The main product of this process is the carbonaceous solid, which is accounted for a relatively high yield range of 35-50 wt%. The fast pyrolysis is characterized by fast heating rate (300-800 °C/min) and relatively shorter vapor residence time (0.5-10 s). The process typically operates in the temperature range of 400-600 °C and generates a high yield of bio-oil with only 15-25 wt% of bio-carbon. The flash pyrolysis uses even faster heating rate (~1000 °C/min) and relatively shorter vapor residence time (<2 s). Only 10-20 wt% of carbon solid could be produced with syngas as the main product. Unlike pyrolysis, flash carbonization uses air flow and elevated pressure reaction condition. No liquid product was reported to be found using this method.\textsuperscript{113} Gasification is another process that involves partial combustion as a controlled oxygen gas is included in the reaction condition. The method is designated to produce syngas as the main product with some carbon solid as by-products. Hydrothermal carbonization is another different process that involves wet feedstock. The method requires elevated temperature and pressure to transform the feedstock material into the carbon-rich material. The resultant carbon from this method would contain a high amount of oxygen (~20 wt%).\textsuperscript{114} Regardless the discrepancy in the carbonization methods, the main mechanism associated with the carbon network formation often does not change. There are three main reactions involved: dehydration, decarboxylation, and polycondensation.\textsuperscript{106, 109, 114, 115}
Figure 2.5  Example of cellulose pyrolysis mechanism. Three products are produced: cellulose-derived carbon, bio-oil, and syngas. Adapted with permission from Liu et al.\textsuperscript{[106]} Copyright 2016 American Chemical Society.

The obtained carbonaceous material from cellulose is often referred as bio-carbon. The predominant aim for the development of bio-carbon is stemmed from the desire to create sustainable carbon nanomaterials. With the increasing attention for nanocarbon, such as carbon...
nanotube (CNT) and graphene as illustrated in Figure 2.6, toward high-performance applications, it would not be surprising that bio-carbon products could also be utilized as the substitute for some of the petroleum-based nanocarbon. The main interest in nanocarbon lies in their excellent intrinsic properties. Nanocarbons have shown to exhibit excellent mechanical properties (up to 130 GPa for tensile strength and 1 TPa for Young’s modulus), high surface area (up to ~1300 m$^2$/g), outstanding electrical properties ($10^2$-$10^5$ S/cm), low optical absorption, chemical inertness, superhydrophobic property, and good thermal stability.$^{[116-120]}$

![Publication Analysis](image)

**Figure 2.6** Development of nanocarbon research based on publication analysis. Reprinted from Shearer et al.$^{[116]}$ with permission of John Wiley and Sons.
In order to compete with the petroleum-based nanocarbon, it is important that the synthesized bio-carbon have comparable properties. The properties of bio-carbon are influenced by the precursor properties of cellulosic materials and treatment condition. Carbonization of cellulose typically would yield a hard carbon, which is a non-graphitizable carbon class.\textsuperscript{112} However, the graphitization capability for cellulose-derived carbon could be achieved to a certain extend for some high purity cellulose with very high crystallinity.\textsuperscript{112} Aside from the source of feedstock, carbonization temperature is another important aspect that greatly affects the properties of bio-carbon. The difference in carbonization temperature would change the composition of aromatic arene-like network\textsuperscript{[112,115]}, the growth of carbon crystallite\textsuperscript{[121]}, electronic properties\textsuperscript{[112,121,122]}, and surface area\textsuperscript{[106,122]}. In general, the graphite-like layers would not start to form until the temperature reach 350 °C, in which large amount of furanic-group is expected. As the temperature increases up to 900 °C, aromatic arene-like network dominates the structure of bio-carbon and form semi-ordered carbon crystallite. Above 900 °C, the obtained bio-carbon is subjected to graphitization, in which more ordered carbon crystallite and increasing crystalline thickness are expected (Figure 2.7).
Figure 2.7  (a) Observable changes in Raman spectra for carbonization of microcrystalline cellulose using various heat treatment temperature (HTT). (b) Deconvolution of each Raman spectrum. (c) Schematic illustration of crystalline carbon growth. (d) Intensity ratio of D band and G band derived from Raman spectra. Reprinted from Rhim et al.\cite{121}, with permission from Elsevier.

The bio-carbon with low defect carbon-rich structure would allow the material to have more favorable electrical properties. The electrical conductivity of cellulose is $10^{-8}$ S/cm.\cite{112} The effect of carbonization temperature on the electrical properties of cellulose-derived carbon has been studied by Rhim et al.\cite{121}, as shown in Figure 2.8. As cellulose was carbonized at the temperature of 350 °C, the electrical conductivity of carbonaceous material could increase up to $10^{-5}$ S/cm. Cellulose-derived carbon prepared at 600 °C would have electrical conductivity around $10^{-3}$ S/cm.
A further increase in the temperature up to 1000 °C would improve the electrical conductivity to reach $10^2$ S/cm. However, no significant change was detected while increasing the temperature up to 2000 °C. The average electrical conductivity of 33 S/cm has been reported for various carbonized CNFs. It should be noted that the inherent electrical conductivity of cellulose-derived nanocarbon would always be inferior compared to the typical petroleum-based nanocarbon.

The effect of carbonization temperature on the development of the surface area and pore structure for bio-carbon have been studied by Brown et al. At carbonization temperature of 450 °C, the surface area of the obtained bio-carbon showed less than 10 m$^2$/g. With increasing temperature to 750 °C, the surface area of bio-carbon increased sharply to reach 400 m$^2$/g. A lower surface area is then expected at 1000 °C because of the microstructural arrangement at high temperature. In comparison to the surface area for petroleum-based nanocarbon, the surface area

![Figure 2.8](image-url) Electrical conductivity measurement for carbonized microcrystalline cellulose at various heat treatment temperature (HTT). Reprinted from Rhim et al., with permission from Elsevier.
of bio-based carbon is still comparable. Additionally, even though the surface area of the material is expected to be slightly lower, CNFs-derived carbon nanofiber may have better interconnected nanocarbon structure that could facilitate better carbon network continuity.

Since carbonization of cellulosic material could lead to a carbon-rich material with O/C ratio of 95%\cite{121}, only limited surface functionality is inherently present. In this regard, surface functionalization methods used for petroleum-based nanocarbon can also be performed for bio-carbon to give the similar surface functionality. There are three typical routes for the surface functionalization of bio-carbon: surface chemistry, heteroatoms doping, and surface recombination.\cite{106, 116} Surface chemistry, such as oxidation, amination, and sulfonation, is a process of introducing new surface functional groups. This method is often used as a preliminary step for further chemical grafting, the same step used to surface engineer CNFs. In addition to surface chemistry, heteroatoms doping is another functionalization by incorporating non-carbon atoms to replace some carbon atoms in the carbon network. Several heteroatoms dopants, such as nitrogen, phosphor, sulfur, and boron, are used to induce chemical heterogeneity that would affect the electronegativity of aromatic carbon atoms.\cite{123} Surface recombination is the other surface functionalization step. In surface recombination, other nanoparticles from different materials, i.e. metals, semiconductors, or oxides, or similar nanomaterials with different nanostructure are imparted on the bio-carbon template to introduce new functionality, nanostructure, or a combination of both.

\section*{2.3 Applications of cellulose nanofibrils}

\subsection*{2.3.1 Cellulose nanofibrils-based applications}

As sustainable nanomaterial with a potential of industrial-size production, the physiochemical, thermal, and mechanical properties of CNFs have been found useful as
reinforcing fibers in commodity polymers and concretes, aerogels and foams, colloid particles, and films. The combination of excellent strength originated from the crystalline region, the high aspect ratio of nanofiber, and surface compatibility with various hydrophilic polymers (i.e. chitosan\textsuperscript{[124]}, polyethylene oxide\textsuperscript{[24]}, and polyvinyl alcohol\textsuperscript{[125]}), has shown to improve the overall mechanical properties of the nanocomposite. Moreover, the surface modified CNFs can be used to reinforce some hydrophobic polymers such as natural rubbers\textsuperscript{[126]}, polylactic acid\textsuperscript{[127]}, polypropylene\textsuperscript{[128]}, and polyethylene\textsuperscript{[129]}. Similarly, the addition of CNFs to the cement paste could facilitate an increase in fracture toughness.\textsuperscript{[130]}

CNFs-based foams and aerogels could be prepared from drying water/air emulsion stabilized by CNFs and octylamine\textsuperscript{[131]} and freeze-drying CNFs suspension\textsuperscript{[132, 133]}, respectively. The resultant aerogels or foams could have low density with a highly porous structure, which is suitable as porous templates for scaffolding\textsuperscript{[132]}, liquid or gas absorbent\textsuperscript{[134-137]}, and conductive material\textsuperscript{[138]}. In addition, the good dimensional stability of neat CNFs offers a potential advantage as thermal insulations.\textsuperscript{[139]}

Owing to their unique nanofiber morphology, CNFs, as colloid particles, can be used as thickeners and suspension stabilizer in various emulsion products. CNFs have been tested to stabilize salad dressing\textsuperscript{[140]}, fracturing fluids of oil recovery\textsuperscript{[140]}, and water-based paint\textsuperscript{[141]}. Films prepared from neat CNFs showed high intrinsic oxygen barrier\textsuperscript{[8, 142]} and oil resistance capabilities\textsuperscript{[142]}. Moreover, the films can act as selective permeation of hydrogen gas filtration membrane.\textsuperscript{[143]}

\textit{2.3.2 Cellulose nanofibrils-derived carbon-based applications}
CNFs-derived carbon nanofibers have been found useful as pollutant adsorption, energy storage material, electrical component, and catalyst. As pollutant adsorption, the carbonized CNFs possess high surface area and hydrophobicity to provide excellent adsorption capacity and selectivity for oils, dyes, and heavy ions removal.\cite{144,145} In addition to the high surface area, the obtained CNFs-derived carbon can be tuned during the carbonization process to enhance their specific capacitance performance and increase the amount of energy stored in the supercapacitor.\cite{146} The CNFs-derived carbon nanofiber composites could also provide better electromechanical stability than conventional CNT- or graphene-based composites, which make the material suitable for a stretchable electrical conductor.\cite{147} Moreover, the functionalized CNFs-derived carbon nanofibers showed promising potential as lithium ion battery anodes\cite{118,148}, catalyst (i.e. electrocatalyst for oxygen reduction reaction and hydrogen evolution reaction)\cite{29-31}, and supercapacitor\cite{149-151}.
CHAPTER III

PROBLEM ANALYSIS AND OBJECTIVES

As reviewed in chapter II, CNFs as nanocellulose are one of promising next generation sustainable building block due to their inherent physio-chemical-mechanical properties. Furthermore, the material can easily undergo modification that will further expand their potential applications. Although extensive investigations on nanocellulose process and characteristics have been reported, developing economical and environmentally-friendly modification technologies for CNFs are still a great challenge that limits the practical feasibilities in diverse engineering applications. In this thesis, we seek various functionalization approaches to introduce hydrophobic surface for each individual nanofiber and demonstrate their applicability as effective bio-fillers and bioabsorbent. The synthesis method and the impact of each modification on the material properties were extensively studied. In addition, we investigated the thermochemical transformation of CNFs and exploited the utilization of CNFs as potential renewable nanocarbon resources. Thus, the objectives of this research work are:

- to synthesize hydrophobic CNFs using coupling agent polymer and ascertain the reinforcing ability of surface functionalized CNFs on mechanical properties of hard, brittle thermoplastic polymer
- to synthesize hydrophobic CNFs in an aqueous medium, elucidate the mechanism of in situ modification approach, and comprehend the impacts of surface functionalized CNFs on the characteristics of aerogels
• to synthesize CNFs-derived carbon nanofibers, exploit different carbon surface functionalization methods, and ascertain the implication of surface functionalized CNFs-derived carbon nanofibers toward effective electrocatalyst material

3.1 Objectives

3.1.1 The synthesis of hydrophobic CNFs using coupling agent polymer and the reinforcing ability of surface functionalized CNFs on mechanical properties of hard polymer

In the fabrication of nanocomposite, excellent filler dispersion and surface compatibility between the filler and the matrix are the key aspects of producing outstanding mechanical properties. As reinforcing bio-fillers for hydrophobic polymers, neat CNFs possess a high number of surface hydroxyl groups that lead to the incompatible filler-matrix surface interaction and self-aggregation tendency. While surface hydrophobization of CNFs is one of the approaches taken to solve this issue, most of the reported methods in literature aimed toward hydrophobization of aggregated CNFs or adding compatibilizer agent simultaneously with polymer processing. In this regard, comprehensive investigations on facile hydrophobization method of individual nanofibrils, characterization of hydrophobic CNFs, and the role of hydrophobic CNFs toward the mechanical properties of nanocomposite are important. Moreover, the excellent reinforcing capability of CNFs should be ascertained by reinforcing hard polymer.

3.1.2 The synthesis of hydrophobic CNFs in aqueous medium, the mechanism of in situ modification approach, and the impacts of surface functionalized CNFs on the characteristics of aerogels

Following up on the reported hydrophobization method for CNFs, an organic solvent often used as the dispersion medium. Because CNFs are often prepared as a suspension in water to
prevent the aggregation of their nanofiber, preparing CNFs as a suspension in the organic solvent requires energy extensive method (i.e. through drying process to remove all water) or excess usage of solvent (i.e. through repetitive solvent-exchange). In most cases, the method causes nanostructure change due to unavoidable aggregation. Furthermore, it has been reported that some solvent could disrupt the crystalline region of CNFs. In this regard, finding an economical, non-toxic surface hydrophobization approach using aqueous medium is important. In addition, the method should also be optimized to accommodate minimal changes in terms of nanofiber morphology. The investigation on the properties of surface modified CNFs should be elucidated in form of low density material, such as aerogel. The use of aerogel could easily magnify the modification impact on overall CNFs properties.

3.1.3 The synthesis of CNFs-derived carbon nanofibers, the exploration of different carbon surface functionalization methods, and the implication of surface functionalized CNFs-derived carbon nanofibers toward effective electrocatalyst material

As a sustainable and inexpensive material, CNFs can be designed as bio-carbon nanofiber. The information available on carbonization method and the resultant properties of CNFs-derived carbon nanofibers are still very limited. Moreover, the pyrolysis and gasification method requires dry CNFs, which often generate CNFs aggregated form that could induce material heterogeneity during carbonization. On the other hand, hydrothermal CNFs would change the morphology of CNFs into aggregated sphere nanoparticles. Thus, it is necessary to find an alternative method that can produce carbon nanofibers from CNFs to satisfy this requirement. Additionally, investigating functionalization methods for CNFs-derived carbon nanofibers that would allow the material to compete with the traditional nanocarbon (i.e. graphene-based) is of particular interest. With the recent interest toward metal-free carbon electrocatalyst in the progress of fuel cell and hydrogen
gas generation, surveying the potential usage of CNFs-derived carbon nanofibers in this field is significant.

3.2 Approach determination

3.2.1 Surface hydrophobization

In order to achieve hydrophobic CNFs with high water repellency, the covalent interaction via grafting of the hydrophobic polymer is the preferred method to minimize the probability of wet leaching. While grafting of hydrophobic molecules can reduce the accessible hydroxyl group of CNFs surface, the presence of long carbon chain in the hydrophobic polymer will ensure that the introduction of non-polar entities can adequately block the surface hydroxyl groups of CNFs. In addition, the amount of grafting should be low enough to have lower surface energy without significantly affecting the morphology and mechanical properties of CNFs. Ideally, it is desirable to have uniform grafting across individual fibers. While more complex methods such as ATRP (atom transfer radical polymerization), NMP (nitroxide mediated polymerization), and RAFT (reversible addition-fragmentation chain transfer) could provide a robust control on the grafted polymer, the use of these methods often does not substantiate an economical benefit of the end-products. On the other hand, conventional methods such as free-radical polymerization is readily available in the larger-scale.

