PHOTONIC MATERIALS BASED ON CELLULOSE NANOCRYSTALS

by

Amber Marie Shukaliak

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Abstract

The self-assembly of cellulose nanocrystals (CNCs) into a chiral nematic structure exhibiting photonic properties has garnered much interest in recent years. The development of free-standing chiral nematic films composed of mesoporous silica and organosilica using CNCs as a template has led to a number of studies on producing photonic films composed of inorganic compounds. These films can be tuned to reflect light within the visible spectrum, yielding an assortment of films that exhibit structural colour that is retained once formed, and can no longer be modified. The incorporation of a photonic structure into a flexible material, such as a hydrogel, would allow for colour changes to transpire after the film is formed. Here, the integration of a chiral nematic photonic structure into hydrogel films prepared from different monomers is reported. The swelling of the photonic hydrogels was explored through the use of UV-visible spectroscopy, and the strength of the gels was investigated.

In addition to the formation of tunable photonic structures based on CNCs, also reported is the formation of hybrid photonic structures produced by combining two classes of photonic crystals. These films build onto the chiral nematic mesoporous silica films by introducing a secondary photonic structure, based on the close packed arrangement of nanospheres. These novel hybrid photonic structures were synthesized, and characterized using electron microscopy. The successful formation of composite photonic materials, such as CNC-hydrogels, and hybrid photonic films displays the potential for CNC to be used as a template to build photonic structures in a wide array of systems.

Preface

Professor Mark J. MacLachlan supervised all of the worked presented in this thesis. Dr. Wadood Hamad of FPInnovations, Vancouver, BC, Canada was a collaborator, and provided the cellulose nanocrystals for the experiments conducted. All of the work was done in collaboration with Dr. Joel A. Kelly.

Part of the results from Chapter 2 have been previously published as: J.A. Kelly, A.M. Shukaliak, C.C.Y. Cheung, K. E. Shopsowitz, W.Y. Hamad, M. J. MacLachlan, "Responsive Photonic Hydrogels Based on Nanocrystalline Cellulose" *Angew. Chem. Int. Ed.* **2013**, *52*, 8912–8916. Dr. Joel Kelly was the principal author of this work; I contributed sample preparation and characterization of the materials. Dr. Joel Kelly and Kevin Shopsowitz first developed the CNC hydrogel procedure, and I continued the studies in collaboration with Dr. Joel Kelly. Dr. Joel Kelly synthesized and characterized via SEM the initial PAAm films. He also synthesized the PAAc films I used to investigate pH sensitivity, and assisted with characterizing the swelling times of PAAm I synthesized, and swelling characterization of the different monomer films. James Hammond at FPInnovations carried out the tensile strength testing. I synthesized and characterized all of the samples for the tensile testing. I synthesized and characterized all other films included in Chapter 2.

I conducted all experiments, including sample preparation and characterization of the work presented in Chapter 3. Dr. Joel Kelly provided useful guidance and suggestions throughout.

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List of Symbols

θ	angle of incidence
<i>n</i> _{avg}	average refractive index
Δn	birefringence
°C	degrees Celsius
Δπ	equilibrium swelling
Р	helical pitch
М	molarity
M _n	number average molecular weight
d	periodicity/spacing
n	refractive index
λ	wavelength
wt. %	weight percent

List of Abbreviations

AAc	acrylic acid
AAm	acrylamide
CNCs	cellulose nanocrystals
HEMa	2-hydroxyethylmethacrylate
LC	liquid crystal
NIPAm	N-isopropylacrylamide
PAAc	poly(acrylic acid)
PAAm	polyacrylamide
PC	photonic crystal
PEGMa	poly(ethylene glycol) methacrylate
PHEMa	poly(2-hydroxyethylmethacrylate)
PNIPAm	poly(N-isopropylacrylamide)
POM	polarized optical microscopy
SEM	scanning electron microscopy
TEOS	tetraethyl orthosilicate
TMOS	tetramethyl orthosilicate
UV-Vis	ultraviolet-visible

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Chapter 1 – Introduction

1.1 Structural Colour

Colour is an integral part of the world around us. Flowering plants that rely on animals for pollination often display colour for a variety of purposes: to indicate their species, to make obvious the location of the flower, to indicate ripeness, and to indicate the location of nectar and pollen within the flower.¹ Certain animal species use colour to entice mating partners, like the male peafowl (the peacock). Studies have shown that peacocks direct their train feathers at certain angles to the sun to best display their iridescent eyespot feathers when a female peafowl is present.² Other species have distinct colouring that can aid to camouflage the animal in order to hide from predators. For example, certain crustaceans display colouration that is similar to the habitat in which they live, allowing the shrimp to blend in with their surroundings when predators are nearby.³ Being able to perceive colour is invaluable for humans in order to be able to easily identify objects and distinguish between them. Our perception of colour is the result of photoreactions in our retinas that are triggered by electromagnetic radiation in the visible region of ca. 400 – 800 nm.

The manifestation of colour may be a result of pigment absorption, or through the selective reflection of light with certain wavelengths, based on the structure of an object. This type of colour display is referred to as structural colour, and has long been present in nature.⁴ Fossils dating back 515 million years, recovered from Burgess Shale in the Canadian Rockies in British Columbia, have been reported to display metallic iridescence

based on diffraction gratings formed on the external shell of the animals.⁵ The development of electron microscopy techniques has allowed scientists to investigate the structures responsible for the production of vibrant colours observed in nature.⁶ For example, the fruit *Pollia condensate* and the tiger beetle, both display bright, iridescent structural colour as seen below.^{7,8} The ordered microstructures on the surface of the *Pollia condensate* berry and the shell of the tiger beetle shell (C) and F), Figure 1 – 1) give rise to the fantastic colour we observe, images A), B) and E).



Figure 1 – 1 Images of structural colour observed in nature. The *Pollia condensate* berry displays bright blue iridescent colour A) and B), as a result of the chiral nematic structure C).⁷ The tiger beetle D), shows bright colour E) based on structure F). Reprinted by permission from Macmillan Publishers Ltd: [Polymer Journal] Reference 8 copyright (2014).

The brilliant display of colour from structurally ordered surfaces in nature has caught the interest of many scientists, leading to extensive investigation into understanding and producing structurally coloured materials.⁷⁻¹⁰ It has been shown that well ordered structures display reflection based on Bragg's law, where the wavelength of diffracted or reflected light (λ) depends on the spacing between particles or layers (d),

the angle of incidence (θ) , and the order of diffraction (n). This is analogous to the diffraction of X-rays used to obtain the solid-state structure of molecules. The relationship between the periodicity of a photonic crystal (d) and the wavelength reflected from the structure (λ) can be described by equation (1), Bragg's law.

$$n\lambda = 2d\sin\theta \tag{1}$$

The term photonic crystal (PC) is used to describe materials displaying structural colour based on a periodic change in refractive index within a structure, where the periodicity is on the order of magnitude of the wavelengths of visible light. Following Bragg's law, some wavelengths of light are reflected from the structure, and can be referred to as a photonic band gap. Light with energies outside the bandgap may be transmitted through the material. Typically, PCs are composed of substances that are transparent; only the periodic nature of the structure gives rise to the observed colour. The periodicity of a PC can occur in one, two, or all three dimensions (Figure 1 - 2), depending on the method of formation, and will dictate the properties and applications for these materials.