Because the homogeneity of hydrophobic CNFs is another important aspect, optimization of grafting preparation/procedure is often necessary. In order to mitigate any heterogeneity during functionalization step, a homogeneous mixture should always be prepared through adequate mixing or with the aid of rotor/stator homogenizer. In addition, multiple replications should be conducted to minimize any possible discrepancy. Good isolation of the modified CNFs after the synthesis is also important to eliminate the effect of excess impurities or unreacted reactants.
Repetitive steps of centrifugation, filtration, or Soxhlet extraction were used in all experimental work and could satisfy a good isolation method of the product.

3.2.1 Carbonization

Carbonization methods of CNFs would use two-step approaches: solvothermal (wet state condition) and pyrolysis (dry state condition). First, the solvothermal method was utilized to produce dispersed carbonized CNFs and avoid morphology change associated with hydrothermal. As the carbonized CNFs would solve nanofiber hornification issue, the dry carbonized CNFs could be easily dispersed to undergo pyrolysis. The pyrolysis was aimed to improve the inherent electrical property and surface area of CNFs-derived carbon.

In order to generate additional functionality to the CNFs-derived carbon, various surface functionalization methods were tested. Heteroatoms-doping, such as N, S, and P-doping, has been found as an effective method to improve the electrochemical properties of carbon material. Simultaneous doping and carbonization in the solvothermal method were adapted to avoid excess use of a doping agent that is commonly needed using pyrolysis method. Furthermore, surface recombination was also used to enhance the material effectiveness of carbon materials further as an electrocatalyst.
CHAPTER IV

WATER-FREE GRAFTING OF HYDROPHOBIC POLYMER VIA COUPLING AGENT

4.1 Introduction

In the recent developments of renewable and sustainable resources, cellulose nanofibrils (CNFs) have received major attentions because of their properties as high-performance biomaterials. Owing to their excellent mechanical strength, biodegradability, and low density,[152, 153] CNFs are attractive as potential nanoparticle reinforcement fillers in composite and often comparable to the conventional reinforcement fillers, such as aramids and glass fibers. CNFs commonly produced by mechanical disintegration of cellulose fibers are composed of both crystalline and amorphous regions and have typical dimensions of 20-40 nm in width and several micrometers in length.[8] CNFs dimensions display relatively high length-to-diameter aspect ratios with averaged value of 100.[152, 153] CNFs’ high aspect ratio could significantly improve the mechanical properties of the composite at very low contents.[154] Yet, one of the challenges in the current development lays in the limited performance of CNFs as filler reinforcement in hydrophobic polymeric matrices due to CNFs’ self-aggregation tendency and incompatible matrix-CNFS interfacial interaction.

Surface modification of CNFs has been an essential technique for engineering composite materials. Grafting the designed polymer onto CNFs surface is an effective and straightforward method to improve CNFs properties without affecting its biodegradability. The addition of a long
chain of the hydrophobic polymer would help in masking accessible hydroxyl groups of CNFs and limiting irreversible agglomeration of fibers upon drying.\cite{155,156} In addition, reducing the degree of hydrophilicity will lead a better interfacial adhesion with hydrophobic polymer matrix. Surface modification with polymer could be achieved by esterification of the coupling agent. One of the most common coupling agents reported in the literature is anhydride-modified copolymers such as maleated styrene block copolymer.\cite{157} Maleic anhydride-grafted styrene–ethylene/butylene–styrene (MA-SEBS) is one of the convenient maleated styrene block copolymers that displays balanced elasticity, excellent processability, and good thermal stability due to the properties of the SEBS thermoplastic elastomer. The anhydride group of this coupling agent reacts rapidly when in contact with the surface hydroxyl group of CNFs at elevated temperature. Thus, grafting coupling agent onto CNFs can be performed in their solid-state mixture, which has the main advantage of a very rapid process on the minute time scale compared to the typical solution grafting method, which requires hours or even days.\cite{158} Blending the coupling agent together with fillers and matrix polymer/monomer in a master batch is a common strategy of using coupling agent.\cite{159,160} To our knowledge, no attention has been devoted to determine CNFs functionalized by anhydride-modified copolymer prior to final composite processing. In this work, the modification process involving solvent treatment followed by coupling polymer agent grafting is subjected to chemical, physical and thermal characterizations. Furthermore, the work provides a mechanical evaluation of using both solvent-treated and surface-modified CNFs as reinforcement fillers for brittle-hard polymers such as polystyrene (PS).

4.2 Experimental Section

4.2.1 Materials
Cellulose nanofibrils (CNFs) prepared from mechanically refined bleached softwood kraft pulp were purchased from the University of Maine Process Development Center. Maleic anhydride-grafted polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (MA-SEBS) containing approximately 2 wt% maleic anhydride and polystyrene pellets with average molecular weight of 230,000 were obtained from Sigma-Aldrich. The 99% Tetrahydrofuran (THF) containing BHT as inhibitor was supplied by Alfa Aesar.

4.2.2 Grafting procedure

Modified CNFs were prepared from a solid mixture of CNFs and coupling polymer agent. In this study, a 0.35 wt% CNFs suspension in THF was prepared using solvent exchange method by successive centrifugation-redispersion steps. Maleated styrene block copolymer, MA-SEBS, added to the 0.35 wt% CNFs/THF suspension at a weight ratio of MA-SEBS to CNFs of 4:1 and mixed using mechanical stirring until completely dissolved. The mixture was dried by casting and evaporating all the solvent at room temperature. The completely dry solid was then cured to undergo grafting reaction at 150 °C over a 15-min period. The grafting chemistry followed the esterification mechanism as shown in Figure 4.1. The resulting cured solid was dispersed and homogenized in THF solution, followed by washing with THF to extract free polymer. After successive washing, a small amount of the modified CNFs/MA-SEBS in THF suspension sample was dried for characterization and the rest was stored for composite preparation.

![Figure 4.1 Esterification reaction between CNFs and maleated styrene block copolymer coupling agent](image)
4.2.3 Characterization of the grafted cellulose nanofibrils

A quantitative amount of polymer after grafting was measured by gravimetric method. The chemical structures of neat CNFs, THF treated CNFs and grafted CNFs were identified using Bruker Vertex 80 V attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The scan range was 4000 to 400 cm\(^{-1}\) with a resolution 4 cm\(^{-1}\). Surface morphology of samples was imaged with a LEO 1530 thermally assisted field emission scanning electron microscope (FE-SEM) in which all samples were gold-sputtered. Sessile drop contact angle measurement of film samples was captured using FTÅ200 Dynamic Contact Angle Analyzer (First Ten Ångstroms). Thermogravimetric analysis (TGA) and its first derivative were operated to assess moisture absorption, thermal degradation profile, and amount of grafted polymer using the PerkinElmer STA 6000. A 20 mg portion of the sample was heated from 35 to 600 °C at a rate of 10 °C/min under a flowing nitrogen atmosphere. X-ray diffraction analysis performed by scanning angular range (2\(\theta\)) from 5° to 35° at a step size of 0.02° on the X’Pert PRO X-ray diffractometer (PANalytical) was applied to estimate the percent crystallinity (\(\%\ Cr\)) of samples. The resulting diffraction patterns were deconvoluted using curve-fitting software (Fityk 0.9.8) based on Voigt functions to separate amorphous and crystalline contributions. The crystalline contribution of cellulose was fitted according to five peaks [(1-10, 110, 102, 200, and 004)] with the position of the maximum peak at 14.8°, 16.7°, 20.8°, 22.8°, 34.5°, respectively.\(^{[161]}\) Percent crystallinity was calculated as the ratio of the sum of non-overlapping areas of crystalline peaks to the total area of the crystalline peaks and the amorphous region, with a minimum value of intensity at 2\(\theta\) of 18°, as indicated in Equation (4.1)\(^{[162-164]}\)

\[
\%Cr = \frac{A_{101} + A_{101T} + A_{021} + A_{002} + A_{040}}{A_{101} + A_{101T} + A_{amp} + A_{021} + A_{002} + A_{040}}
\]  

(4.1)
Colorimetric titration was used to measure the amount of unesterified anhydride and its isomeric acid form. A small amount (0.175 g) of dried samples was dispersed in 75 mL of xylene at room temperature. 15 mL of 0.05 N potassium hydroxide solution in methanol was added and the mixture was agitated for 1 h at room temperature. The formed mixture was back titrated with 0.05 N sulfuric acid solution in methanol using methyl red as an indicator. The acid number was calculated as:

\[
\text{Acid Number} = AN = \frac{(A - B)N \times 56.1}{W}
\]  

(4.2)

where \( A \) is the volume (in milliliter) of the acid solution used to titrate the blank, \( B \) is the volume (in milliliter) of the acid solution used to titrate the sample, \( N \) is the normality of the acid solution, \( W \) is the weight (in gram) of the sample. The hydrolysis effect in this procedure was validated as commercial cellulose acetate showed only 3 wt% mass loss.

**4.2.4 Composite film and characterization**

Polystyrene pellets were mixed with the desired amount of CNFs suspension in THF at room temperature (0−2.0 wt% filler composite). The mixture was adjusted to 7.5 wt% solid content by adding THF and magnetically stirred for 1−2 h until all polystyrene pellets were dissolved. The polymer mixture was homogenized for 1 min and casted on an aluminum pan. Dry composite films were obtained after solvent evaporation overnight at room temperature. Sample films were placed in an oven for 60 min at 50 °C to ensure complete solvent removal.

Uniaxial tensile testing of composite films was carried out using Instron 5566 equipped with a 10 kN load cell. Strip specimens were prepared by cutting films into 100 mm × 10 mm strips with 0.12 mm average thickness. Sample conditioning and testing were prepared according to ASTM D882-12. Strip specimens were exposed in a temperature- and humidity-controlled
chamber (23 °C and 50 % RH) for at least 48 h prior to the test. The speed of testing was 5 mm/min. Sample break within the grip area was mitigated by lining a Kapton tape. A minimum of four samples was tested for each composite film and the average values were reported.

4.3 Results and Discussion

4.3.1 Effect of grafting on cellulose nanofibrils

The average weight of samples was found to increase by 33.7% gravimetrically after the grafting reaction, and the total polymer fraction of modified CNFs was estimated around 25.2 wt%. This value was relatively consistent with the value determined by the percent area of two consecutive peaks in the rate of mass loss curves from TGA. The peak area above 380 °C, which corresponded to polymer chain scission, showed 29.6 wt% polymer content.

![Estimated polymer fraction from thermal decomposition analysis for the modified cellulose nanofibrils](image)

Figure 4.2 Estimated polymer fraction from thermal decomposition analysis for the modified cellulose nanofibrils

To assess the changes in chemical structure due to polymer grafting, ATR-FTIR spectra were measured for each step of the grafting treatment. Figure 4.3 shows the ATR-FTIR spectra of neat CNFs from water suspension, THF pretreated CNFs, and polymer modified CNFs. All CNFs
features were observed in the three spectra: notably, a broad band of hydroxyl groups stretching at 3327 cm$^{-1}$, $\text{--CH}$ stretching at 2885 cm$^{-1}$, $\text{--CH}_2$ bending at 1427 cm$^{-1}$ and wagging at 1315 cm$^{-1}$, $\text{C}--\text{O}--\text{C}$ stretching of glycosidic linkage at 1161 cm$^{-1}$, $\text{C}--\text{O}$ stretching in the 1000–1100 cm$^{-1}$ range, and anomeric $\text{C}--\text{H}$ deformation at 895 cm$^{-1}$.[165-170] A slight change in band intensity was observed after solvent treatment, notably, at 986 cm$^{-1}$ associated with $\text{C(6)}--\text{O(6)}$ stretching in the crystalline region of cellulose.[165, 167, 169] In the case of the polymer modified CNFs sample, the additional absorption bands at 1700–1750 cm$^{-1}$ was identified as the monoester functional group.[171, 172] In addition, significant changes in the frequency of $\text{C}--\text{O}$ stretching in the 1000–1100 cm$^{-1}$ interval confirmed that esterification occurred. Reduction in peak intensity at 1034 cm$^{-1}$ corresponding to $\text{C(6)}--\text{O(6)}$ stretching may suggest that the new ester linkages arise from the primary alcohol. There was, however, no reduction of band intensity for hydroxyl groups stretching observed. It is possible that the unchanged hydroxyl group peaks originated from isomeric acid groups of anhydride from the coupling polymer agent. The characteristics of the grafted polymer could be witnessed through new absorption peaks of polystyrene aromatic ring deformation at 698 and 756 cm$^{-1}$, $\text{C}=$$\text{C}$ stretching ring vibration at 1583 and 1601 cm$^{-1}$, and $\text{--CH}_2$ asymmetric and symmetric stretching at 2922 and 2852 cm$^{-1}$.[173] Thus, these infrared spectra provided supporting evidence of a grafting reaction that occurred between cellulose and the coupling polymer agent.
Further information on the reaction between the hydroxyl group of cellulose and anhydride group of the coupling agent was inferred from acid number using colorimetric titration. The acid number (AN) values for THF-pretreated CNFs, pure coupling polymer agent, and polymer modified CNFs were 3.23, 19.32, and 13.78, respectively. The higher value of acid number value given by the coupling polymer agent suggested the presence of anhydride group and/or its isomeric acid, while a low acid number value for THF pretreated CNFs indicated that the presence of CNFs has little or no significant effect on acid-base reaction. For modified CNFs, the acid number value was closer to that of the neat coupling polymer agent than that of THF-pretreated CNFs. The trend concluded that only a small amount of maleic anhydride moieties from the polymer was actually grafted onto CNFs, while most of the non-grafted maleic anhydride moieties were transformed to their isomeric acids.

Figure 4.3 ATR-FTIR of neat CNFs, THF-pretreated CNFs, and polymer-modified CNFs.
Figure 4.4  FE-SEM images of (a,b) neat CNFs, (c,d) THF-pretreated CNFs, and (e,f) polymer-modified CNFs at two different magnification

Scanning electron micrographs revealed the surface morphology of neat CNFs, THF-pretreated CNFs, and modified CNFs. Figure 4.4 highlights the distinction of between cellulose and polymer surface. The characteristics of the cellulose surface can be observed by the entanglement of nanofibrils as they agglomerate as indicated in Figure 4.4a,b. Figure 4.4c,d shows that the surface morphology of solvent-treated CNFs remains the same as that of neat CNFs. In
comparison to the surface morphology of neat CNFs and THF-pretreated CNFs, the polymer surface on modified CNFs depicted on Figure 4.4e,f has a smoother surface as they entangle.

![Image](image1.png)

**Figure 4.5** Contact angle images of (a) neat CNFs, (b) THF-pretreated CNFs, and (c) polymer-modified CNF film

![Image](image2.png)

**Figure 4.6** Estimation of critical surface tension for modified CNFs film using Zisman plot

Surface wetting of CNFs samples was assessed using the sessile drop contact angle method. Figure 4.5 shows the captured images as water droplet was in contact with CNFs samples. As expected from neat CNFs and THF-pretreated CNFs film, the hydrophilic surface showed averaged contact angles of 48.2° and 46.4°, respectively. In comparison, the presence of grafted polymer on CNFs surface exhibited a hydrophobic property given the maximum contact angle of 130°. The hydrophobic property of the modified CNFs was also indicated by the low surface
energy of the material. Figure 4.6 shows the estimated critical surface tension of 25 mN m\(^{-1}\) for modified CNFs film samples using Zisman plot.

The moisture content of CNFs film before and after modification was also measured. The values indicated that polymer-modified CNFs contained 60% less water than neat CNFs. The decrease in moisture content was consistent with the higher contact angle value, in which hydrophobic polymer surface of modified CNFs can block the access of water to the hydrophilic part of CNFs. It is also found that moisture content of THF-pretreated CNFs was 28% lower than that of neat CNFs. Considering surface wetting characteristic was unchanged and a more highly porous film structure was obtained because of the lower capillary force acting on the cellulose nanofibrils\(^{174}\) the smaller amount of adsorbed moisture indicated that THF was successfully replaced water after the solvent-exchange, which corresponds to the assumption that the organic molecules introduced during solvent-exchange step are retained and included on drying\(^{175}\).