Figure 1 – 2 Schematic representations of typical examples of different dimensional photonic structures.

Photonic crystals can be fabricated in different ways, from simple self-assembly to lithography methods.¹¹⁻¹³ Simple methods producing consistent, high quality structures are most desirable. A classic example of a one-dimensional PC is a Bragg reflector, which is a PC composed of alternating layers of two materials with different refractive indices. Another route to produce photonic crystals is through self-assembly of macroscopic components into an ordered structure. This process is often used for the formation of three-dimensional PCs such as opals or inverse opal structures. Opal structures consist of closely packed spheres, shown in Figure 1 – 2. In opal and inverse opal structures, the contrast in refractive index exists between the substance composing the opals and the medium filling the voids between the opals (the inverse opal). Certain types of opal and inverse opal structures have been shown to be of use for sensing applications, for example as refractive index sensors, and are therefore interesting for scientific investigation.¹⁴

1.2 Hydrogel Materials

Soft, flexible gel materials are of great interest to many biological researchers due to their tissue-like structure.¹⁵⁻¹⁷ In order to be relevant for this kind of research, these materials need to be compatible with biological, aqueous conditions. Hydrogels are swellable polymer networks that maintain their network structure upon being soaked in aqueous solutions. Over the last half century, there has been a great deal of investigation into the biological applications of hydrogel materials.¹⁵ Drahoslav Lím synthesized the first hydrogel in 1954, after starting a research program with Otto Wichterle in Prague,

with the primary goal of designing biocompatible polymers for ophthalmic uses.^{15,18} This discovery led to the development of the first hydrogel based-product, the soft contact lens, by Lím and Wichterle.¹⁹ Since that time, hydrogels have continued to be used and investigated as contact lenses, as platforms for tissue engineering and drug delivery, along with other uses that take advantage of their responsive nature, such as actuators for optics and fluidics.^{15,17,20} Many researchers have investigated tuning the responsiveness of hydrogels, which has contributed to the establishment of these types of materials as useful tools for sensing applications.²¹

Hydrogels can undergo vast swelling upon being soaked in aqueous media due to hydrophilic substituents bonded to a crosslinked backbone. The substituents interact with water molecules encouraging swelling, while crosslinking of the backbone prevents dissolution of the network.²² Depending on the composition of the hydrogel, crosslinking may exist through chemical and/or physical means. Composite hydrogels typically exhibit both chemical and physical bonding; polymer backbone chains are commonly cross-linked via chemical photopolymerization, while hydrogen and ionic bonds exist between the solutes and substituent chains. The combination of the cross-linked network and significant water content gives rise to both solid- and liquid-like properties, typically resulting in flexible materials when swollen. Figure 1 - 3 depicts the general changes in structure upon swelling a hydrogel film.



Figure 1 – 3 Representation of a swellable hydrogel network.

The extent and rate that a hydrogel will swell depends on the composition of the gel as well as the conditions to which the hydrogel is subjected. Swelling of the polymer as it is placed in an aqueous solution is a result of polymer-solvent interactions that produce an osmotic pressure ($\Delta \pi_{mix}$) within the gel. This can be coupled with the restrictive polymer-polymer interactions that resist expansion ($\Delta \pi_{elast}$), the expansive pressure of electrostatic interactions of polyelectrolyte hydrogels with the solvent ($\Delta \pi_{ion}$), and the ionic strength of the solvent-polymer matrix ($\Delta \pi_{bath}$), to describe the swelling equilibrium of the hydrogel, as shown in equation (2).²³

$$\Delta \pi = \Delta \pi_{mix} + \Delta \pi_{elast} + \Delta \pi_{ion} + \Delta \pi_{bath} = 0$$
(2)

In the fully swollen state, osmotic pressure due to polymer-solvent interactions is the dominant factor influencing the phase of the hydrogel, whereas in the dry state the phase is determined by polymer-polymer interactions that expel solution from the hydrogel.²³ The composition of the hydrogel will influence the polymer-polymer interactions, while both polymer and solvent conditions will influence the polymersolvent interactions, as well as the electrostatic and ionic contributions to the overall osmotic pressure. Polyelectrolyte hydrogels are composed of weakly acidic or basic groups that undergo deprotonation/protonation in basic or acidic conditions, respectively. Functional groups with distinct responses to certain solvents or other variables, such as temperature or pH, can be incorporated to develop hydrogels with specific sensing capabilities in mind.

Hydrogels composed of polymers such as poly(acrylic acid) and poly(*N*-isopropylacrylamide) have been widely studied as responsive materials for use in sensing due to their ability to swell in response to various stimuli.²⁴⁻²⁷ The swelling of hydrogels can be monitored in different ways, for example through changes in mass,²³ pressure,²⁸ or colour.^{26,29} The ability to introduce photonic colour into hydrogel materials provides a simple route towards monitoring changes in swelling. When a photonic hydrogel expands, the photonic structure is affected and affords a change in colour. This response is completely physical and allows for colour changes to occur without interfering with possible chemical states related to the responsiveness of the gel, making this colour production method applicable to any type of gel. Examples of photonic hydrogels that can be tuned to display colour changes in response to certain stimuli include hydrogels based on colloidal crystalline arrays and microgel-etalons.²⁹⁻³¹

1.3 Cellulose Nanocrystals

Cellulose is a bountiful, renewable resource whose properties are taken advantage of for use in everyday materials. As the main structural component in plant cell walls, as well as being produced by certain bacteria, fungi and even some sea creatures, cellulose is said to be the most abundant renewable resource on Earth.³² The use of cellulose-based precursors to produce materials for numerous applications, such as wood for constructing housing, or cotton for clothing, has been prevalent for many centuries. Interestingly, the word 'material' is derived from the Latin word materia, referring to 'wood, material, substance'.³³ More recently, cellulose fibres or cellulose derivatives have found widespread use in many of the products we rely on today, and are of interest as an additive component in forming new composite materials for a wide variety of applications.³⁴ An example of cellulose that displays exceptional properties is nanocrystalline cellulose; this form of cellulose has been shown to have, among other properties, remarkable strength and has been used to improve the strength and other properties of composites.³⁵⁻³⁷ The fantastic attributes of cellulose nanocrystals (CNCs), in additional to the abundance and renewability of cellulose make it an attractive component to incorporate into composites as a basis for developing new materials.