**Table 4.1** Sessile drop contact angle values, moisture absorption, onset temperature, and temperature at maximum weight loss rate from TGA, and crystallinity from XRD pattern.

<table>
<thead>
<tr>
<th></th>
<th>Contact angle (°)</th>
<th>Moisture absorption (%)</th>
<th>Onset temperature, (T_o) (°C)</th>
<th>Temperature at maximum weight loss rate, (T_m) (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs/Water</td>
<td>48.2 ± 2.8</td>
<td>5.0 ± 0.9</td>
<td>296.2 ± 7.3</td>
<td>332.7 ± 9.0</td>
<td>62%</td>
</tr>
<tr>
<td>CNFs/THF</td>
<td>46.4 ± 5.6</td>
<td>3.6 ± 0.9</td>
<td>305.4 ± 5.5</td>
<td>340.7 ± 8.7</td>
<td>55%</td>
</tr>
<tr>
<td>CNFs/MA-SEBS</td>
<td>130.0 ± 4.1</td>
<td>2.0 ± 0.4</td>
<td>314.7 ± 2.2</td>
<td>348.8 ± 4.6</td>
<td>42%</td>
</tr>
</tbody>
</table>

Figure 4.7a,b shows the TGA data on weight loss (Figure 4.7a) and the first derivative of weight loss (Figure 4.7b) as a function of temperature. The decomposition onset temperature (\(T_o\)) and temperature at maximum weight loss rate (\(T_m\)) are given in Table 4.1. The weight loss curve showed that the characteristics shape of the curve was unchanged after organic solvent treatment.
Treatment of CNFs with an organic solvent, however, showed an increase in both the onset temperature and the temperature at maximum weight loss rate. For polymer-modified CNFs, a two-step degradation curve was observed, in which the first step corresponded to the decomposition of CNFs and the second step corresponds to the decomposition of grafted polymer. A further increase in both the onset temperature and the temperature at maximum weight loss rate was found for polymer-modified CNFs. Furthermore, a higher temperature at the maximum weight loss rate for grafted polymer at 461.0 °C was achieved in comparison to that of the neat coupling polymer agent at 442.0 °C.

**Figure 4.7**  Thermogravimetric analysis: (a) weight loss curve and (b) the rate of weight loss curve for neat CNFs, THF-pretreated CNFs, and polymer-modified CNFs

Figure 4.8 shows the XRD pattern for neat CNFs, THF-pretreated CNFs, and polymer-modified CNFs. The spectra revealed a similar pattern for all samples, which suggests that original crystalline structures of CNFs could be well preserved after modification. Table 4.1 presents the calculated crystallinity for each CNFs film. A reduction in crystallinity was observed after exposure with THF and grafting with the polymer. The decrease in crystallinity after organic solvent treatment suggested that the solvent-exchanged process with THF was capable of
disrupting the ordering of cellulose crystal.\textsuperscript{[176]} A further crystallinity decrease after polymer grafting was also observed. However, instead of a disruption of the cellulose crystalline region, the decrease in the ratio of crystallinity was caused primarily because of an increase in the amorphous region originating from the grafted polymer.

\textbf{Figure 4.8} (a) XRD pattern for neat CNFs, THF-pretreated CNFs, and polymer-modified CNFs film. Deconvoluted of XRD pattern for: (b) neat CNFs, (c) THF-pretreated CNFs, and (d) polymer-modified CNFs.
4.3.2 Reinforcing effect of modified cellulose nanofibrils

Mechanical properties of polystyrene reinforced with CNFs was assessed using uniaxial tensile testing. Figure 4.9 and Table 4.2 show typical tensile stress-strain curves of brittle-hard polymer films and their measured tensile strength, Young’s modulus, and elongation at break for all the composites. The tensile strength, Young’s modulus, and elongation at break for control polystyrene film were 20.6 MPa, 1,764 MPa, and 1.32%. Significant improvement in the tensile strength and elongation at break for the composite at lower loadings of 0.5 wt% was observed. The composite showed a tensile strength of 27.5 MPa and elongation at break of 1.77%, which are 33 and 34 % higher than those of neat PS film, respectively. The improvements in both tensile strength and elongation at break are attributed to the high mechanical properties of CNFs and the ability of CNFs to bridge numerous crazes induced by the tensile stress.\cite{177} However, as a higher concentration of CNFs filler was added, a lower tensile strength and elongation at break of composites were observed. This behavior can be attributed to extensive fiber-fiber entanglement and self-agglomeration tendency of CNFs.

![Representative tensile stress-strain curves for neat PS and composite films with (a) THF-pretreated CNFs and (b) polymer-modified CNFs.](image)

Figure 4.9
The mechanical percolation effect of CNFs fillers was demonstrated by the measured Young’s modulus. It has been previously reported that cellulose nanoparticle would form a rigid continuous three-dimensional network linked through hydrogen bonding above the percolation threshold.\cite{178}

The percolation threshold based on the volume fraction for the filler can be estimated by the following Equation (4.3) \cite{177, 178}

\[
\varphi_c = \frac{0.7}{(L/D)}
\] (4.3)

where \( L \) and \( D \) are length and diameter of fillers respectively. In this manner, a CNFs percolation threshold of 1.0 wt% was obtained when using CNFs L/D of 100 and density values of 1.59 and 1.05 g cm\(^{-3} \) for CNFs and PS, respectively. The experimental percolation threshold as shown in Table 2 was captured by a large increase in Young’s modulus of composite comprising 1.5 wt% CNFs to 2,717 MPa compared to those of the composite comprising 0.5 and 1.0 wt% CNFs at 1,864 and 1,993 MPa, respectively.

**Table 4.2**  Tensile Strength, Young’s Modulus, and Elongation at Break of the PS composite at various loadings.

<table>
<thead>
<tr>
<th>Filler Content (wt%)</th>
<th>Filler</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>20.6 ± 1.4</td>
<td>1,764 ± 49</td>
<td>1.32 ± 0.04</td>
</tr>
<tr>
<td>0.5</td>
<td>CNFs/THF</td>
<td>27.5 ± 0.3</td>
<td>1,864 ± 29</td>
<td>1.77 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>CNFs/MA-SEBS</td>
<td>29.5 ± 0.7</td>
<td>2,150 ± 29</td>
<td>1.69 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>CNFs/THF</td>
<td>25.9 ± 2.1</td>
<td>1,993 ± 73</td>
<td>1.49 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>CNFs/MA-SEBS</td>
<td>30.2 ± 1.7</td>
<td>2,421 ± 96</td>
<td>1.50 ± 0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>CNFs/THF</td>
<td>23.3 ± 1.0</td>
<td>2,717 ± 82</td>
<td>1.10 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>CNFs/MA-SEBS</td>
<td>26.2 ± 1.6</td>
<td>3,060 ± 166</td>
<td>1.00 ± 0.03</td>
</tr>
<tr>
<td>2.0</td>
<td>CNFs/THF</td>
<td>20.4 ± 1.4</td>
<td>2,003 ± 124</td>
<td>1.17 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>CNFs/MA-SEBS</td>
<td>27.6 ± 0.9</td>
<td>2,781 ± 91</td>
<td>1.16 ± 0.07</td>
</tr>
</tbody>
</table>
The high improvement of tensile strength and elongation at break for the PS composite reinforced with modified CNFs was found to be relatively the same as that with unmodified CNFs at 0.5 wt%. This result suggested that the optimal reinforcing effect of CNFs filler could be achieved for 0.5 wt% loading without surface modification in PS matrices. The behavior, however, deviated as modified CNFs fillers loading increased above 0.5 wt%. In comparison to the unmodified CNFs suspension, polymer-modified CNFs fillers show a better-reinforcing effect as they could consistently maintain the strength of composite films in between 26.2 and 30.2 MPa. It can be inferred that the difference in tensile strength is attributed to the stronger filler-matrix interaction. In contrast, Young’s modulus and elongation at break of PS composite reinforced with surface-modified CNFs exhibit the similar trend as those with unmodified CNFs, in which a large jump of modulus is observed at 1.5 wt% CNFs and the highest elongation at break is obtained at 0.5 wt% CNFs. The result suggested that surface modified CNFs has little effect on Young’s modulus and elongation at break. It could also be inferred that fiber-fiber entanglement leading to a percolation network highlighted the changes in Young’s modulus and elongation at break for brittle-hard polymer reinforced with CNFs. The slight differences in both Young’s modulus and elongation at break for composites with the same amount of filler content could possibly be attributed to the introduction of some fiber aggregates during surface modification method leading to changes in the CNFs dimension.

4.4 Conclusions

Surface modification of CNFs through a solvent-exchanged followed by grafting of a maleated block copolymer coupling agent is reported. SEM showed a distinct difference in CNFs surface morphology before and after polymer grafting. The presence of the grafted polymer promoted the hydrophobic surface and better thermal stability. A decrease in the crystalline phase of CNFs was
found after organic solvent treatment, but no further significant reduction of CNFs crystals was observed during grafting. As a reinforcement filler of a brittle-hard polystyrene matrix, the addition of high-aspect-ratio CNFs at 0.5 wt% exhibited the best mechanical properties among those tried as portrayed by the higher tensile strength, Young’s modulus, and elongation at break. Surface-modified CNFs for higher filler loading supported the assertion that stronger interfacial compatibility between the CNFs and hydrophobic polymer matrix contribute to greater strength, while fiber-fiber interaction in the polymer matrix contributes more significantly to the changes in Young’s modulus and elongation at break.
CHAPTER V

IN-SITU HYDROPHOBIC POLYMER GRAFTING IN AQUEOUS MEDIUM

5.1 Introduction

With increasing environmental and ecological concerns to reduce water pollutants from organic contaminants frequently occurring from industrial wastewater and oil spills,[135, 179-182] there is a growing demand for more efficient, economical, and environmentally conscious methods to remove oil contaminants or improve oil–water separation. The use of 3D porous sorbent materials that possess outstanding absorption capacity, high oil–water selectivity, and low density appears as a promising approach.

Aerogels, defined as a class of light-weight nanoporous materials,[183-185] show appropriate characteristics in liquid absorption applications. Various types of aerogels as sorbent materials such as carbon nanofiber,[179] carbon nanotube,[180, 186] graphene,[180, 187] silica,[188, 189] cellulose nanofibrils,[95, 136, 190] polymers,[191, 192] and any combination of these with other polymers have been recently reported in the literature. Among these newly developed aerogels, the one based on cellulose nanofibrils (CNFs) provides advantages from an environmental and economical perspective as CNFs are the most abundant renewable resources and their aerogel fabrication requires neither solvent involvement nor complex processes. In addition, it has been well-documented that cellulosic-based aerogels are capable of absorbing a variety of organic solvents.[95, 145] Unfortunately, neat CNFs aerogels exhibit a poor tendency for oil/solvent pick up

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from water as abundant free hydroxyls on the CNFs surface can easily be saturated with water. Thus, modification of CNFs into the hydrophobic material is necessary.

Hydrophobic CNFs aerogels have been demonstrated to improve oil/solvent absorption from the water.[95, 135, 136, 182] Most literature reported methods for fabricating hydrophobic CNFs aerogels involve surface hydrophobization after freeze-drying by chemical vapor deposition.[95, 136, 182] This process often requires relatively expensive and toxic fluorine chemicals. Furthermore, the treatment may be a diffusion-limited process such that nonuniform functionalization between the outer layer and inner layer may occur for thick aerogel. For aerogel as an oil absorbent, it is necessary to functionalize the whole aerogel. Mechanical action may be applied to the aerogel, and the deformation of aerogel may occur (such as squeezing) during the application process. As it occurs, the exerted pressure could cause the water to penetrate the hydrophobic outer layer, and the hydrophobic inner layer would prevent water from being stored inside. Another possible approach for improving CNFs hydrophobicity is chemical grafting methods. Although a large variety of chemical grafting methods has been reported,[193] almost all available approaches require an organic solvent medium such as chlorosilane in toluene.[26, 104] Such a process will make aerogel fabrication more complex. In addition, the aerogel would contain inorganic species, Si, which could become an environmental concern upon chemical incineration for product disposal. Surface modification based on adsorption has also been widely used. However, in a comparison to a covalent bond, physical or ionic absorption is reversible, and hydrophobicity could be easily lost due to desorption of the modifiers. Thus, the more environmentally friendly method for CNFs surface modification directly in water to produce hydrophobic aerogel upon freeze-drying remains a challenge. In this study, we report an in situ surface modification method that can convert hydrophilic CNFs to hydrophobic species in aqueous medium directly, which has many advantages
compared to an organic solvent or vapor deposition methods. Furthermore, our method does not use expensive and toxic fluorine chemical or inorganic Si, which is an environmentally friendly method to convert hydrophilic cellulose surface to hydrophobic material *in situ*.

Practically, one pot surface modification of CNFs using hydrophobic styrene-acrylic monomer was conducted in an aqueous medium. Hydrophobic aerogels are prepared by freeze-drying of modified CNFs dispersion. The objective is to improve aerogel uptake of oil/solvent from water using nontoxic, less expensive materials and noncomplex equipment. The physical properties of aerogels, such as their low density, highly porous structure, large specific surface area, and excellent elastic property, are also maintained.

5.2 Experimental Section

5.2.1 Materials

Never dried cellulose nanofibrils prepared from mechanically refined bleached softwood kraft pulp were purchased from the University of Maine Process Development Center. The CNFs was mechanically produced without any chemical (carboxymethylation nor TEMPO) pretreatment. The charge density of CNFs is $-133 \text{ µeq g}^{-1}$, which was measured by charge titration. Potassium persulfate (KPS), sodium hydrogen carbonate (NaHCO$_3$), pyridine (99.8%, anhydrous), and toluene (99%) were obtained from Sigma-Aldrich. Isopar M Fluid was received from ExxonMobil Chemical. Methanol (HPLC grade) was obtained from Fisher Scientific. Dimethylformamide (DMF) was supplied by EMD Chemicals. Chloroform (99.8%) and dimethyl sulfoxide (DMSO) were provided by BDH Chemicals. Styrene (99%) containing TBC inhibitor, n-butyl acrylate (≥98%) stabilized with 4-methoxyphenol, and n-hexane (≥95%) were supplied by Alfa Aesar. Ethylene dimethacrylate (EDMA) was provided by Acros. Kymene™ 920A (a polyamide-epichlorohydin resin, a cross-linking agent for papermaking) was procured from
Ashland. All chemicals and solvents were used as received without further purification. Deionized water was used in all experiments. See Table 5.1.

### 5.2.2 Synthesis of hydrophobic CNFs

Polymerization with a monomer dropwise-feeding method was adapted. Specifically, 0.8 wt% CNFs suspension in water was charged into a 250 mL three-necked round-bottom flask connected with a nitrogen gas inlet, a reflux-condenser, and a mechanical stirrer, and mounted in an oil temperature-controlled bath. Nitrogen was bubbled through the suspension under 350 rpm stirring for at least 45 min at 80 °C to remove dissolved and vapor space oxygen. KPS was added as an initiator and the mixture was stirred for 15 min. A 1 mL portion of a monomer mixture containing n-butyl acrylate, styrene, and ethylene dimethacrylate was introduced dropwise over a period of 35 min. During monomer addition, the flask was continuously purged with a nitrogen atmosphere and the stirring rate was kept at 350 rpm. In this condition, monomer drops were presented in emulsion forms in the solution. After monomer addition was completed, the polymerization system was stirred for another 145 min to ensure complete reaction. A buffer was added at the end of the reaction to neutralize pH, and the mixture was allowed to reach room temperature. The suspension was washed with excess water through centrifugation–redispersion for 5 repetitions; 2.3 wt% hydrophobic polymer modified CNFs suspension in water was stored for further use.
Table 5.1 Basic recipe of *in situ* grafting method

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>1.0</td>
</tr>
<tr>
<td>Water</td>
<td>125</td>
</tr>
<tr>
<td>KPS</td>
<td>0.156</td>
</tr>
<tr>
<td>n-butyl acrylate</td>
<td>0.6 (dropped in)</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.25 (dropped in)</td>
</tr>
<tr>
<td>EDMA</td>
<td>0.08 (dropped in)</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.15</td>
</tr>
</tbody>
</table>

5.2.3 Preparation of hydrophobic CNFs aerogel

A 50 mL plastic tube was used as the mold to produce aerogels; 2 wt% kymene with respect to the solid weight of hydrophobic CNFs was added to the suspension. The mixture was stirred under mechanical stirring and transferred into the mold. The hydrophobic CNFs hydrogel was frozen in liquid nitrogen (−196°C) for 5 min. Aerogels were obtained by freeze-drying under 20 mTorr vacuum (VirTis Freezemobile 25EL Sentry 2.0) at room temperature for 4 days. The freeze-dried samples were cured in an oven at 120 °C for 3 h to allow the formation of cross-linked network between kymene and CNFs. The final aerogels were stored in the ambient environment before further use.