Cellulose is a linear chain of β -D-glucose, consisting of hundreds to thousands of units that aggregate to form microfibrils located in the cellular walls of plants.³³ Both intra- and interchain hydrogen bonds hold the microfibrils together in a linear, parallel arrangement referred to as cellulose I (Figure 1 – 4), the crystalline arrangement of cellulose found in plants.³⁸ This extensive interchain hydrogen bonding of cellulose leads

to poor solubility, which calls for chemical modifications in order to afford soluble forms of cellulose.



Figure 1 – 4 Chemical structure of cellulose a) and the hydrogen-bonding patterns of cellulose I b). Reprinted with permission (*Biomacromolecules* **2004**, *5*, 1333-1339). Copyright (2004) American Chemical Society.

As a microfibril, cellulose is composed of both closely packed crystalline regions that make up the majority of the microfibril, as well as less ordered amorphous regions that develop as a result of defects along the fibril axis.³⁴ Due to the lack of close packing within the amorphous regions of the microfibrils, acid hydrolysis can be used to cleave these regions, allowing for the facile isolation of crystalline cellulose, as depicted in Figure 1 – 5. The use of acid hydrolysis to obtain colloidal cellulose particles was first reported by Ränby in 1949, where sulfuric acid was used to degrade the non-crystalline regions of cellulose fibres, leaving only the crystalline cellulose behind.³⁹ The hydrolysis of cellulose with sulfuric acid generates a negatively charged surface, as sulfate esters are covalently bonded to the surface of the nanocrystals. The charged surface of the nanocrystals leads to inter-particle repulsion, rendering them soluble in water.⁴⁰ Other acids, such as hydrochloric, hydrobromic and phosphoric acids can be used to prepare cellulose nanocrystals, however, sulfuric acid hydrolysis tends to be the most appealing due to the superior solubility of the resulting nanocrystals.³⁴



Figure 1 – 5 Schematic representation of a cellulose microfibril composed of amorphous and crystalline regions. Sulfuric acid can be used to cleave the amorphous regions to afford sulfate terminated cellulose nanocrystals.

Depending on the source of the cellulose and the method used to prepare CNCs, different dimensions and morphologies of crystalline cellulose can be obtained. Sulfuric acid treatment of cellulose from wood sources yields cylindrically shaped CNCs with widths between $\sim 5 - 30$ nm and lengths of $\sim 100 - 250$ nm.⁴¹ The rod-like shape of cellulose nanocrystals plays a role in the liquid crystalline behaviour of CNCs. Liquids crystals (LCs) are a form of matter that maintains the flow-like properties of liquids yet

exhibits some degree of positional and/or orientational order.⁴² CNCs are lyotropic LCs, where the transition of the solution into a liquid crystal phase occurs as the composition of the solution is changed.⁴³ Lyotropic LCs can be influenced by temperature, concentration and other factors. Marchessault *et al.*⁴⁴ first described CNCs as displaying LC properties by observing their birefringence under a cross polarized microscope.

A nematic liquid crystalline phase can be described as the assembly of rod-like structures into an arrangement where each rod is oriented in the same direction, yet the position of the rods is not ordered, schematic a), Figure 1 – 6. Layers of nematic liquid crystals can stack in a twisting manner, where the orientation of the rods is shifted in a continuous, specific direction. The resulting helical structure is described as a cholesteric or chiral nematic structure, schematic b) in Figure 1 – 6. The arrangement of CNCs into a chiral nematic phase was first described by Revol *et al.* in 1992⁴⁰ and typically occurs above ~5 wt.% for CNCs in water.



Figure 1 - 6 Representations of a liquid crystal nematic phase a) and a chiral nematic phase b).

The chiral nematic phase formed by the assembly of CNCs in solution can be maintained upon slow evaporation of the solvent, resulting in a solid chiral nematic film. The chiral nematic structure formed by CNC assembly forms a periodical helix that will selectively reflect certain wavelengths of light based on the pitch of the structure, acting as a photonic crystal. The pitch (P) is the distance over which one full director rotation occurs. The relationship between the pitch of chiral nematic structure, the average refractive index (n_{avg}) and the wavelength of light (λ) that will be reflected from the structure at a certain angle (θ) relative to the plane perpendicular to the pitch can be described by equation (3).⁴⁵

$$\lambda = P n_{avg} \sin \theta \tag{3}$$

Due to the birefringence of chiral nematic structures, equation (3) describes only the centre of the reflection peak from the structure. Equation (4) describes the width of the reflectance peak ($\Delta\lambda$), the range of wavelengths that will be observed as being reflected from the chiral nematic structure, based on the birefringence (Δn) and the pitch.⁴⁵

$$\Delta \lambda = P \Delta n \tag{4}$$

The chiral nematic structure formed by CNCs can be incorporated into other materials, for example as a template for inorganic species to produce mesoporous one-dimensional PCs.^{46.49} These types of porous structures could prove effective for optics and sensing. Based on the straightforward colour production through the self-assembly of

CNCs into a chiral nematic structure, this process lends itself towards colour incorporation into otherwise uncoloured substances that could prove beneficial to many applications.

1.4 Overview of this Thesis

This thesis presents and discusses the integration of the chiral nematic photonic structure formed by cellulose nanocrystals with polymer and inorganic species to produce composites. The preservation of the chiral nematic structure in combination with the formation of cross-linked polymer materials to yield photonic hydrogels is discussed in Chapter Two. Studies into the swelling, responsiveness and mechanical strength of the hydrogels are presented, and potential applications for these hydrogels are proposed. Chapter Three examines the compatibility of the self-assembly process of cellulose nanocrystals with polymer nanospheres and inorganic species to create hybrid photonic structures. The novel structures are characterized by electron microscopy. This thesis shows examples of how the chiral nematic structure of cellulose nanocrystals can be used to form a variety of composite materials, demonstrating the widespread potential for CNC-based photonic materials.

Chapter 2 – Cellulose Nanocrystal-based Hydrogels

2.1 Introduction

Cellulose nanocrystals (CNCs) have fascinating properties that make them an ideal candidate to integrate into new composites and materials.^{50,51} Two properties of CNCs of significant interest include the excellent mechanical strength of CNCs^{52,53}, and the ability of CNCs to self-assemble into a chiral nematic photonic structure.⁴⁰ Both of these functional properties have captured the attention of many researchers, who are now investigating developing new materials that exploit these features.^{46,49,54,55} The integration of CNCs into various composites to increase strength has been fairly well studied,^{36,55,56} while the incorporation of the chiral nematic structure of CNCs into composites to produce colour is a relatively new area. The sensitive nature of the chiral nematic formation has been a limiting factor towards widespread studies on incorporating this structure into new materials. A composite that would display both high strength and structural colour from the integration of CNCs would be of great value as a mechanically strong, coloured material. These new materials could have potential applications in photonics and sensing.

The high mechanical strength observed for crystalline cellulose fibres⁵² has also been demonstrated for CNCs.⁵³ Both forms of crystalline cellulose have been used as reinforcing agents to improve the mechanical strength of composites.^{54,55,57,58} The use of CNCs instead of crystalline cellulose fibers to increase the strength of composites provides some advantages, such as better stability of the composites, and a more efficient increase in strength due to better dispersibility of the CNCs, and higher surface area.⁴¹ These advantages, along with the great abundance and renewability of cellulose, make CNCs an excellent component for strong materials. An example of one material that has displayed improved strength upon CNC incorporation is the hydrogel.⁵⁹

Hydrogels are swellable polymers that undergo volume changes when immersed in water. This dynamic property makes hydrogels useful for many applications, including different types of biological research and sensing studies.^{15,22} In order for a material to be useful as a sensor, it must undergo a measurable change upon exposure to specific stimuli. Hydrogels can be tuned to respond to a variety of stimuli by changing its chemical structure.²¹ Upon swelling, solvent and/or solute molecules enter the hydrogel network, contributing to network expansion. When certain functional groups are present on the polymer chain, exposure to complementary solute molecules can lead to further swelling. For example, a weakly acidic functional group on a polymer chain can be deprotonated in a basic solution, leading to negatively charged groups within the hydrogel network. This leads to electrostatic repulsion, and thereby further expansion of the hydrogel network. Other types of polymers, for example the temperature responsive poly(*N*-isopropylacrylamide), can be used to generate an assortment of responsive hydrogels.²⁹

One potential drawback of the hydrogel network expansion is that as the gel swells, it can also become less strong.⁶⁰ One method that has been used to increase the strength of hydrogels is to integrate cellulose into the hydrogel network.^{37,56} Previously, there has been a great deal of focus on finding suitable solvents for the dissolution of cellulose⁶¹⁻⁶³, or using water soluble cellulose derivatives such as hydroxypropyl cellulose or carboxymethyl cellulose^{51,64} to form cellulose-based hydrogels. As an alternative to

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these two methods, other researchers have looked to using CNCs as a water-soluble component to synthesize cellulose-based hydrogels.^{36,37,59,65}

Studies have shown that the incorporation of CNCs into hydrogels can have many advantageous effects to improve properties of the hydrogel, in addition to improved mechanical properties. For example, the integration of CNCs into hydrogels can lead to hydrogels with improved thermal properties, crosslink densities and better formation.^{36,37,65} There has also been interest in transferring more unique properties of CNCs to hydrogel materials. Tatsumi *et al.*⁶⁶ showed that the liquid crystalline phase formed by CNCs can be transferred to a hydrogel material. The polymeric materials synthesized in Tatsumi's study did not show any photonic properties, however the ability to maintain the LC structure formed by CNCs demonstrates the potential to produce photonic chiral nematic hydrogels.

Photonic hydrogels display colour changes upon swelling, and can be tuned to respond to certain stimuli, to act as a colourimetric sensor. As a hydrogel swells, the cross-linked network expands, which in turn extends the structure of the photonic crystal within the hydrogel. A change in the structure of a photonic crystal leads to a change in reflected wavelengths, and therefore a change in colour. The Asher group has developed a series of photonic hydrogels composed of three-dimensional photonic crystals within a hydrogel network. They have shown that their systems can be modified to respond to a variety of stimuli, for example glucose,^{31,67} pH,^{30,68,69} or ionic strength,⁶⁸ demonstrating the vast potential of sensing capabilities of these types of hydrogels. Other groups have shown that a photonic hydrogel can be developed based on microgel etalons using monolayers of gold, and can also be tuned for responsiveness.²⁹ Photonic hydrogels that

derive colour from the chiral nematic structure formed by CNCs would be unique, and could provide additional benefits towards applications. For example, cellulose is an abundant, natural resource that is non-toxic, meaning these hydrogels could be used in biological studies as well as for sensing applications. In addition to providing colour, CNC incorporation into a hydrogel could also lead to improved mechanical properties of the gel.

This chapter discusses our investigation into the properties of photonic CNCbased hydrogels. The swelling properties of CNC hydrogels composed of different polymers are examined and the responsiveness of the gels to various stimuli and conditions is analyzed. Polymers studied include polyacrylamide, poly(acrylic acid), poly(*N*-isopropylacrylamide), poly(2-hydroxyethyl methacrylate) and poly(ethylene glycol) methacrylate (Figure 2 – 1). The responsive swelling and ability to display patterns upon swelling of the photonic hydrogels are presented. Investigation into the mechanical properties of the photonic hydrogels based on different monomers is also described.



Figure 2 – 1 Monomers studied for the production of CNC hydrogel composites.

2.2 Experimental

Materials

Cellulose nanocrystals (CNCs) were received in an aqueous solution, pH 2.4 from our collaborators at FPInnovations. Acrylamide (AAm), acrylic acid (AAc), *N*, *N'*methylenebisacrylamide, *N*-isopropylacrylamide (NIPAm), 2-hydroxyethyl methacrylate (HEMa), poly(ethylene glycol) methacrylate Mn 550 (PEGMa), and poly(ethylene glycol) dimethacrylate were obtained from Sigma Aldrich and used without further purification. Sodium chloride and 2,2-diethoxyacetophenone were obtained from Fisher Scientific and used as received.

Preparation of Cellulose Nanocrystals

CNCs were prepared according to a literature method⁴⁶ from fully-bleached, commercial Kraft softwood pulp. Following dispersion by ultrasonication, the CNC dispersion was diluted to the desired concentration (3 wt. %). The final CNC suspension was measured to have a zeta potential of -59 mV and a pH of 2.4.

Preparation of Photonic CNC Hydrogels

CNC hydrogel materials were prepared by combining a 3 wt. % aqueous CNC dispersion with an ethanolic solution of hydrogel precursors: the desired monomer species, a crosslinker and 2,2-diethoxyacetophenone as the photo-initiator. In some samples aqueous sodium chloride was also added to increase the ionic strength. After combining, the mixture was stirred for one hour to ensure homogeneity before casting into a polystyrene petri dish to allow evaporation to dryness. A representative procedure for casting in a 60 x 15 mm petri dish is given: first, 78 mg of monomer species dissolved in 1.25 g of ethanol was combined with 5 mg of cross linker dissolved in 0.2 g of ethanol and 7.5 μ L of photo-initiator. To this was added 5.0 g of a 3 wt. % solution of CNCs, and 150 μ L of a 0.25 M NaCl solution, followed by stirring with a magnetic stir bar and casting in a petri dish. Upon complete evaporation, photo-polymerization was carried out using an 8 W 300 nm UV-B light source for one hour. Hydrogel samples were rinsed and dried multiple times prior to characterizing in order to remove excess oligomers. Polymers studied include polyacrylamide (PAAm), poly(acrylic acid) (PAAc), poly(Nisopropylacrylamide) (PNIPAm), poly(2-hydroxyethyl methacrylate) (PHEMa), and poly(ethylene glycol) methacrylate (PEGMa).