5.2.4 Characterization of aerogels

FT-IR spectra of hydrophobic aerogel samples were measured as KBr pellets on a Bruker Vertex 80 V spectrometer in the scan range of 4000–400 cm⁻¹ with a resolution 4 cm⁻¹.

Stability of leaching of the surface polymer was evaluated by Soxhlet extraction of aerogel sample using chloroform for 24 h. Samples were dried overnight at room temperature after extraction and subsequently dried under vacuum for 6 h at room temperature. The stability of polymer on CNFs surface to solvent leaching was confirmed by comparing the weight, water contact angle, chemical structure, and thermal decomposition before and after extraction.
Thermogravimetric analysis (TGA) and its first derivative were performed to estimate the amount of polymer on the surface and to assess thermal degradation profile using PerkinElmer STA 6000. A 20 mg portion of the sample was heated from 35 to 600 °C at a rate of 10 °C/min under a flowing nitrogen atmosphere.

Static sessile drop contact angle measurement of aerogel samples was captured using FTÅ200 dynamic contact angle analyzer (First Ten Ångstroms).

Surface morphology of samples was imaged by LEO 1530 thermally assisted field emission scanning electron microscope (FE-SEM), in which all samples were gold-sputtered.

The apparent density of aerogels was calculated by measuring the mass and dimensions using caliper and balance. Porosity of aerogels was evaluated as

\[
\text{Porosity (\%)} = \left(1 - \frac{\rho_{\text{aerogel}}}{\rho_s}\right) \times 100
\]

where \(\rho_{\text{aerogel}}\) is the apparent density of aerogels and \(\rho_s\) is the bulk density of hydrophobic cellulose, respectively.

The bulk density of hydrophobic cellulose was estimated as a composite of cellulose, polyamide-epichlorohydrin (PAE), and a styrene-acrylic copolymer

\[
\rho_s = \frac{1}{\frac{w_{\text{cellulose}}}{\rho_{\text{cellulose}}} + \frac{w_{\text{PAE}}}{\rho_{\text{PAE}}} + \frac{w_{\text{copolymer}}}{\rho_{\text{copolymer}}}}
\]

where \(w_{\text{cellulose}}\) is the weight fraction of cellulose, \(w_{\text{PAE}}\) is the weight fraction of kymene, and \(w_{\text{copolymer}}\) is the weight fraction of styrene-acrylic copolymer estimated from TGA. The bulk density of cellulose (\(\rho_{\text{cellulose}}\)) is taken as 1,600 mg·cm\(^{-3}\), while the bulk densities of PAE (\(\rho_{\text{PAE}}\)) and styrene-acrylic copolymer (\(\rho_{\text{copolymer}}\)) are assumed 1,150 and 1,080 mg·cm\(^{-3}\), respectively.
Moisture uptake of the hydrophobic CNFs aerogels was evaluated by measuring the total mass change as samples exposed to a temperature- and humidity-controlled chamber for 7 days given by

$$\Delta M(\%) = \left| \frac{W_s - W_b}{W_b} \right| \times 100$$

where $W_s$ is the current mass of aerogels after being exposed to a temperature- and humidity-controlled chamber (23 °C and 50 % RH) and $W_b$ is the baseline mass of aerogels after preconditioning under vacuum for 24 h at room temperature.

BET specific surface area was evaluated from nitrogen adsorption isotherms. Samples were conditioned overnight under vacuum at room temperature. Nitrogen adsorption isotherms were measured at −196 °C using a Quadrasorb EVO system from Quantachrome Instruments. BET analysis was performed in the low relative pressure range between 0.05 and 0.25. Measured BET specific surface area was compared with its theoretical value assuming individual nanofibrils given by

$$BET_{calc} (m^2/g) = \frac{4}{D \cdot \rho_{cellulose}}$$

where $D$ is nanofibrils width and $\rho_{cellulose}$ is the bulk density of cellulose. The average width of nanofibrils was assumed 37 nm corresponding to image analysis.

Compression tests of hydrophobic CNFs aerogels were performed using Instron 5566 equipped with a 10 kN load cell. Cylinder aerogels were compressed with a speed of 1 mm/min to 80% of its original length.

5.2.5 Oil/Solvent absorption performance

Cylindrical shaped aerogels with a dimension of 20 mm in length and 25 mm in diameter were dried under vacuum at room temperature for a minimum of 24h. Mass of dry aerogels ($m_0$)
was recorded and immersed in 50 mL of solvent/oil for 1 min. Solvent/oil-saturated aerogels were removed, and excess liquid on the surface was blotted using blotting paper. Mass of wet aerogels ($m_w$) was measured, and the absorption capacities ($C_{abs}$) were evaluated as

$$C_{abs}(w/w) = \frac{m_w - m_0}{m_0}$$

Theoretical solvent/oil absorption capacity of aerogels was also calculated on the basis of aerogel pore volume assuming a constant volume of soaked aerogels.

$$C_{calc}(w/w) = \frac{\text{Porosity} \times \rho_{solvent/oil}}{\rho_{aerogel}}$$

Aerogel reusability was evaluated by repetitive cyclic toluene absorption and evaporation sequence. Evaporation of wet aerogels was performed at room temperature overnight and subsequently dried under vacuum for 24 h.

Solvent-induced shape recovery of aerogels was investigated. Aerogels were immersed in an equal volume of pyridine and allowed to be fully saturated. The sample was compressed to 80% of its original length for 10 s and the weight was unloaded. Shape recovery was calculated by the shape change of aerogel measured by the length of cylinder shaped aerogel.

### 5.3 Results and Discussion

#### 5.3.1 In situ surface hydrophobization of CNFs

The principle of polymer surface modification based on suspension (surfactant-free emulsion) in the heterogeneous systems has been reported for various nanoparticles, such as carbon black,[194] silica,[195-198] and iron oxide.[199] As shown in Figure 5.1, free radical polymerization could occur on the CNFs surface. Specifically, aqueous free radicals initiate polymerization on dissolved monomer to form living oligomers. Although these living oligomers will further grow to form a homopolymer particle in water, in the absence of surfactant, these
living oligomers are unstable and have a tendency to improve their stability through adsorption onto a solid surface such as CNFs. Besides, the free radicals formed in water can also directly attach to the CNFs surface, which causes direct surface initiation of the polymerization. Further growth of the polymer chain on the surface is continued through coagulation of oligomers and polymerization of adsorbed monomers. Both homopolymerization and grafting take place simultaneously in the system and cause competitive reactions. The presence of competitive reactions highlights the importance of controlling the reaction condition to hinder homopolymerization and promote grafting. This was achieved by keeping the concentration of monomer in the reactor relatively low such that aggregation tendency of oligomers was limited. For this reason, a monomer dropwise method was adopted in this study. In addition to free radical formation on monomer, potassium persulfate has also been reported to generate cellulosic radicals. It was reported that free radicals could be formed through hydrogen abstraction at C1 or oxidative ring opening at C3.

Figure 5.1 Schematic representation of polymer surface modification based on dropwise suspension (surfactant-free emulsion) polymerization.
In the early attempt with n-butyl acrylate and ethylene dimethacrylate, the results showed that some large agglomerates of CNFs were present in the products. This is because self-adhesive characteristics of poly(butyl acrylate)\textsuperscript{[205, 206]} and the cross-linking of ethylene dimethacrylate would lead to bridging effects among fibrils. Reducing the amount of cross-linker is undesirable as the cross-linker promotes resistance toward organic solvent that could dissolve deposited polymer. In order to mitigate the agglomeration problem, a small part of n-butyl acrylate was substituted with styrene. The change in surface wetting of CNFs could be indirectly observed through the sedimentation of CNFs suspension, as reported in similar work using carbon black.\textsuperscript{[194]} Rapid sedimentation of CNFs suspension indicates the presence of high polymer content which completely masks the surface hydroxyl group. However, it is important to have some available hydroxyl groups on CNFs for aerogel preparation. This could be accomplished by controlling the total concentration of styrene-butyl acrylate monomer mixture in the system. Our synthesized surface-modified CNFs suspensions settled slowly after a day.

\textbf{5.3.2 Hydrophobic CNFs aerogels as bioabsorbent}

The as-prepared hydrophobic CNFs aerogels obtained using the styrene-acrylic modified CNFs showed an average density of 23.2 mg cm\textsuperscript{3}, the porosity of 98.5\%, and BET specific surface area of 18.4 m\textsuperscript{2} g\textsuperscript{-1}. The measured density, porosity, and BET specific surface area are consistent with data reported previously for CNFs aerogel prepared under similar conditions.\textsuperscript{[136, 183, 185, 190]} The lower value of measured BET specific surface area as compared to the theoretical BET surface area for an individual fibril, 67.6 m\textsuperscript{2} g\textsuperscript{-1}, indicated the presence of CNFs aggregation upon freeze-drying.

The grafting of polymer on the surface of CNFs was identified from ATR-FTIR spectra of hydrophobic CNFs aerogels as shown in Figure 5.2. The pronounced band appearing at 1732 cm\textsuperscript{-1}
together with the less pronounced bands at 1261, 2937, and 2959 cm\(^{-1}\) correspond to C=O ester, C─O acrylate, ─CH\(_2\) asymmetric, and ─CH\(_3\) asymmetric stretching of n-butyl acrylate and ethylene dimethacrylate. The peak at 702 cm\(^{-1}\) is associated with the presence of the polystyrene aromatic ring. These results suggest that copolymerization of n-butyl acrylate, styrene, and ethylene dimethacrylate is present as attached polymer. The spectra also show that the characteristics of CNFs were maintained as indicated by anomeric C\(_1\)─H deformation at 899 cm\(^{-1}\), C─O stretching in 1034─1111 cm\(^{-1}\) range, C─O─C stretching of glycosidic linkage at 1161 cm\(^{-1}\), ─CH\(_2\) wagging at 1317 cm\(^{-1}\), ─CH\(_2\) bending at 1429 cm\(^{-1}\), and a broad band of hydroxyl groups stretching at 3339 cm\(^{-1}\).\(^{[167, 169, 170, 207, 208]}\)

![Figure 5.2 ATR-FTIR of hydrophobic CNFs aerogels.](image)

A two-step degradation profile was observed from TGA weight loss curve as indicated in Figure 5.3. The second degradation step starting from 380 °C confirmed the coated polymer chain scission. The amount of polymer deposited on the surface of cellulose nanofibrils was further estimated using the rate of weight loss curves in TGA through the percent area of the second peak.
The as-prepared hydrophobic CNFs aerogels contained 15.3 wt% copolymer located on CNFs surface.

![Figure 5.3](image1.png) **Figure 5.3** Weight loss curve and the rate of weight loss curve as a function of temperature.

The presence of styrene-acrylic copolymer covered on the surface of cellulose nanofibrils would create lower surface energy.\cite{209-212} Furthermore, microporous structure of aerogels can form air pockets that exhibit a Cassie-Baxter wetting state leading to greater surface hydrophobicity. Such hydrophobic CNFs aerogels demonstrated neither water-wettable nor water-absorbing characteristics, as shown by apparent water contact angle of 149° (Figure 5.4a) and aerogel ability to stay afloat on the water surface (Figure 5.4b,c). The hydrophobic CNFs aerogels, however, still allow organic solvent/oil to be absorbed (Figure 5.4d). Excellent oil extraction from water by hydrophobic aerogels was also observed (Figure 5.4e–h). Typical neat CNFs aerogels would be fully wetted as they are in contact with water leading to their inability to pick up chloroform under water. In contrast, hydrophobic CNFs aerogels form water barriers around themselves and only collect chloroform. Similar wetting behavior was also reported in other hydrophobic CNFs aerogels performed using different modification methods.\cite{95, 135, 136, 182, 190} Experiments on water vapor absorption and water uptake upon immersion were conducted for the
as-prepared hydrophobic CNFs aerogels. The aerogels showed 4.1% mass increase after processing for 7 days at 23°C and 50% RH, while their water uptakes were up to 0.5 g/g aerogels. As a comparison, neat CNFs aerogels exhibited 37.3 g water uptake/g aerogels, which is 70 times higher than the hydrophobic CNFs aerogels. These results indicate the aerogels reported in this work have high selectivity in absorbing oil from water.

![Figure 5.4 Wetting characteristics of hydrophobic CNFs aerogels.](image)

The hydrophobic aerogel prepared in this method has hydrophobicity for the whole aerogel and not just for the outermost layer. Although treating just the outermost layer of aerogel would provide the described water barrier characteristic, a small amount of water could still penetrate the aerogel through the presence of large pores. The hydrophobic inner part of aerogel would prevent any water from swelling the fiber.

The stability of a cross-linked polymer layer on the CNFs surface to solvent leaching was verified (Figure 5.5a,b). Overall mass loss of 9.9 wt% was recorded through gravimetric
measurement, while estimated copolymer loss based on the difference in the peak area of polymer scission using TGA is 3.7 wt% (Calculated based on Figure 5.5b). The slight mass loss upon leaching is originated from desorption of ungrafted polymer and non-cross-linked polymer. The reduced amount of coated polymer on the cellulose surface does not significantly affect surface hydrophobicity of the aerogel as shown by the high water contact angle (144°, Figure 5.5d).

The morphology of hydrophobic CNFs aerogels was examined and compared with neat CNFs aerogels using FE-SEM as shown in Figure 5.6a–f. The micrographs of the internal structure of aerogels taken at radial cross-section show a similar macroporous structure for both neat and
hydrophobic CNFs aerogels. All CNFs aerogels exhibited a highly porous open-structured skeleton that comprises sheets formed by CNFs aggregates and interconnected with individual CNFs (Figure 5.6a,b). The same characteristics have also been reported in the previous literature using the same vacuum freeze-drying method.\textsuperscript{[183, 185, 213]} The similarity between parts a and b in Figure 5.6 suggested that the aggregation tendency of nanofibrils in suspension upon chemical modification prepared in this procedure was minimal compared to the aggregation introduced upon freeze-drying. The change in the surface morphology before and after modification was further observed (Figure 5.6e,f). The presence of the deposited polymer layer generates irregular roughness on fiber surface as indicated by the patchy texture of grafted polymer. The masking of surface hydroxyl groups also leads to lower apparent fibrillar joints in the network (Figure 5.6b,d,f). It is expected that the decrease in fibrillar network is caused by less accessible hydrogen bonding on the surface to form covalently bonded interfiber bond entanglement.
Figure 5.6 FE-SEM images of (a,c,e) neat CNFs aerogels and (b,d,f) hydrophobic CNFs aerogels at different magnification.