Preparation of Non-Photonic CNC Hydrogels

A series of non-photonic hydrogels was prepared following a similar procedure as described above with the following adaptations: no sodium chloride solution was added to the solution and for a 60 x 15 mm dish, the amount of monomer added was increased to 250 mg while keeping all other masses and volumes the same. Additionally, these films were polymerized before complete evaporation; polymerization was carried out when the CNC concentration was around 10 wt. % of the total solution. The CNC concentration was determined by monitoring the mass of the solution throughout the drying process, and initiating polymerization when a certain solution mass was reached. The initial mass of CNCs added was used to calculate CNC wt. % of the total solution.

Characterization Techniques

Ultraviolet-visible light spectroscopy (UV-vis) was carried out using a Cary 5000UV/Vis/NIR spectrophotometer with the hydrogel films mounted normal to the beam path; transmission spectra were collected. Polarized optical microscopy was performed on an Olympus BX41 microscope; all images were taken with the polarizers in a perpendicular (crossed) arrangement. Scanning electron microscopy (SEM) was performed using a Hitachi S4700; samples were sputter-coated with gold or gold/palladium prior to imaging. Solution pH measurements were performed using a pH/ISE meter, model 735P from ISTEK. Tensile data was taken using a Deben microtensile stage, equipped with a 200 N load cell using 7 mm by 15 mm strips at a rate of 0.1 mm min⁻¹.

2.3 Results and Discussion

Chiral Nematic Structured Hydrogels

The lyotropic assembly of acid-hydrolyzed cellulose nanocrystals into a chiral nematic structure has been shown to be sensitive to a variety of conditions such as concentration, pH, ionic strength, sonication, evaporation rate and magnetization.⁷⁰⁻⁷³ To access composites templated by CNC self-assembly that retain the chiral nematic ordering, it is important to understand how these material precursors affect this process. Polarized optical microscopy (POM) is a tool that can be used to determine whether or not chiral nematic ordering is occurring in a solution through the formation of spherulite structures. Spherulite structures are observed using POM as regions consisting of alternating dark and white lines that appear as the solvent evaporates from a solution containing CNCs. As the CNC concentration increases during evaporation, regions of an anisotropic chiral nematic phase form within the isotropic solution, creating these spherulite droplets.⁷⁴ The lines observed result from the twisting of the chiral nematic director; a group of four lines, two white, two dark, correlates to one full turn of the helical structure. The observation of these structures using POM can be used to confirm the formation of a chiral nematic structure. Figure 2 - 2 demonstrates that the formation of spherulite structures will occur in the presence of hydrogel precursors at both high and low concentrations of CNCs.



Figure 2 – 2 Polarized Optical Micrographs of CNC hydrogels; high CNC content a) and low CNC content b).

Upon finding that hydrogel precursors would not affect the chiral nematic organization of the CNCs, we were interested in producing a photonic hydrogel based on the chiral structure formed by CNC self-assembly. To determine the conditions under which a photonic hydrogel could be produced using CNCs, we investigated combining CNCs with hydrogel precursors containing high monomer content and low monomer content, with and without the addition of salts. Figure 2 - 3 depicts a general reaction for the formation of the hydrogel polymer: here acrylamide (AAc) is shown as the monomer, and *N*, *N'*-methylenebisacrylamide as the crosslinker, however different monomers and crosslinkers were also studied in this chapter. A typical procedure for the low monomer to content films involved combining approximately a 16:1:1.5 weight ratio of monomer content films were formed using a 50:1:1.5 weight ratio of monomer, crosslinker, initiator, respectively. Polymerization and crosslinking were initiated through exposure to UV irradiation for one hour.



Figure 2 – 3 Example of typical polymerization/crosslinking reaction to produce the crosslinked polymer hydrogels, showing AAc and N,N'-methylenebis(acrylamide) as the monomer and crosslinker, respectively. The reaction was initiated using 300 nm UV light, with 2,2-diethhoxyacetophenone as the photo-initiator.

It was found that hydrogel films composed of both high and low monomer content showed chiral nematic ordering, evident using SEM, as shown in Figure 2 – 4. However, only hydrogels with low monomer content and salt addition displayed photonic properties. In these micrographs, it can be seen that the helical pitch of the non-photonic hydrogels is much greater, on the order of microns, than that of the photonic hydrogels where the helical pitch is on the order of hundreds of nanometers. The decrease in the pitch of the chiral nematic phase of the photonic hydrogel is associated with the increased ionic strength as a result of the salt addition.⁷¹ Interestingly, the non-photonic hydrogels as compared to the photonic hydrogels. The photonic hydrogels display great order, with a consistent helical pitch throughout the thickness of the film.



Figure 2 – 4 SEM images of CNC hydrogels; non-photonic, high acrylamide content at low magnification a) and high magnification b), and low acrylamide content photonic hydrogel at low magnification c) and high magnification d).⁸⁰

Swelling of Photonic Hydrogels

The photonic CNC hydrogel films could be synthesized using a variety of different monomers. The choice of monomer will dictate the specific properties and stimuli to which the hydrogel films will respond. All of the photonic CNC hydrogels displayed colour upon drying, ranging from blue to yellow, with specific colours being dependent on the monomer used. The dry films can be soaked in aqueous media to induce a red shift in the observed colour where the extent of the shift is also dependent on the monomer used. Due to the hydrophilic nature of the polymer substituents, water molecules can enter the hydrogel network, and the network will expand to accommodate. As the hydrogel network extends, so does the helical pitch of the chiral nematic structure.

The increase in pitch results in an increase of the wavelengths of light being reflected from the hydrogel, shifting to the far end of the visible region, or even into the near infrared region of the electromagnetic spectrum as shown in Figure 2 - 6. Figure 2 - 6 shows the reflected wavelengths of the various polymer hydrogels, as dry films and in swollen states. Due to the strong correlation between the transmitted wavelengths of light, and the swelling of the hydrogels, UV-vis spectroscopy proved to be an invaluable tool to investigate swelling characteristics of the hydrogels.

The colour observed from the dry or swollen hydrogels corresponds to the range of wavelengths being reflected from the films. Transmission of the hydrogels samples is correlated to reflection from the gels, as these films are assumed to not be absorbing any wavelengths in the UV-visible region of the electromagnetic spectrum. The wavelengths correlated to the lowest transmittance in a UV-vis spectrum are associated with the maximum reflectance from the film, and thereby the colour of the films. For example, Figure 2-5 shows that the dry PAAc film displays a minimum transmittance at 350 nm, meaning the maximum wavelength reflected from the film. For each of the films studied in the chapter, the maximum reflectance of the films dry, swollen in water and swollen in ethanol were recorded and plotted in Figure 2 - 6. Figure 2 - 6 shows that all of the films undergo a red shift after immersion in water, indicating that the hydrogel network expands as water is incorporated into the structure, in turn expanding the chiral nematic structure. The response to ethanol varies between samples. Water saturated PAAm and PAAc films immersed in ethanol undergo a blue shift towards the colour of the dry films, indicating that ethanol can be used as an effective drying agent for these films. The PHEMa and PEGMa films in ethanol show partial blue shifts with regard to the observed

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colour of the water swollen films. The PNIPAm film on the other hand, does not show any change in swelling between soaking in ethanol or water. These variations in swelling provide us with a set of photonic CNC-hydrogels that can accommodate an assortment of swelling requirements.



Figure 2 – 5 UV-visible spectra of a PAAc hydrogel dry, soaked in ethanol, and soaked in water.



Figure 2 - 6 Maximum reflected wavelengths of CNC-polymer hydrogels dry, soaked in water, and soaked in ethanol.

Swelling Times

The density of cross-linking within a hydrogel film will affect the swelling ability of the hydrogel, as well as the amount of time it takes for a hydrogel to reach equilibrium swelling.⁷⁵ The photonic CNC hydrogels displayed relatively quick colour changes, typically under a minute, upon soaking in water and ethanol. We were interested in examining how cross-linking would affect the swelling time of the photonic CNC hydrogels. Cross-linking within the photonic CNC hydrogels was initiated through exposure to UV radiation for a period of one hour after complete drying for the standard films studied in this chapter. To study the effect of cross-linking density on swelling time, a set of PAAm hydrogels was prepared that varied only in the exposure time to UV radiation. Longer UV exposure would be expected to increase the cross-linking within the hydrogels, and therefore influence swelling time. Samples were exposed to UV radiation for 0, 1 or 2 hours before UV-vis transmission spectra were collected at one-second intervals as the films were soaked in water and ethanol.

Figures 2 - 7 and 2 - 8 show the maximum absorbance wavelength recorded for each sample as a function of time. These plots show that irradiation time, and thereby crosslinking, does affect the amount of time taken to reach equilibrium swelling of the hydrogel, as well as the level of swelling. Figure 2 - 7 shows the absorbance as the gels were swollen in water. The sample not exposed to UV-radiation (0 hour) to initiate crosslinking reached equilibrium swelling in the least amount of time, in approximately twenty seconds, as water can easily penetrate an uncrosslinked network. In comparison, the sample irradiated for 1 hour took nearly 150 seconds to reach full swelling, and the sample irradiated for 2 hours took just under 100 seconds. The 2-hour sample reached equilibrium swelling at a lower wavelength of transmittance, a less swollen state, than the 1-hour sample, which can account for the faster swelling time. The decreased swelling of the 2-hour sample in comparison to both the 0-hour and 1-hour samples can be attributed to the higher level of cross-linking within the 2-hour polymer hydrogel. Exposing the gel to UV radiation for a longer period of time would allow for more free radical formation, and therefore more cross-linking of the hydrogel network. A more densely cross-linked network would not be as flexible to expand as much as a less dense network.



Figure 2 – 7 Swelling times for PAAm hydrogels soaked in water.

The PAAm films in ethanol contract to equilibrium in approximately 50 seconds, Figure 2 - 8. This reveals that the de-swelling of the CNC hydrogel films is quite rapid and that ethanol is a good drying agent for the PAAm films. The films that have been exposed to UV radiation reach approximately the same transmittance upon drying, whereas the non-cross-linked film does not. This can be attributed to the film partially disintegrating upon being immersed in water, due to the lack of crosslinking. This result reinforces the importance of crosslinking in swellable hydrogel films. The 0-hour sample film does not maintain its properties over multiple swelling cycles.



Figure 2 – 8 Collapse time of PAAm hydrogels upon ethanol soaking.

Photo Patterning of Photonic CNC Hydrogels

The colour of the photonic CNC hydrogels is derived from the pitch of the chiral nematic phase of the CNCs being on the order of magnitude of visible light. As previously discussed, swelling the gels in water can change the pitch of the chiral nematic structure, and therefore the colour, of the hydrogels. In order to ensure crosslinking of the monomer units with the hydrogel films, a photo-initiator was added to the solution mixtures and the dry films were exposed to UV radiation. Cross-linking is important in hydrogel formation in order to ensure the hydrogel will not dissolve upon swelling.²²

The ability to pattern the surface of hydrogels is of interest to many biochemists as a means to control the adhesion of cells and bacteria on the surface of the gels.^{76,77} It has been shown that photo- and electron-lithography are techniques that can be used to pattern poly(ethylene glycol) hydrogels.^{77,78} As materials chemists, we were interested in patterning the hydrogels to display our ability to control swelling within the same film. By controlling the relative swelling within the films, and therefore the colour, there is potential to embed images on the surface of the hydrogels. If these changes in swelling (colour) occur only when the film is exposed to water, this could be potentially useful in security applications.

Initial attempts to differentiate the swelling between various regions of the hydrogel films included increasing the amount of cross-linker added to the initial hydrogel solution mixture. The cross-linking unit has a great influence on the swelling of the hydrogels, and by increasing the density of cross-linking within the hydrogel network it was thought we would have better control over swelling within the gel. In order to form regions with different swelling properties within the same film, parts of the film were covered with a pattern during the UV radiation process, following photolithographic techniques. Covered portions would be expected to have little to no cross-linking, and therefore swell more quickly, as shown in the previous section. Due to the success of patterning PEG hydrogels, we decided to investigate using a PEG-dimethacrylate cross-linker in the acrylamide hydrogels to see if patterning would be possible.

Films were produced with increasing amounts of PEG-dimethacrylate crosslinker, and then a mask was used to cover certain areas of the film during irradiation. It was discovered that, upon using the right mask, and when the cross-linker amount was

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increased to three or four times that of our standard, a latent image of the mask would become apparent when the film was soaked in water. Prior to being placed in water, there was no visible image on the surface of the films, as seen in the inset image in Figure 2 – 9. Films made with standard or lower levels or cross-linker did not show enough variation in swelling for an image to be visible on the surface after irradiation. It should also be noted that exposure to UV radiation to induce crosslinking does not change the colour of the dry films. The procedure to produce the CNC-hydrogels can be scaled up or down easily, and to display the success of our patterning, and ability to control hydrogel swelling, a large, patterned hydrogel film was made (Figure 2 - 9).