Hydrophobic CNFs aerogels are softer than neat CNFs aerogels. Figure 5.7 shows the compressive strain-stress curves for both aerogels of the same density. Neat CNFs aerogels exhibit linear elastic deformation region at low strain below 5% followed by a gradual transition to nonlinear elastic collapse and densification region, while no apparent linear elastic deformation region could be observed for hydrophobic CNFs aerogels. Densification regions for
both CNFs aerogels start gradually above 60% strain. The compressive modulus and maximum stress at 80% strain are significantly reduced for hydrophobic CNFs aerogel. The specific modulus values extracted from a the low strain value for the neat and hydrophobic CNFs aerogels are 2.7 and 0.4 MPa cm\(^{3}\cdot g^{-1}\), respectively. The maximum compressive stress at 80% strain also decreases from 157 kPa for neat CNFs aerogels to 78 kPa for hydrophobic CNFs aerogels. Lower mechanical properties correspond to the lower both interfiber hydrogen bonding and physical entanglement,\(^{95, 184}\) which are consistent with previous FE-SEM images.

\[
\left( \frac{L}{D} \right)^2 = \frac{9E_{\text{CNF}}f}{32E_{\text{aerogel}}} \]

\(E_{\text{CNF}}\) is the modulus of CNFs with a mean width of 37 nm (assumed as 84 GPa), \(E_{\text{aerogel}}\) is the measured compressive modulus of aerogel, and \(f\) is the volume fraction of CNFs in aerogel (given by \(\rho_{\text{aerogel}}/\rho_s\)). The calculated aspect ratios for the interconnected fibrillar joints for both neat and hydrophobic CNFs aerogels are 79.1 and 205.2, respectively. These values suggest that as grafted

![Mechanical properties of neat and hydrophobic CNFs aerogels.](image)

**Figure 5.7** Mechanical properties of neat and hydrophobic CNFs aerogels.
polymer masked the free accessible hydroxyl groups of CNFs surface, interfiber hydrogen bonding area formed during freeze-drying for hydrophobic CNFs aerogels was reduced by a factor of 2.6 compared to that of neat CNFs aerogels.

Oil/solvent absorption performance of hydrophobic CNFs aerogels was investigated for various liquids with different polarity, viscosity, and density. Hydrophobic CNFs aerogels exhibit absorption affinity toward both polar and nonpolar liquids as indicated by similar absorption capacities for Isopar M Fluid and methanol at 29.0 and 28.2 g·g⁻¹, respectively. In addition, the viscosity difference between those liquids has no influence on the amount of absorbed liquid. Absorption capacities of hydrophobic CNFs aerogels depend strongly on liquid density as indicated in Figure 7. The absorption capacities for toluene with a density of 0.863 g·mL⁻¹ and chloroform with a density of 1.49 g·mL⁻¹ are 30.0 and 46.6 g·g⁻¹, respectively. These values are close to the previously reported hydrophobic nanocellulose aerogels prepared by freeze-drying.[136, 190]

The oil removal capacity of CNFs aerogel is governed primarily by total pore volume of aerogel. Calculated pore volume per gram of hydrophobic CNFs aerogels was 42.4 cm³. Figure 5.8 indicates that oil uptake of hydrophobic CNFs aerogels could fill approximately 73-84% of theoretical pore volume. The value suggests that at least 16% of total pore volume is inaccessible to the wetting liquid. This is due to the presence of trapped air, which is indicated by the presence of air bubble upon compressing soaked aerogels in the liquid. Also, the lower volume of the maximum absorption compared to the calculated one may be due to the shape change, such as aerogel shrinking, upon removal of wet aerogels from their immersed liquid. The accessibility of pore volume for higher density liquid, such as DMSO and chloroform, was further lowered by 11%. A literature reported the dependence of aerogel density with liquid absorption capacity, in
which denser aerogels held the absorbed liquid better.\textsuperscript{[95]} These results suggest that small pores with relatively thick walls are important parameters for keeping trapped liquid inside and providing high structural strength against pore deformation. Thus, it is believed that the as-prepared aerogels do not have enough small pores to maintain their optimum liquid sorption capacity for heavy oil. The inadequate amount of small pores was in agreement with the presence of CNFs aggregation upon freeze-drying as shown by previous SEM images in Figure 5.6b,d,f. It is expected that even though CNFs aggregation would not change the total pore volume of aerogel, it may shift the pore size distribution toward larger pores.

![Figure 5.8](image.png)

**Figure 5.8** Absorption capacities of various oils for hydrophobic CNFs aerogels and their theoretical pore volume capacities.

Reusability of hydrophobic CNFs aerogels as oil/solvent absorbents was investigated by successive absorption-evaporation of toluene as shown in Figure 5.9. During liquid evaporation at room temperature in the first cycle, structural deformation of aerogels occurred as macropores collapsed permanently leading to reduced pore volume. The lower pore volume of dry aerogels for the next repeat cycle leads to lower oil uptake. As a result, a 60% decrease in toluene absorption capacity in the second cycle from the first cycle was detected during solvent uptake. The maximum
absorption capacity, however, was not decreased after second repeat cycle as no further structural deformation was observed.

![Graph](image)

**Figure 5.9** Absorbent reusability of hydrophobic CNFs aerogels over five cycles

Neat CNFs aerogels, as shown previously, have a water-induced shape recovery property. As the presence of grafted polymer contributed primarily to alter surface wetting characteristics of aerogels, the solvent-induced shape recovery property of CNFs aerogels could still be retained. However, because the surface modification changes the CNFs’ hydrophobicity so the capillary force of aerogel pores as well as the swellability of CNFs, the solvent that could stimulate the shape recovery of the compressed aerogel should be different for modified and unmodified CNFs aerogels. Instead of water that was used in the previous study for neat aerogel shape recovery, it was found that pyridine could stimulate the shape recovery of hydrophobic aerogel as shown in Figure 5.10a–d. The mechanism for pyridine stimulated shape recovery of hydrophobic CNFs aerogels should be similar to that for water stimulated shape recovery of neat CNFs aerogels. Specifically, a solvent with high polarity and moderate surface energy, such as pyridine and DMSO, would penetrate polymer layer and partially swell the cellulose. The swelled cellulose
would expand and create open pore structure, which leads to more liquid penetration. As liquid diffuses into the cellulose network, a hydrodynamic force is introduced allowing the deformed aerogel to expand and recover its shape within several minutes.

Figure 5.10 Sequential photograph of pyridine-induced shape memory of hydrophobic CNFs aerogel: (a) aerogel initially immersed in equal volume of pyridine, (b) wet aerogel deformation by compressing to 80% its original length, (c) temporary shape upon unloading, (d) shape recovery after 5 min.

5.4 Conclusion

Surface modification of cellulose nanofibrils using styrene-acrylic monomers was successfully obtained in an aqueous medium with a monomer dropwise polymerization method. No fluorine chemical is used in the aerogel and the hydrophobic modification of CNFs was done in water directly rather than in organic solvent. Hydrophobic aerogels were presented using the modified CNFs. The hydrophobic aerogels displayed similar characteristics as those of previously reported CNFs aerogels with fluorine chemical modification, including low density, highly porous structure, and excellent elasticity. The performance of hydrophobic aerogels as absorbents showed high oil removal efficiency from water. The maximum absorption capacities for various oils and solvents are similar to those prepared using chemical vapor deposition method. The hydrophobic aerogels also demonstrated solvent-induced shape recovery ability in several minutes by using pyridine as a solvent.
CHAPTER VI

CELLULOSE NANOFIBRILS-_DERIVED CARBOCATALYST

6.1 Introduction

With a growing interest in renewable energy technologies as well as chemical conversion, developing effective and affordable catalysts is extremely important. Although noble-metal based catalysts have a high intrinsic catalytic activity toward sluggish electrochemical reactions, such as oxygen reduction reactions (ORR), oxygen evolution reactions (OER), and hydrogen evolution reactions (HER), they are expensive and often susceptible to the crossover effects.[216, 217] Commercially-viable strategies are proposed by substituting noble-metal catalysts with metal-free catalysts. Among them, carbon-based catalysts have stimulated enormous interest due to their low cost, environmental friendliness, and abundance. Furthermore, both theoretical and experimental studies have shown that functionalizing carbon-based materials with heteroatoms dopants, such as nitrogen, phosphorus, sulfur, and boron, would improve both electrochemical properties and catalytic activities.[123, 217-221] Doped carbon nanomaterials have been successfully prepared as high-performance HER electrocatalysts.[221-227] In particular, co-doping two heteroatoms with different electronegativities (N/P or N/S) on graphene material could boost its electrocatalytic activity attributed to their synergistic effect. However, to the best of our knowledge, most of the reported literature rely on rather expensive carbon materials, such as graphene oxide, and only limited work has been performed using sustainable materials as their carbon precursors.

This chapter has been modified from the paper submitted: Facile Approach for Synthesis of Doped Carbon Electro catalyst from Cellulose Nanofibrils toward Metal-Free Oxygen Reduction and Hydrogen Evolution
Cellulose nanofibrils (CNFs), as biomass nanomaterials derived from plants, have drawn a great interest as promising raw materials for preparing carbonaceous materials due to their abundant availability, sustainability, biodegradability, inherent nontoxicity, and encouraging potential to be produced in industrial-size quantities.\textsuperscript{[5, 7, 228]} Furthermore, CNFs, owing to its nanoscale diameter and high aspect ratio, can easily form an interconnected three-dimensional network structure, which could facilitate better mass transport and improve electrokinetics in achieving enhanced electrocatalytic performance.\textsuperscript{[229-231]} Recently, N-doped carbon materials derived from nanocellulose have been synthesized and demonstrated experimentally as effective ORR carbocatalysts.\textsuperscript{[29, 30, 232]} The carbocatalysts cannot only promote ORR activity comparable to traditional Pt-based electrocatalysts but also exhibit better electrochemical stability toward methanol contamination. However, there is still no report using N, P, or S-doped nanocellulose based carbon materials as the effective electrocatalysts for HER.

Herein, bifunctional metal-free carbocatalyst toward HER and ORR using N,S-doped carbon nanofibers/N,P-doped graphitic carbon hybrid was synthesized through the deposition of N,P-enriched complex particles onto N,S-doped carbon fiber network. The as-synthesized carbon hybrids showed promising ORR and HER activities, as indicated by their low onset potential and high exchange current density. Thus, this approach is an encouraging method of deriving nanocellulose to construct catalytically active carbon nanofibers toward both HER and ORR.

\section*{6.2 Experimental Section}

\subsection*{6.2.1 Materials}

Never dried cellulose nanofibrils prepared from mechanically refined bleached softwood kraft pulp were purchased from the University of Maine Process Development Center. The CNFs were produced mechanically without any chemical (such as carboxymethylation nor TEMPO)
pretreatment. Tetrahydrofuran (THF) was obtained from EMD. Melamine was provided by BeanTown Chemical. 50 wt% phytic acid was supplied by TCI. Ammonium thiocyanate, 5 wt% Nafion® perfluorinated resin, and potassium hydroxide was procured from Sigma-Aldrich. Reagent alcohol, acetone, and sulfuric acid were received from BDH. Commercial 20 % Pt/C as electrocatalyst reference was purchased from Fuel Cell Store. All chemicals and solvents were used as received without further purification. Deionized water was used in all experiments.

6.2.2 Catalyst preparation

Cellulose nanofibrils suspension in water was solvent exchanged to THF by successive centrifugation-redispersion procedure. 15 g of 1.75 wt% CNFs suspension in THF underwent solvothermal with 0.165 g ammonium thiocyanate at 245 °C for 4.5 h in a 45 mL Parr Teflon-lined stainless steel autoclave. The product was thoroughly washed with acetone followed by DI water to obtain the doped carbon nanofibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NSC (g)</th>
<th>Melamine (g)</th>
<th>Phytic Acid (mL)</th>
<th>MPA:NSC (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>0.020</td>
<td>0.08</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
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<td>5</td>
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<tr>
<td>3</td>
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<td>0.155</td>
<td>0.63</td>
<td>10</td>
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<tr>
<td>4</td>
<td>0.025</td>
<td>0.31</td>
<td>1.25</td>
<td>20</td>
</tr>
</tbody>
</table>

Carbon nanocomposites were prepared by mixing the solvothermal-treated CNFs-derived N,S-doped carbon nanofibers (NSC) with the complex particles of melamine-phytic acid (MPA) according to Table 6.1. For each nanocomposite formulation, 50 wt% phytic acid in water was added into dissolved melamine solution with a molar ratio of 1:1 under stirring for 5 min. The aqueous solution was further cooled down to 5 °C, in which some white precipitates appeared. After at least 2 h, NSC was added and the mixture was further incubated at 5 °C for overnight under static conditions to give the desired NSC/MPA ratio. The solid mixture was separated from
the dissolved excess materials using a centrifuge and further re-dispersed in water. A uniform mixture was obtained under sonication for 30 min. The suspension was allowed to be sedimented before lyophilization under 20 mTorr vacuum (VirTis Freezemobile 25EL Sentry 2.0, USA) at room temperature for 4 days to form the carbon nanocomposite. Pyrolysis of the carbon nanocomposite was performed under nitrogen atmosphere at 400 °C for 2 h followed by another 2 h at 900 °C. The pyrolysis of neat MPA has been tested to yield approximately 2 % solid carbon material.

**6.2.3 Characterization of catalyst material**

Surface morphology of the samples was imaged by LEO 1530 thermally assisted field emission scanning electron microscope (FE-SEM) coupled with INCA 200 X-Sight de Oxford instruments for energy-dispersive X-ray spectroscopy (EDS) analysis. X-Ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo K-Alpha instrument equipped with monochromatic AlKα radiation at 1486.6 eV X-ray source. Charge neutralization was performed using a low energy flood gun. The samples were supported on Cu substrate. The spectra were calibrated by setting the C1s peak at 284.8 eV. Raman spectroscopy was recorded on a Thermo Nicolet Almega XR instrument with a 488 nm excitation laser beam wavelength. The intensity of the D and G bands was measured from the maximum height of the peaks. X-ray diffraction (XRD) was conducted by scanning angular range (2θ) from 10° to 60° at a scan rate of 1°/min on X’Pert PRO X-ray diffractometer (PANalytical) with CuKα radiation. BET specific surface area was determined from the linear region of the nitrogen adsorption curve in the relative pressure range between 0.05 and 0.25, while the total pore volume was measured at P/P0 value of 0.99. The samples were conditioned for 20 h under vacuum at 150 °C. N2 sorption analysis was carried out at -196 °C using a Quadrasorb EVO system equipped with QuadraWIN software to give the
calculated surface area and pore size. Quenched Solid Density Functional Theory (QSDFT) model analysis was used in the evaluation of pore size distribution considering the effects of surface roughness and chemical heterogeneity of carbon.

6.2.4 Electro catalytic activity

The electrocatalytic activities toward ORR and HER were performed using a CHI 760D electrochemical workstation (CH Instruments) in a three-electrode configuration with a working electrode, a graphite rod as a counter electrode and an SCE reference electrode. A working electrode was fabricated by coating a mirror polished glassy carbon electrode with a suspension of carbon sample. Specifically, the suspension was prepared by dispersing 5 mg of each carbon sample in a solution composed of 350 µL of reagent alcohol, 260 µL of water, and 95 µL of 5 wt% Nafion® binder. A homogeneous suspension was obtained after sonication for 30 min. A 2.5 µL of the as-prepared suspension was dropped onto the glassy carbon electrode with a diameter of 3 mm (0.07065 cm² geometric area). The catalyst loading on the electrode was estimated to be 0.25 mg cm⁻². The working electrode was dried at 65°C before electrochemical measurement. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) for ORR tests were conducted in an O₂-saturated 0.1 M KOH electrolyte with a scan rate of 5 and 100 mV s⁻¹, respectively. The electrolyte was bubbled with high-purity oxygen flow for about 20 min before each test and kept constant throughout the whole experiment. The carbon catalyst durability was tested using 1,500 continuous CV cycles and a constant voltage of its maximum cathodic peak. The HER activity was performed in an N₂-saturated 0.5 M H₂SO₄ electrolyte using LSV with a scan rate of 2 mV s⁻¹. The stability of catalyst material was also tested by 1,500 continuous CV cycles from 0 to -0.8 V (vs. SCE) and 15,000 s of continuous operation at a constant potential of -0.7 V (vs. SCE). All potentials are referenced to the reversible hydrogen electrode (RHE) based on the Nernst equation:
\[ E_{RHE} = E_{SCE} + 0.059 \text{ pH} + 0.2412. \]

The electrochemical double layer capacitance \( (C_{dl}) \) of carbon catalysts was conducted to estimate their effective electrochemical surface area. The measurement was performed by sweeping CV at different rates in the region of 0.15-0.25 V (vs. RHE) using a 0.5 M Na\(_2\)SO\(_4\) electrolyte. The values of \( C_{dl} \) were calculated as half value of the slopes in a linear relationship between the capacitive current (\( \Delta \mid J_a - J_c \mid \)) at 0.2 V (vs. RHE) and the CV scan rates. The calculated electrochemical double layer capacitance was further utilized to normalize the catalyst activities in relation to both their surface area and loading.\[^{222, 226, 233}\]

### 6.3 Results and discussion

#### 6.3.1 N,S-doped CNFs carbon nanofibers (NSC)

In the present study, highly porous N,S-doped 3D carbon nanofibers (NSC) was first prepared using \textit{in situ} solvothermal carbonization of CNFs in the presence of ammonium thiocyanate salt. In this step, salt molecules decomposed into reactive N/S species (NH\(_3\), H\(_2\)S, and CS\(_2\)), in which both nitrogen and sulfur atoms are easily fixed onto the polycyclic aromatic carbon framework formed from the dehydration and polycondensation of cellulose.\[^{234, 235}\] The average yield of an insoluble solid upon solvothermal carbonization was 55.8 \% by gravimetric measurement. An additional weight loss up to 75.3 wt\% was observed after high-temperature pyrolysis.

The morphology of the resulting N,S-doped carbon aerogel was characterized by scanning electron microscopy. As shown in Figure 6.1a and 6.1b, the use of solvothermal carbonization followed by pyrolysis could retain the morphology of neat CNFs, in which an interconnected three dimensional porous network is clearly observed. In addition, no agglomerated microsphere is found on the fiber surface, which is different from other reported carbonized cellulose.\[^{114, 118, 236}\]

The interconnected carbon network is beneficial to facilitate efficient long-range transport of
electrons. Composition mappings of pyrolyzed NSC were analyzed using EDS. Figure 6.1d and 6.1e show homogeneous distributions of nitrogen and sulfur heteroatoms across the surface of carbon nanofibers.

Figure 6.1 (a) SEM image of neat CNFs aerogel. (b) SEM image of carbonized NSC revealing its 3D network nanostructure and the corresponding EDS elemental mapping of (c) carbon (red); (d) nitrogen (green); (e) sulfur (yellow); and (f) oxygen (blue)

The carbon structure, quantitative amount of doping, and chemical state of dopants greatly influence the electrocatalytic performance of carbon-based material.[237] Raman spectroscopy is an important tool to investigate the structural information of carbon-based materials and to give an
insight into the electrochemical properties of the carbon material. As presented in Figure 6.2a, Raman spectra show the characteristic peaks of graphitic layers (G band) at around 1,587 cm$^{-1}$, disordered carbon at around 1,362 cm$^{-1}$ (D band), and the second order of the D band (2D band) at around 2,830 cm$^{-1}$. The presence of a broad and weak 2D band indicates the characteristic feature of few-layered graphene lattices in the as-prepared carbon samples. Figure 6.2a also indicates sharper first-order D and G bands with increasing pyrolysis temperature. This trend suggests that NSC undergoes an increase in carbon crystallite size and more graphitic domains with increasing pyrolysis temperature. The same result has also been confirmed in literature.[238] Larger crystallite size, which consists of a highly-ordered carbon structure, is a preferred structural property for carbocatalysts as it would enhance the electron migration into or out of deeper carbon structure. In addition, Figure 6.2a depicts an increasing intensity ratio of the D band and G band ($I_D/I_G$) with increasing pyrolysis temperature. The Raman $I_D/I_G$ ratio is a good indicator to represent the level of defects in carbon material caused by the integration of heteroatoms species in the carbon framework. Therefore, an increasing $I_D/I_G$ ratio until a pyrolysis temperature of 900 °C may indicate that more in-plane heteroatoms (graphitic-like) exist, which agrees with the results of XPS presented in Table 6.2. Correspondingly, the decrease in $I_D/I_G$ ratio with pyrolysis temperature of a 1,050 °C implies the severe decomposition of in-plane heteroatoms. Thereby, pyrolysis of NSC at 900 °C (NSC900) should be assumed as the most optimal functionalized carbon structure.
Table 6.2 Physiochemical properties of various NSC samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (At. %)</th>
<th>Raman $I_D/I_G$ ratio</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume at $P/P_0=0.99$ (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
<td>S</td>
<td>O</td>
</tr>
<tr>
<td>NSC</td>
<td>68.2</td>
<td>9.4</td>
<td>2.5</td>
<td>19.9</td>
</tr>
<tr>
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<td>78.1</td>
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<td>1.1</td>
<td>5.3</td>
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<td>13.4</td>
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<tr>
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<td>7.5</td>
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<tr>
<td>NSC1050</td>
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<td>1.6</td>
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<td>4.3</td>
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Figure 6.2 (a) Raman spectra of NSC samples pyrolyzed at different temperatures, (b) XRD pattern of NSC900, (c) $N_2$ physisorption isotherms, and (d) corresponding pore size distribution of NSC samples pyrolyzed at different temperatures

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Further structural characterization of carbon material was conducted by XRD. Figure 6.2b indicates that NSC900 exhibits two diffraction peaks at 24.9° and 43.5°. The two broad peaks of the XRD pattern suggest that there are partially disordered carbon structures. The higher graphitic interlayer spacing at 3.53 Å compared to that of perfect graphite at 3.35 Å indicates a turbostratic structure. Based on the Scherrer equation, the crystal thickness of (002) lattice is 7.85 Å and the carbon structure could be modeled as 2-3 (averaged at 2.2) layer-stacked sheets, which is in agreement with the previous 2D band of Raman spectra.

Nitrogen adsorption-desorption measurements were performed to quantify the specific surface area. Figure 6.2c shows that the specific surface area of different pyrolyzed NSC varies between 241 and 612 m² g⁻¹ with pore volume in the range of 0.61 to 1.3 cm³ g⁻¹. In addition, the pore size of pyrolyzed NSC is dominated by mesopores with pore radii in the range of 5 to 25 nm, as highlighted in Figure 6.2d. It has been reported that an electrocatalyst with sufficient mesopores would produce an effective electrochemical activity.[239, 240] Increasing specific surface area was also found with increasing pyrolysis temperature with a maximum at 900 °C. The observed trend is supported by the results in the literature.[223, 241] Figure 6.2d further suggests that when the pyrolysis temperature is above 900 °C, decomposition of some carbon structure causes the collapse of mesopores to generate more micro- and macropores. In addition, it may also be possible that a tar-like substance at 1,050 °C would form an intermediate melt that could easily block some pores.

The elemental composition and chemical state of the pyrolyzed NSC were further investigated using XPS. As shown in Figure 6.3a and Table 6.2, the quantitative elemental analysis yields carbon-based material consisted of integrated nitrogen and sulfur atoms. Higher pyrolysis temperatures lead to the reduction of oxygen, nitrogen, and sulfur content, which stipulates the thermal instability of nitrogen and sulfur dopants in the carbonaceous nanofiber. The as-prepared
NSC900 is composed of 3.4 % N, 0.5 % S, and 4.7 % O. The amount of nitrogen atoms has been found to be similar to other nitrogen-doped carbon materials, prepared through different synthetic routes, with the capability to enhance their electrocatalytic performance.\textsuperscript{[242-245]}

Figure 6.3  (a) XPS survey spectrum and high-resolution scans of (b) C1s (c) N1s and (d) S2p electrons of NSC900

Further analysis on high-resolution XPS spectra of individual elements was utilized to evaluate their chemical states, in which more detailed information are given in Table 6.3. The high-resolution C1s spectrum could be deconvoluted into seven components.\textsuperscript{[242, 246-249]} The sp\textsuperscript{2} C=C or aromatic group and sp\textsuperscript{3} C-C are centered at 284.5 and 285.1 eV, while carbon atoms connected to N, S, and O heteroatoms are represented by C-N/C-S at 285.8 eV, C-O at 286.7 eV,
C=O/C=N at 288.1 eV, and O-C=O at 289.7 eV. The small peak at 291.5 eV corresponds to π-π shake up. Fitting the N1s signal shows the presence of six nitrogen states denoted by pyridinic-N at 398.3 eV, pyrrolic-N at 399.9 eV, graphitic-N at 401.0 eV, pyridinic N-oxide at 402.4 eV, π-π* satellite at 404.3 eV, and entrapped NO at 406.8 eV. The chemical states of sulfur in the S2p spectrum contain the covalently bonded S atoms in aromatic carbon network, indicated by S2p\textsubscript{3/2} and S2p\textsubscript{1/2} doublet peaks centered at 163.8 and 165.2 eV, and the oxidized species attributed to -C-SO\textsubscript{x}-C- with peaks at 167-171 eV. It should be noted that some samples treated at low temperature have polysulfide-like S\textsuperscript{2-} species with a peak centered at 161.6 eV. The O1s signal is fitted into four components: C=O at 530.9 eV, C-O/-O- at 532.1 eV, O=C-OR at 533.2 eV, and NO\textsubscript{x} at 534.5 eV.
The high resolution carbon spectrum in Figure 6.3b reveals that the majority fraction of carbon species is sp² C=C carbon, while the fitted spectra of nitrogen and sulfur species are dominated with graphitic nitrogen and thiophenic sulfur, as shown in Figure 6.3c,d. It was also
noted that pyrolysis temperature was found to affect the transformation of unstable heteroatoms dopant (pyrrolic nitrogen and $S^{2-}$) toward more stable structurally-bound heteroatoms (pyridinic/graphitic nitrogen and thiophenic sulfur), as presented in Table 6.3 and Figure 6.4, which is in agreement with the previously reported literature.$^{[242, 258]}$ The appearances of oxidized species are also identified across all samples, which strongly denote the existence of an oxidation reaction due to the presence of residual oxygen species of carbonized CNFs upon solvothermal treatment.

![Figure 6.4](image)

**Figure 6.4** Summary of nitrogen and sulfur compositions for NSC samples pyrolyzed at different temperature

The effectiveness of various pyrolyzed NSC as an electrocatalyst material was studied based on their activity toward ORR. The ORR activities of pyrolyzed NSC, pyrolyzed non-doped carbon nanofibers from solvothermal-treated CNFs (C900), and commercial Pt/C were tested using cyclic voltammetry (CV) curve and linear sweep voltammetry (LSV) in 0.1 M KOH as electrolytes. NSC900 has the highest activity compared to the other pyrolyzed NSC samples, as suggested by its lowest onset potential (Figure 6.5). An onset potential of 60 mV lower than that of Pt/C catalyst was recorded. The as-synthesized NSC900 could also reach a cathodic peak potential of 0.66 V
(vs. RHE), which is comparable to that of most reported N-doped carbon materials.\textsuperscript{[29, 217]} Indeed, the electrocatalytic performance of NSC900 is well-aligned with both structural and chemical analysis that suggest the as-synthesized NSC900 is the most optimal carbocatalyst among other NSC samples. In this regard, carbonization of NSC at 900°C is confirmed as the best annealing temperature to generate a carbocatalyst with a strong balance between a highly crystalline carbon structure, large surface area, and active catalytic sites. It should be noted, however, that although NSC900 was found to improve both ORR and HER activity compared to C900, the improvement obtained by the N,S-doping toward HER is not significant and the performance is still far from competitive compared with Pt/C electrocatalysts.

![Figure 6.5](image)

**Figure 6.5** CV curves and onset LSV for different electrodes (GC, Commercial 20% Pt/C, C900, NSC750, NSC900, and NSC1050) toward ORR in 0.1 M KOH solution

6.3.2 N,S-doped CNFs carbon nanofibers coated with N,P-doped carbon derived from melamine-phytic acid complex particles (NSC/MPA)

Concerning the limited improvement on HER activities for the as-synthesized NSC900, further functionalization strategies were considered to enhance its activity. An attempt to incorporate an additional doping element of phosphor using a hydrothermal reaction between NSC and phytic acids followed by pyrolysis at 900 °C was performed. The resulting carbon nanofibers were consisted of 3.9 % N, 0.5 % S, 1.9 % P, and 4.9 % O. Still, no significant improvement in HER activity was observed even after the addition of phosphor as a third doping element. It was
believed that the as-prepared N,S- or N,S,P-doped carbon nanofibers derived from the mechanically-treated CNFs were not able to provide sufficient active doping sites to promote good HER activity. In this regard, an alternative approach of coating layers of N,P-doped carbon nanoparticles onto N,S-doped carbon nanofiber network (sample NSC900) was investigated. Both computationally simulated and experimental studies reported in literature have demonstrated that several carbon materials co-doped with N/P heteroatoms are able to induce outstanding HER activities.[123, 221, 227] In this work, the synthesis of N,S-doped carbon nanofibers coated with N,P-doped carbon (as described by the carbon hybrid in this study) was obtained through Figure 6.6. Initially, NSC samples obtained after solvothermal treatment were dispersed with complex particles of melamine-phytic acid (MPA) via the aid of sonication prior to pyrolysis. Owing to the accessible hydrogen bonding and π-π interactions, a relatively well-dispersed mixture was achieved. Subsequently, the dry mixture of NSC/MPA was annealed at 900 °C, a pyrolysis temperature at which optimal N,S-doped carbon nanofiber was exhibited. As carbonization occurred, complex particles of MPA were converted to N,P-doped carbon. At the same time, due to the cooperative interaction between MPA complex particles and solvothermal-treated NSC in their vicinity, the synthesized N,P-doped carbon could be easily integrated with the pyrolyzed NSC and use the nanofibers morphology as a template to form shell-like carbon hybrids.

Figure 6.6 Carbon hybrids preparation
Optimization of carbon hybrids was assessed by formulating NSC/MPA composite mixtures with different mass ratios that could give a sensible N,P-doped carbon coverage on the surface of carbon nanofibers while maintaining the 3D nanofiber network. As represented in Figure 6.7a, carbonization of neat MPA complex particles would lead to uniform aggregates of carbonaceous material. In contrast, the carbonization of MPA from the NSC/MPA mixture would lead to the formation of less aggregated carbonaceous material. Figure 6.7c-f reveal that all carbon hybrids may still have the entangled nanofiber network as part of their carbon morphology similar to NSC900, as displayed in Figure 6.7b. However, noticeable changes in the nanofiber morphology of carbon hybrids were identified with the increasing mass loading of MPA complex particles in the NSC/MPA mixture prior to pyrolysis. At a very low loading of MPA, represented by NSC/MPA-1 in Figure 6.7c, the surface of the carbon nanofibers is relatively unchanged from neat NSC900 in Figure 6.7b. As the MPA mass loading increases, the nanofiber surfaces become more uneven and look as if some sections of nanofibers are “swollen” due to the presence of coating layers made from aggregated carbon, which can be represented by NSC/MPA-5 and NSC/MPA-10 in Figure 6.7d,e. It is believed that the coating of aggregated carbon layers on the surface of the nanofiber would closely resemble the characteristic of non-uniform core-shell-like nanofiber. The aggregated carbon shell layers also tend to promote a bridging effect between nearby entangled networks and result in a diminishing amount of pores in the 3D nanofibers network. A further increase of the MPA loading in the mixture would eventually lead to higher carbon shell content in carbon hybrids, as represented in NSC/MPA-20. When the carbon shell layers start to dominate the composition of carbon hybrids, as shown by Figure 6.7f, each individual nanofiber becomes fully covered with a relatively thick and smooth surface assembled from carbon shell layers. Furthermore, excessive carbon shell layers could induce extensive bridging effects. As a result,
the formation of entangled carbon networks from NSC morphology is replaced with formation of continuous aggregated carbon networks, which results in more densely-packed 3D carbon materials.