Figure 2 – 9 Photograph of a patterned PAAm hydrogel upon swelling in water. The inset photo shows the hydrogel before the addition of water, when the pattern is barely visible.⁸⁰

Solute Effects on Swelling

One of the most prominent features of a hydrogel is its ability to swell in water and exhibit volume changes in response to various stimuli. Parameters that have been shown to influence volume changes within hydrogel materials include temperature, pH, ionic strength, solvent quality, and electric fields.⁷⁹ These changes may occur at a critical stimulus level or over a range, how the changes occur will dictate the potential application for the gel.²² Regarding the photonic CNC hydrogels, we were interested in studying how to tune the responsiveness of the hydrogel swelling. To this end, we synthesized hydrogels using various monomers, choosing species known to respond to certain stimuli, in order to develop a series of responsive photonic hydrogels. Examples of some of the stimuli we investigated include pH, temperature, ionic strength, and the introduction of various cations.⁸⁰ Discussed here will be my contributions to the ionic strength and solvent pH studies.

The swelling of hydrogel materials can be affected by the nature of the aqueous solution; ionic strength, solution pH or temperature can influence the extent of hydrogel swelling. Depending on the nature of the hydrogel network, the influence of the introduction of ionic species will vary. As earlier noted, the swelling equilibrium of a hydrogel network is affected by polymer-polymer interactions, polymer-solution interactions, the electrostatic interactions of the hydrogel itself, as well as the ionic strength of the solution in which the hydrogel is soaked.

To investigate the influence of solution ionic strength on the swelling of photonic CNC hydrogels, samples of each polymer hydrogel were soaked in solutions of

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increasing concentrations of salt, and the resulting films were characterized by UV-vis spectroscopy.



Figure 2 – 10 Maximum reflected wavelengths for hydrogel samples soaked in aqueous sodium chloride solutions.

Transmission spectra were recorded for concentrations in the range of 0.075 to 2.0 M. Figure 2 – 10 shows the maximum reflected wavelength for each polymer hydrogel after being soaked in the corresponding NaCl solution. From the plot, it can be seen that while changes in swelling are minimal overall, the PNIPAm and PHEMa hydrogels undergo the largest changes in swelling as the ionic concentration is increased, while the PAAm and PAAc hydrogels are affected slightly. The swelling of the PEGMa hydrogel was the most stable towards ionic strength changes.

The slight collapse of the PHEMa hydrogel as the ionic concentration increases can be attributed to polyelectrolyte shielding by the salt ions, leading to a decrease in the repulsion between HEMa chains, while the slight collapse of the PNIPAm hydrogel is a result of interactions between the salt and neutral gel.⁸¹ The otherwise unaffected nature of the hydrogels to ionic strength displays the stability of the CNC polymer composite hydrogels, and is likely related to the strong hydrogen bonding interactions between the CNCs and polymer network. This effect is not observed for all hydrogels, and in fact ionic strength can have large effects on the swelling of regular polymer hydrogels.⁸² This has led to the use of hydrogels as ionic strength sensors,⁶⁸ and in one interesting example, the swelling of a hydrogel was used to monitor changes in ionic strength through coupling to a piezoresistive sensor.²⁸

Upon displaying the stability of the photonic CNC hydrogels towards ionic strength, we also wanted to investigate the specific responsiveness of stimuli sensitive hydrogels. For this purpose, the pH sensitivity of a PAAc hydrogel was studied. Acrylic acid (AAc) is a weak acid with a pKa of ~ 4.25 in water with a polymer pKa of ~ 4.7, above these pH levels the AAc functional groups will begin to be deprotonated.²³ Due to this sensitivity towards pH, poly(acrylic acid) has been studied for use in pH sensing hydrogels.^{24,29,83}

As a neutral film, the PAAc hydrogel contains hydroxyl groups that can be deprotonated to carboxylate ions in basic solutions. When deprotonation occurs, the hydrogel becomes negatively charged, leading to repulsion within the polymer network, and thereby expanding the gel. The swelling can be monitored through the use of UV-vis transmission spectroscopy to measure the change in reflected colour. The pH of the solutions used in these studies was controlled through the addition of HCl or NaOH to distilled water, and monitored using a pH meter. Samples of PAAm hydrogels were soaked in pH-controlled solutions overnight before transmission spectra were recorded.

Subjecting the PAAc hydrogels to a range of basic pH solutions led to a pronounced, incremental red shift in the UV-vis transmission spectrum as shown in Figure 2 – 11. As the pH was increased from 8 to 13, a red shift of approximately 45 nm was observed for each increase of one pH unit until pH 11, when a larger shift of \sim 120 nm to pH 12 was observed. These incremental shifts in swelling occurred as the PAAc hydrogel became more deprotonated, and thereby experienced greater repulsion within the polymer network. The larger shift to pH 12 and pH 13 could be due to some decomposition of the gel upon exposure to such basic conditions.



Figure 2 – 11 UV-vis transmission spectra of PAAc hydrogels soaked in basic conditions.

Typically, hydrogel samples display reversibility towards stimuli, allowing the gels to be reusable.⁷⁹ In order to reprotonate the PAAc hydrogels after being subjected to basic conditions, the hydrogels were soaked in acidic conditions for a week before recording new transmission data. Ideally, by soaking the gels in acidic solutions, the carboxylate groups would become reprotonated and the gels would return to their initial swelling behaviour. However, we found this was not the case for the CNC-hydrogels, as shown in Figure 2 - 12. After being subjected to acidic conditions, the gels still showed an incremental increase in swelling associated with the basic pH to which the gels were originally exposed. However, the range of swelling was decreased to a difference of 100 nm between pH 8 and pH 13, as compared to the range of nearly 300 nm for the samples before the acid soak. As described by Hu et al.²⁹, some hysteresis of swelling may be observed as the pH of the hydrogel bath solution is decreased. After deprotonation, the negatively charged carboxylate ions may start to interact with positive counter ions from the solution. When the pH of the solution is lower by the addition of HCl, both positive H⁺ and negative Cl⁻ ions will initially enter the network, causing some further repulsion within the network. In order for protonation to occur, the protons would have to overcome the carboxylate-counter ion binding energy.²⁹ This could explain the swelling observed for the hydrogels after being subjected to acidic conditions, where the gels do not return to their initial swelling, some expand further, and some contract. These results indicate that the PAAc gels would be best suited for sensing pH when reversibility is not desired. Also noted is the disintegration of the pH 11 sample after immersion in acid, further suggesting single use applications would best fit the properties of these gels.



Figure 2 – 12 Swelling of the PAAc films soaked in acidic conditions after being immersed in basic solutions.

In order to display that the pH responsiveness of the PAAc hydrogels is confined to basic solutions, we also looked at the responsiveness of the hydrogels in acid solutions. Figure 2 - 13 shows the transmission spectra of the PAAc hydrogel in acidic solutions, where the peak reflection of the gel remains around 540 nm for all of the acidic solutions measured. This is as expected, based on the pKa of PAAc.



Figure 2 – 13 PAAc hydrogels display no change in swelling after being immersed in acidic solutions.