Figure 6.7  SEM images of the as-synthesized (a) N,P-doped carbon from MPA, (b) NSC900, and NSC/MPA hybrids with different loading ratio: (c) NSC/MPA-1, (d) NSC/MPA-5, (e) NSC/MPA-10, and (f) NSC/MPA-20
Compositional mappings for carbon hybrids were also identified using EDS to indicate the distribution of carbon shell layers originated from carbonization of MPA on N,S-doped carbon nanofiber. As shown in Figure 6.8, well-distributed nitrogen and phosphor species are observed for carbon hybrid formulated based on NSC/MPA-5. This result provides supporting evidence that N,P-doped carbon is dispersed along the surface of the nanofibers. Additionally, the dispersion of sulfur atoms is shown across the surface of carbon hybrids. Although the uncoated section of N,S-doped carbon nanofiber is one possible reason for the presence of sulfur atoms, it is also possible that cooperative integration of the carbon framework was obtained during the formation of N,P-doped carbon shell layers and N,S-doped carbon nanofibers as core material.

Figure 6.8 The morphology and corresponding N, P, S-heteroatoms distribution of NSC/MPA-5

BET analysis (Figure 6.9a,b) was evaluated to give further insight on the change in morphology of N,S-doped carbon nanofibers coated with N,P-doped carbon prepared from different NSC/MPA mixture formulations. As listed in Table 6.4, the synthesis of N,P-doped carbon from carbonization of neat MPA complex particles typically generates carbon material with
surface area of ~1,000 m² g⁻¹. In contrast, the surface area of carbon hybrid networks prepared using mixture formulation varies in the range of ~560 to ~1,220 m² g⁻¹. For NSC/MPA-1, the calculated BET surface area of 565 m² g⁻¹ is relatively close to that of NSC900 (612 m² g⁻¹). This insignificant change in the specific surface area implies that carbon nanofiber morphology is still relatively unaltered in the presence of very low amounts of N,P-doped carbon, which is also supported by the previous SEM images in Fig. 4c. By increasing the MPA loading in the NSC/MPA composite mixture prior to pyrolysis, the calculated specific surface area starts to increase due to the large surface area originating from the coating layers of N,P-doped carbon. An increase in the surface area to 682, 1,217, and 954 m² g⁻¹ was obtained for NSC/MPA-5, NSC/MPA-10, and NSC/MPA-20, respectively. Furthermore, it should also be noted that the surface area of ~1,200 m² g⁻¹ for NSC/MPA-10, which is even higher than the value for both NSC/MPA-20 and neat MPA (~1,000 m² g⁻¹), may imply the synergistic effect between coating layers of N,P-doped carbon and highly porous 3D nanofibers network originating from N,S-doped carbon nanofibers.

Figure 6.9 (a) N₂ physisorption isotherms and (b) pore size distribution of MPA-derived N,P-graphitic carbon and NSC/MPA carbon hybrids prepared using different mixture formulation
Table 6.4  Surface elemental composition, Raman intensity ratio, BET surface area, and pore volume of various carbon materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (At. %)</th>
<th>Raman (\text{I}_D/\text{I}_G) ratio</th>
<th>BET surface area (m² g⁻¹)</th>
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</thead>
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<tr>
<td>MPA</td>
<td>84.0 4.4 2.8 - 9.0</td>
<td>0.91</td>
<td>1,044</td>
</tr>
<tr>
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<td>0.83</td>
<td>565</td>
</tr>
<tr>
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<td>0.88</td>
<td>682</td>
</tr>
<tr>
<td>NSC/MPA-10</td>
<td>83.8 4.3 2.7 0.9 8.3</td>
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<td>1,217</td>
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<tr>
<td>NSC/MPA-20</td>
<td>84.2 4.2 2.4 0.8 8.4</td>
<td>0.85</td>
<td>954</td>
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</tbody>
</table>

XPS measurements on N,S-doped carbon nanofibers coated with N,P-doped carbon were performed to quantitatively evaluate the elemental composition of the samples, as shown in Figure 6.10 and summarized in Table 6.4. As presented in Table 6.4, carbonization of neat MPA complex particles leads to carbonaceous materials consisting of ~4.4 % nitrogen and ~2.8 % phosphor atoms. It is expected that while aromatization and intramolecular condensation occur during pyrolysis to form graphitic carbon, nitrogen and phosphor heteroatoms can be concurrently incorporated into its carbon framework. For N,S-doped carbon nanofibers coated with N,P-doped carbon, Table 6.4 provides evidence that their elemental compositions are relatively close among different formulations of the precursor mixture, in which ~2.5 to 4.3 % nitrogen, ~1.5 to 2.7 % phosphor, and ~0.6 to 0.9 % sulfur are detected. In particular, the relatively consistent sulfur composition at the surface of carbon hybrids reveals that the sulfur atoms originated from N,S-doped carbon nanofibers may be well integrated with N,P-doped carbon upon pyrolysis. In addition, a quantitative increase in the composition of nitrogen and phosphor atoms with increasing mass loading of MPA in the composite precursor supports the evidence on the progress of N,P-doped carbon shell surface coverage. Analogous to the SEM and BET analysis, NSC/MPA-1 has the least amount of nitrogen and phosphor detected, which corresponds well to the fact that only minimal amount of coated N,P-doped carbon layer is expected. With the increasing MPA content in the NSC/MPA mixtures prior to pyrolysis, the formation of more coating layers can be expected.
up to a saturation point where extensive coverage of N,P-doped carbon layers on N,S-doped carbon nanofibers generates similar composition to the bulk N,P-doped carbon synthesized from neat MPA. Table 2 points out that the saturation point could be achieved with a mixture formulation between NSC/MPA-5 and NSC/MPA-10. This trend from the XPS results corresponds accordingly with both the SEM and BET analysis.
Figure 6.10 (a) XPS survey spectrum and high-resolution scans of (b) C1s (c) N1s (d) S2p (e) P2p and (f) O1s electrons of NSC/MPA-5

Characterization of the carbon structures of N,S-doped carbon nanofibers coated with N,P-doped carbon was conducted with Raman spectra analysis. The spectra (Figure 6.11) reveal that the coupling of N,S-doped carbon nanofibers with N,P-doped carbon bears no significant change
in the carbon structure. The characteristics of broad and weak 2D bands with intensity ratio ($I_D/I_G$) in the range of 0.83 to 0.88, similar to the carbon characteristics of NSC900, were observed. It should be noted, however, that the $I_D/I_G$ ratio for N,S-doped carbon nanofibers coated with N,P-doped carbon is lower than just N,P-doped carbon synthesized from neat MPA complex particles. The result may imply that the presence of carbon nanofibers does not induce more disordered carbon structure, instead the cooperative integration between N,S-doped carbon nanofibers and N,P-doped carbon may enhance the lack of graphitic carbon structure of N,P-doped carbon from neat MPA.

![Raman spectra](image.png)

**Figure 6.11** Raman spectra of MPA and NSC/MPA hybrids at different mixture formulation

The electrocatalytic functionalities of the as-synthesized N,S-doped carbon nanofibers coated with N,P-doped carbon were investigated toward both HER and ORR. HER measurements were carried out in an acidic solution of 0.5 M H$_2$SO$_4$ solution. The N,S-doped carbon nanofibers coated with N,P-doped carbon prepared using different NSC/MPA composite precursors exhibit different catalytic activities, as shown in Figure 6.12a. The optimal HER performance of a hybrid carbocatalyst can be obtained for either NSC/MPA-5 or NSC/MPA-10, which corresponds well with the physiochemical analysis of the carbon material. Given that NSC/MPA-5 could already
provide a high HER activity with a minimal amount of N,P-doped carbon coating layers, a further evaluation of the electrocatalytic properties on N,S-doped carbon nanofibers coated with N,P-doped carbon will be based on NSC/MPA-5. The polarization curve of NSC/MPA-5 shows a potential of 331 mV to achieve a cathodic current density of 10 mA cm\(^{-2}\) with an onset potential of 233 mV. Compared to either NSC900 or neat MPA based carbon particles, the HER performance of NSC/MPA-5 is superior. The result provides a good evidence that a synergistic integration between carbon nanofiber architecture and catalytically active graphitic carbon layers on the surface could lead to a more effective electrocatalytic activity.
Figure 6.12 (a) HER polarization curves in 0.5 M H₂SO₄ with (b) the corresponding Tafel plot. (c) Cyclic voltammetry curves for NSC/MPA-5 electrode at different scan rates and (d) the extracted capacitive current. (e) ORR polarization curves in 0.1 M KOH with (f) the corresponding Tafel plot.

In order to better understand the electrocatalytic enhancement achieved from NSC/MPA-5, quantitative evaluations on both the Tafel slope and the exchange current density ($J_0$) derived from
Tafel plot were conducted and compared with both NSC900 and MPA-derived N,P-doped carbon. Figure 6.12b shows that the Tafel slopes between these three samples are all in the approximate range of ~90 to ~120 mV decade\(^{-1}\), in which the NSC/MPA-5 displays the lowest slope at 99 mV decade\(^{-1}\). The Tafel slope is a tool often used to determine the rate-determining step involved in electrocatalysis of HER, OER, and ORR. There are three generally accepted steps for the HER mechanism in acidic conditions:\(^{[259]}\) the discharge step (Volmer reaction, Equation 6.1), the desorption step (Heyrovsky reaction, Equation 6.2), and the recombination step (Tafel reaction, Equation 6.3).

\[
\begin{align*}
H_3O^+ + e^- &\rightarrow H_{\text{ads}} + H_2O \quad (6.1) \\
H_{\text{ads}} + H_3O^+ + e^- &\rightarrow H_2 + H_2O \quad (6.2) \\
H_{\text{ads}} + H_{\text{ads}} &\rightarrow H_2 \quad (6.3)
\end{align*}
\]

Based on these mechanisms, it has been reported that Tafel slopes of 120, 40, and 30 mV decade\(^{-1}\) are involved when the rate-limiting step is the Volmer, Heyrovsky, and Tafel reaction, respectively. All doped-carbon samples prepared in this work is close to a slope of 120 mV decade\(^{-1}\), which suggests that Volmer reaction is the rate-determining step. Although the detailed HER mechanism for the as-synthesized carbon samples remains unclear, it is believed that higher Tafel slope is often undesirable as it would lead to lower HER rate in the high overpotential region.\(^{[225,259]}\)

The exchange current density \(J_0\) of N,P-doped carbon from neat MPA, NSC900, and NSC/MPA-5 was evaluated by extrapolating the Tafel plot, as presented in Figure 6.12b and Table 6.5. The highest exchange current density of 4.8×10\(^{-3}\) mA cm\(^{-2}\) was obtained for the NSC/MPA-5. This relatively high value (see Table 6.6 for comparison with other reported materials) may be attributed to the additive effect of the high intrinsic activity of N,P-doped carbon.
shell layers and the mesoporous-rich nanofiber morphology that can provide more accessible active sites and more rapid electron transport to the electrode. In an attempt to further understand these effects, the electrochemical double-layer capacitances ($C_{dl}$), which are often used as an indicator of the electronically-active surface area, for the as-synthesized carbon samples were measured from Figure 6.12c. Figure 6.12d compares the calculated slopes for N,P-doped carbon from neat MPA, NSC900, and NSC/MPA-5, in which these materials exhibit $C_{dl}$ of 14.5, 5.0, and 24.4 mF cm$^{-2}$, respectively. These results suggest that NSC/MPA-5 allows ~1.6× and ~4.9× higher exposure of active surface area than that of N,P-doped carbon from neat MPA and NSC900 alone. Furthermore, the normalization of the exchange current density by relative surface area (Table 6.5) suggests that the discrepancy in the intrinsic activity between N,P-doped carbon from neat MPA and NSC/MPA-5 is minimal and that the integrated N,P-doped carbon shell layers on N,S-carbon nanofibers are the driving forces to enable good HER activity for NSC/MPA-5.

### Table 6.5 Summary of electrochemical properties of the as-prepared catalysts toward HER

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_{onset}$, mV</th>
<th>$\mu$ @ 10mA cm$^{-2}$, mV</th>
<th>Tafel slope, mV dec$^{-1}$</th>
<th>$J_0$, mA cm$^{-2}$</th>
<th>$C_{dl}$, mF cm$^{-2}$</th>
<th>Relative Surface Area</th>
<th>Normalized $J_0$, mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC900</td>
<td>450</td>
<td>572</td>
<td>121</td>
<td>2.0×10$^{-4}$</td>
<td>5.0</td>
<td>0.2</td>
<td>9.9×10$^{-4}$</td>
</tr>
<tr>
<td>MPA</td>
<td>274</td>
<td>409</td>
<td>114</td>
<td>3.4×10$^{-3}$</td>
<td>14.5</td>
<td>0.6</td>
<td>5.8×10$^{-3}$</td>
</tr>
<tr>
<td>NSC/MPA-5</td>
<td>233</td>
<td>331</td>
<td>99</td>
<td>4.8×10$^{-3}$</td>
<td>24.4</td>
<td>1.0</td>
<td>4.8×10$^{-3}$</td>
</tr>
</tbody>
</table>
Table 6.6 Comparison electrochemical properties of various catalyst materials toward HER

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_{\text{onset}}$, mV</th>
<th>$\mu_{10 \text{mA cm}^{-2}}$, mV</th>
<th>Tafel slope, mV dec$^{-1}$</th>
<th>$J_0$, mA cm$^{-2}$</th>
<th>Catalyst loading, $\mu$g cm$^{-2}$</th>
<th>$C_{dl}$, mF cm$^{-2}$</th>
<th>$C_{dl}$, mF $\mu$g$^{-1}$</th>
<th>Normalize factor by mass and surface area</th>
<th>Normalized $J_0$, mA cm$^{-2}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC900</td>
<td>450</td>
<td>572</td>
<td>121</td>
<td>2.0×10^{-4}</td>
<td>250</td>
<td>5.0</td>
<td>0.02</td>
<td>0.2</td>
<td>9.9×10^{-4}</td>
<td>This Work</td>
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<tr>
<td>MPA</td>
<td>274</td>
<td>409</td>
<td>114</td>
<td>3.4×10^{-3}</td>
<td>250</td>
<td>14.5</td>
<td>0.06</td>
<td>0.6</td>
<td>5.8×10^{-3}</td>
<td>This Work</td>
</tr>
<tr>
<td>NSC/MPA-5</td>
<td>233</td>
<td>331</td>
<td>99</td>
<td>4.8×10^{-3}</td>
<td>250</td>
<td>24.4</td>
<td>0.10</td>
<td>1.0</td>
<td>4.8×10^{-3}</td>
<td>This Work</td>
</tr>
<tr>
<td>N-graphene</td>
<td>331</td>
<td>490</td>
<td>116</td>
<td>7.0×10^{-5}</td>
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<td>[123]</td>
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<tr>
<td>P-graphene</td>
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<td>553</td>
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<td>9.0×10^{-6}</td>
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<td></td>
<td></td>
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<td></td>
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<td>N,P-graphene</td>
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<td>422</td>
<td>91</td>
<td>2.4×10^{-4}</td>
<td>200</td>
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<td>0.05</td>
<td>0.5</td>
<td>4.4×10^{-4}</td>
<td>[123]</td>
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<tr>
<td>N,S-graphene</td>
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<td>276</td>
<td>81</td>
<td>8.4×10^{-3}</td>
<td></td>
<td></td>
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<td></td>
<td>[224]</td>
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<tr>
<td>S-graphene</td>
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<td>671</td>
<td>124</td>
<td>9.0×10^{-4}</td>
<td>20</td>
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<td>0.67</td>
<td>6.8</td>
<td>1.3×10^{-4}</td>
<td>[226]</td>
</tr>
<tr>
<td>g-C$_3$N$_4$@NG</td>
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<td>240</td>
<td>51.5</td>
<td>3.5×10^{-4}</td>
<td>100</td>
<td>5.0</td>
<td>0.05</td>
<td>0.5</td>
<td>6.8×10^{-4}</td>
<td>[225]</td>
</tr>
<tr>
<td>g-C$_3$N$_4$@G</td>
<td>80</td>
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<td>54</td>
<td>4.0×10^{-2}</td>
<td>143</td>
<td>13.0</td>
<td>0.09</td>
<td>0.9</td>
<td>4.3×10^{-2}</td>
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</tr>
<tr>
<td>g-C$_3$N$_4$@SG</td>
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<td>346</td>
<td>84</td>
<td>5.6×10^{-3}</td>
<td>20</td>
<td>5.8</td>
<td>0.29</td>
<td>2.9</td>
<td>1.9×10^{-3}</td>
<td>[226]</td>
</tr>
<tr>
<td>g-C$_3$N$_4$@PG</td>
<td>76</td>
<td>340</td>
<td>90</td>
<td>3.3×10^{-3}</td>
<td>20</td>
<td>4.2</td>
<td>0.21</td>
<td>2.2</td>
<td>1.5×10^{-3}</td>
<td>[227]</td>
</tr>
<tr>
<td>SA900Z</td>
<td>236</td>
<td>387</td>
<td>80.2</td>
<td>5.4×10^{-4}</td>
<td>152</td>
<td>11.0</td>
<td>0.07</td>
<td>0.7</td>
<td>7.3×10^{-4}</td>
<td>[222]</td>
</tr>
<tr>
<td>SA900ZC</td>
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<td>204</td>
<td>58.4</td>
<td>1.7×10^{-2}</td>
<td>152</td>
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<td>[222]</td>
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<tr>
<td>HPC-900</td>
<td>12</td>
<td>97</td>
<td>57.4</td>
<td></td>
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</tr>
<tr>
<td>MPSA/GO-1000</td>
<td>163</td>
<td>32</td>
<td>1.6×10^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[221]</td>
</tr>
<tr>
<td>g-C$_3$N$_4$@S- Se-G</td>
<td>92</td>
<td>300</td>
<td>86</td>
<td>6.3×10^{-3}</td>
<td>20</td>
<td>4.4</td>
<td>0.22</td>
<td>2.2</td>
<td>2.8×10^{-3}</td>
<td>[226]</td>
</tr>
<tr>
<td>pBC-N/MoS$_2$</td>
<td>108</td>
<td>215</td>
<td>61</td>
<td>3.0×10^{-3}</td>
<td>210</td>
<td>10.4</td>
<td>0.05</td>
<td>0.5</td>
<td>5.9×10^{-3}</td>
<td>[260]</td>
</tr>
<tr>
<td>MoS$_2$/G</td>
<td>42</td>
<td>3.0×10^{-3}</td>
<td>210</td>
<td>210</td>
<td>10.4</td>
<td>0.05</td>
<td>0.5</td>
<td>5.9×10^{-3}</td>
<td>[260]</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$ nanosheet</td>
<td>120</td>
<td>186</td>
<td>55</td>
<td>1.3×10^{-2}</td>
<td>285</td>
<td>37.7</td>
<td>0.13</td>
<td>1.4</td>
<td>9.3×10^{-3}</td>
<td>[261]</td>
</tr>
<tr>
<td>Cu$_2$MoS$_4$</td>
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<td>337</td>
<td>95</td>
<td>4.0×10^{-2}</td>
<td>41.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[262]</td>
</tr>
</tbody>
</table>
It should be noted that the evaluated electrochemical properties of the as-synthesized NSC/MPA-5 toward HER are better than previously reported N,P-graphene\cite{225} and comparable to some other recently reported carbon catalysts and metallic catalysts such as N,P-doped carbon derived from bacterium strain before cathodic post-treatment\cite{222}, g-C₃N₄ at S-graphene\cite{226}, g-C₃N₄ at P-graphene\cite{227}, and Cu₂MoS₄\cite{262}. However, in comparison to the most current state-of-the-art Pt/C, carbon hybrids based on MPSA/O\textit{G}\textit{O}\cite{221}, or carbon derived from amino acids-rich biowaste from human hair\cite{223}, the apparent electrocatalytic activity of the as-prepared carbon hybrids still need to be improved.

The effect of coating N,S-doped carbon nanofibers with N,P-doped carbon layers on the electrochemical activity toward ORR in alkaline solution was also assessed. It was found that ORR activity could be significantly enhanced. Fig. 6.12e shows a more positive shift in the onset potential closer to that of commercial Pt/C for NSC/MPA-5. The onset potential of NSC/MPA-5 is only 10 mV higher than the onset potential of Pt/C. Furthermore, the pronounced cathodic peak of 0.84 V (vs. RHE) was demonstrated from CV measurements in O₂-saturated 0.1 M KOH (Figure 6.13). Based on these results, NSC/MPA-5 exceeds the performance of typical N-doped carbon material as ORR carbocatalyst (Table 6.7). The positive improvement of NSC/MPA-5 from NSC900 is assumed to have originated from better exposure of active dopants, which is also in agreement with other reported result\cite{29,242}. A Tafel plot for ORR in an alkaline medium was also derived from its polarization curves, as depicted in Figure 6.12f. Tafel slopes in the range of ~40 to ~60 mV decade⁻¹ were observed in the low overpotential region for the as-synthesized carbon samples and commercial Pt/C. Although the mechanism steps of ORR often vary widely and are still not well-understood\cite{263}, a relatively similar Tafel slope for the as-synthesized carbon samples to that value of Pt/C may imply that the same rate-determining step is highly possible in the low
overpotential region. For comparison, Tafel slopes in the range of 47 to 57 mV decade\(^{-1}\) have also been reported for some carbon-supported metal oxides.\[^{264}\]

**Figure 6.13** CV curves for NSC/MPA-5 carbon hybrid toward ORR in 0.1 M KOH solution

**Table 6.7** Comparison onset potential and cathodic peak potential of various catalyst materials toward ORR

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon precursor</th>
<th>(\mu_{\text{onset}}, \text{V (vs. RHE)})</th>
<th>(\mu_{\text{cathodic peak}}, \text{V (vs. RHE)})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC900</td>
<td>CNFs</td>
<td>0.94</td>
<td>0.66</td>
<td>This Work</td>
</tr>
<tr>
<td>NSC/MPA-5</td>
<td>CNFs + Melamine + Phytic acid</td>
<td>0.99</td>
<td>0.84</td>
<td>This Work</td>
</tr>
<tr>
<td>N-CNF</td>
<td>Bacterial Cellulose</td>
<td></td>
<td>0.85</td>
<td>[29]</td>
</tr>
<tr>
<td>N-CNTs</td>
<td>Carbon Nanotube</td>
<td></td>
<td>0.78</td>
<td>[29]</td>
</tr>
<tr>
<td>N-RGO</td>
<td>Reduced Graphene Oxide</td>
<td></td>
<td>0.68</td>
<td>[29]</td>
</tr>
<tr>
<td>SA-CN900-900</td>
<td>Spider Silk</td>
<td>0.98</td>
<td>0.83</td>
<td>[265]</td>
</tr>
<tr>
<td>NGSH</td>
<td>Graphene + Single-walled Carbon Nanotube</td>
<td></td>
<td>0.88, ~0.64</td>
<td>[266]</td>
</tr>
<tr>
<td>NG</td>
<td>Graphene Oxide</td>
<td>0.86</td>
<td>0.64</td>
<td>[217]</td>
</tr>
<tr>
<td>CNT@NCNT</td>
<td>Carbon Nanotube</td>
<td>0.99</td>
<td></td>
<td>[267]</td>
</tr>
<tr>
<td>CFO/CNF</td>
<td>Bacterial Cellulose + Co + Fe</td>
<td>0.88</td>
<td></td>
<td>[268]</td>
</tr>
</tbody>
</table>
Besides the electrocatalytic activity, long-term stability is another important feature of electrocatalyst materials. In order to assess this parameter, the as-prepared NSC/MPA-5 sample was exposed to continuous 1,500 cyclic voltammetry tests for continuous HER or ORR process under a constant voltage. Figure 6.14a,b suggest that the carbon material suffers from some degree of degradation during the long-term HER process in an acidic environment since the onset potential after the durability test is shifted to a higher value. In this regard, there is a strong possibility that owing to the characteristic of limited high-ordered, graphitic carbon structures from both N,S-doped carbon nanofibers as the core material and N,P-doped carbon from MPA as shell layers, the as-prepared NSC/MPA-5 is still relatively susceptible to an oxidation or decomposition reaction. In contrast, the NSC/MPA-5 has been found to have better long-term stability toward a long-term ORR process in an alkaline medium. A relatively stable ORR performance before and after the test is shown in Figure 6.14c-e. It is also expected that the as-synthesized NSC/MPA-5 still has a good tolerance toward methanol contamination, which is confirmed in Figure 6.14f. In this regard, although the current HER stability is a concern, it is believed that a further optimization process and incorporation of a highly-ordered, graphitic carbon filler might offer significant enhancement in both carbocatalyst activity and durability.
Figure 6.14 Stability of NSC/MPA-5 electrocatalyst: (a,b) Polarization curves toward long-term HER process, (c,d) cyclic voltammetry curves toward long-term ORR process, (e) amperometric curve at constant applied voltage of 0.84 V (vs. RHE) and (f) methanol tolerance
6.4 Conclusion

In summary, nitrogen- and sulfur-codoped porous carbon nanofibers were prepared from inexpensive, naturally abundant, and potentially mass-producible cellulose nanofibril precursors for carbon electrocatalyst. The physiochemical properties of samples were thoroughly characterized and the electrochemical properties were tested. Both ORR and HER using pyrolyzed N,S-doped CNFs-derived carbon nanofibers were still not competitive. However, hybridization of N,S-doped CNFs-derived carbon nanofiber network coated with N,P-doped carbon has been found to significantly increase both HER and ORR electrocatalytic activity. The carbon hybrids demonstrated a low onset potential of 233 mV (vs. RHE), a current density of 10 mA cm$^{-2}$ at 331 mV (vs. RHE), and a Tafel slope of 99 mV decade$^{-1}$ toward HER in an acidic medium. Improvement in ORR performance was also displayed. The electrochemical properties were comparable to that of commercial Pt/C as the onset potential of hybrid carbon was only 10 mV lower than that of commercial Pt/C, and a high cathodic peak at 0.84 V was obtained from hybrid carbon nanofiber network. The high activity of N,S-doped CNFs-derived carbon nanofibers coated with N,P-doped carbon can be attributed to the synergistic effects of heteroatoms-doping, structural morphology, and large accessible active sites. Overall, the results in this study offer a new insight into designing and engineering metal-free carbocatalyst using easily available, affordable, and sustainable material toward a more effective electrocatalytic activity.
7.1 Conclusions

In this dissertation, we have demonstrated several modification routes of CNFs, the tailored properties after modification CNFs, and fabrication of high value-added applications using the altered CNFs. In all attempted modification methods, the synthesis of homogeneous functionalized CNFs has been very challenging. We designed the processing techniques to meet this requirement and optimized the modification conditions to maximize the functionalization impact while preserving the essential properties of CNFs.

In the first part of the work, coupling agent polymer was employed to exploit a facile route of CNFs surface hydrophobization. The maleic anhydride groups could easily react with the accessible surface hydroxyl groups of CNFs. However, the long chain of the hydrophobic backbone in the coupling agent may provide steric hindrance such that only very limited amount of ester bonding was obtained. Nevertheless, the long hydrophobic backbone of the coupling agent were able to cover most of the surface hydroxyl groups of CNFs as indicated by high water contact angle and low critical surface tension. The characterization study also showed that the inherent CNFs properties remained relatively unchanged. The preparation of polystyrene/CNFs nanocomposite further highlighted the effect of CNFs as excellent reinforcing filler and the important of surface interaction between CNFs filler and hydrophobic polymer matrices. The superior mechanical properties of nanocomposite at very low loading suggest that the inherent amphiphilic surface of CNFs was sufficient to provide a good dispersion and filler-matrix surface
interaction. Nevertheless, as filler loading was increased, surface hydrophobization was necessary to provide the optimal surface interaction.

Following the first part of the work, it has been noted that the modification approach required the use of an organic solvent as the dispersing medium and a dry condition for the grafting reaction. These conditions were unfavorable since potential aggregation tendency could still be present. Since CNFs have a good dispersion in an aqueous medium, the second work adopted suspension (surfactant-free emulsion) polymerization to graft hydrophobic polymer on their surface. By adjusting the monomer mixture, salt content in the solution, and polymerization condition, the optimal hydrophobic CNFs dispersed in water could be accomplished. Since the primary objective of this work is on homogeneous surface hydrophobized CNFs, no attempt was made on optimizing the experiment to control the molecular weight of grafted polymers. The as-obtained hydrophobic CNFs were used to prepare hydrophobic aerogels. It was found that the characteristics of the hydrophobic CNFs aerogels closely resembled those of the neat CNFs aerogels. The main differences were limited only to the surface wetting and the low compression strength. The hydrophobic CNFs aerogels were used to demonstrate oil/water separation and wet-solvent shape recovery capability.

The third part of the work involved both carbonization and its surface functionalization. Carbonization was studied as the technological possibility to obtain bio-based nanocarbon to compete with other recent nanosized carbon materials (i.e. carbon nanotubes and graphene). With the increasing interest in nanocarbon for energy-related materials, the use of bio-based CNFs could offer a competitive material for electrocatalyst application. Simultaneous carbonization and heteroatoms doping were obtained through solvothermal treatment. The as-obtained carbon material exhibited heteroatoms-doped carbon nanofiber with the same morphology as their
precursor CNFs but with higher surface area. An additional step using high temperature pyrolysis was required in order to obtain bio-based carbon nanofibers with good conductivity. Although enhanced surface active site could be detected from the pyrolyzed heteroatoms-doped carbon nanofibers, recombination of heteroatoms-doped CNFs-derived carbon with a more active carbon materials could generate better electrocatalytic performance. The improvement obtained from carbon hybrids may be attributed to the synergistic effect between the architectural templates provided by CNFs-derived carbon, the interactions among heteroatoms dopants, and the mesopore-rich of graphitic carbon hybrids.

Overall, the main objectives of this thesis work were achieved. Several modifications approached for CNFs were reported, and the enhanced properties of highly functionalized CNFs were clearly elucidated. The modification mechanism and the influence of modified CNFs were deduced using various analytical techniques. A broad range of applications for the altered CNFs-based materials was demonstrated and identified as high-performance nanofiber materials that are comparable with other reported advanced materials. Herein, the current study established the promising high value-added products obtained using both CNFs as the building blocks and different modification routes as the pathways.

7.2 Future works

As indicated in Chapter IV and V of this thesis work, the effect of surface hydrophobization for CNFs played significant roles to open new applications. Future attention should focus on the innovative approaches to obtain hydrophobic CNFs using an aqueous medium with better control on grafted material and more robust process to provide greater flexibility on the properties of grafted material. In addition, exploiting different applications of surface hydrophobized CNFs beyond their reinforcing capacity should be considered, especially regarding the gas barrier, light
scattering, and biocompatibility. The result will be valuable to develop CNFs as multifunctional nanofiber materials.

Given the limited technical knowledge on CNFs-derived carbon shown in Chapter VI, an extensive study in a demonstration of CNFs-derived carbon nanofibers could facilitate more technical knowledge to open new potential roadmap toward different applications that are beyond surface functionalized CNFs. The fundamental understanding of the effects of each carbonization parameters on CNFs-based carbon would give better tuning on the properties of the carbon materials and allow the CNFs-based carbon to be more competitive toward other nanocarbon, i.e. carbon nanotubes and graphene. Recombination with another nanomaterial has been found useful to improve the surface functionality of CNFs-based carbon nanofibers significantly. Therefore, it may be of great interest to scientists to further focus on the innovative recombination approach for CNFs-based carbon nanofibers.
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