Mechanical Properties of Dry and Wet Composites

In addition to sensing, hydrogel materials have been studied for use in many other applications such as for scaffolds in tissue engineering, and as drug delivery tools.^{16,17,84} Important properties to understand for these applications include the strength of the hydrogel, as well as the elasticity of the gels which can allow for compounds to diffuse through the hydrogel, for example to allow the release of drugs.¹⁷ As discussed earlier, the incorporation of CNCs into hydrogel materials has been shown to improve the mechanical properties of the hydrogels, where higher amounts of CNCs have shown greater strength.³⁶ The photonic hydrogels studied in this chapter contain a relatively high

percent of CNCs as compared to other CNC-polymer materials shown to have improved mechanical properties,^{36,66}, so it was of interest to investigate the mechanical properties of our photonic hydrogels. We were interested in quantitatively examining the difference in mechanical properties between the dry, brittle hydrogel films and the wet, swollen films. Standard methods of tensile testing require large sample fragments, which were difficult to obtain for the hydrogel films due to their brittleness when dry. My attempts at acquiring tensile data using standard equipment were unsuccessful, and in order to obtain reasonable data, measurements were performed using a Microtensile instrument where small sample pieces can be used. Measurements were taken for both dry and wet films of the different polymer hydrogels. The Young's modulus for each polymer film, dry and swollen, was calculated by taking the average from all the samples run.

From the stress-strain curves shown in Figure 2 – 14, it can be observed that for all of the polymers tested, the dry films do indeed show brittle characteristics; high stress can be endured at low strain, with little deformation before fracture. The polyacrylamide samples showed the greatest reproducibility, and the highest maximum stress and maximum extension of the dry polymer hydrogel films with an average Young's modulus of 17 GPa for the samples tested, Table 2 – 1. Based on averages, the PAAc hydrogel showed the next highest Young's modulus at 16 GPa, but these samples also showed the greatest variation between results with a calculated standard deviation of 13 GPa. This variation is most likely a consequence of inhomogeneity due to defects within the PAAc films. The PHEMa and PEGMa samples showed Young's modulus results of 11 GPa and 9 GPa, respectively. This decrease in modulus between different polymer samples is attributed to the amount of crosslinking within the samples. Presumably, the HEMa and PEGMa samples have less crosslinking than the PAAm and PAAc samples due to the longer substituent chains of HEMa and PEGMa, interfering with the ability of the cross linking agent to bond with two backbone chains. Of course this would depend on the orientation of the substituent chains, but could explain the variation in modulus. The PEGMa sample has the longest substituent chain, with the least amount of crosslinking, and it shows the lowest Young's modulus.

The results from the PHEMa hydrogel can be compared with results reported by Tatsumi et al.⁶⁶. In their study, the authors prepared samples of PHEMa-CNC films where the CNCs had either arranged isotropically or anisotropically, or a mixture of the two phases, and tensile mechanical data was reported. The authors found that the PHEMa-CNC anisotropic sample showed the highest Young's modulus at 2.03 GPa, compared to the PHEMa-CNC isotropic at 1.84 GPa and the mixed sample at 1.58 GPa. A sample of PHEMa without CNCs was reported to have a Young's modulus of 1.28 GPa. These values are much lower than the Young's modulus determined for our CNChydrogel films, which is most likely related to the high proportion of CNCs used in our films. Our photonic hydrogels have a final CNC content of approximately 64 wt. %, whereas the PHEMa films studied by Tatsumi were estimated to be about 7 wt. % CNCs. This nine-fold increase in CNC content would be expected to produce more rigid films with a higher Young's modulus, based on the estimation of cellulose nanocrystals having a modulus of elasticity of 130 GPa.³⁵ Comparing the results from Tatsumi's study, who reported films with a Young's modulus of 2.03 GPa, with our results of a Young's modulus of 11 GPa, it seems the greater CNC content substantially improves the elastic modulus. Based on these comparisons, it can be concluded that the introduction of CNCs into polymer hydrogel films increases the rigidity of the films, and that higher CNC content can be correlated with higher rigidity.

Polymer Film	Average Young's Modulus (GPa)	
	Dry	Wet
PAAm	17 ± 1	$0.6 \pm N/A$
PAAc	16 ± 13	1.4 ± 0.3
PHEMa	11 ± 4	0.66 ± 0.02
PEGMa	9 ± 3	0.39 ± 0.08

Table 2 – 1 Summary of Young's Modulus of dry and swollen photonic CNC hydrogels



Figure 2 – 14 Stress-strain curves for dry CNC hydrogel films composed of PAAm a), PAAc b), PHEMa c), and PEGMa d).

The wet hydrogel composites showed much greater extension than the dry samples, as one would expect due to the greater flexibility of the wet samples. The tensile strength results for the wet samples, Figure 2 - 15, show that the PAAc film has the highest average Young's modulus, while the PAAm film showed the greatest overall elongation. Tensile measurements were to be taken for 3 - 4 samples of each polymer gel, however due to the fragile nature of the gels, dry and swollen, only two samples were recorded for the wet PAAm hydrogel. This small sample size makes it difficult to assess the nature of the PAAm wet film, but it can be noted that the wet film easily tears, most likely due to variability within the film, limiting reproducibility. Both PHEMa and PEGMa samples showed good reproducibility in terms of stress within the wet measurements. The PEGMa sample showed some bilateral results, with half the samples exhibiting maximum stress around 3.5 MPa, and the other half around 7 MPa, implying there is some inhomogeneity within these films.

Aside from the lack of data for the wet PAAm hydrogels, the PAAc films showed the greatest variation in results as compared to the other films, further suggesting inhomogeneity within the films. The swollen hydrogel films all showed a decreased Young's modulus, a decreased maximum stress and an increased maximum extension as compared to the dry films, with the exception of the PAAc maximum extension. These results indicate that the wet films are less tough, but have more ductile characteristics than the dry films.



Figure 2 – 15 Stress-strain curves for CNC hydrogels synthesized with PAAm a), PAAc b), PHEMa c) and PEGMa d).

The mechanical testing results show that the incorporation of CNCs into hydrogel films improves the mechanical properties of the film, and that a higher CNC content will further increase the rigidity of the films. The dry films displayed higher Young's moduli, and greater toughness than the wet films, while the wet films showed more ductile characteristics. The relatively small sample size used to determine these values, as well the large standard deviation for some of the samples should caution against regarding these values as absolute. Rather, these results give us a general idea of the rigidity of our films as compared to results reported by other groups and as to the variation in rigidity between the different monomers chosen to produce these films. In order to gain a better representation of the mechanical properties of the photonic CNC hydrogels, a more indepth study using large sample sizes would need to be conducted.

2.4 Conclusions and Future Work

Polymer hydrogels containing cellulose nanocrystals arranged in a chiral nematic structure were synthesized and characterized according to their swelling. The chiral nematic structure of CNCs was successfully combined with many different monomers to produce an array of responsive photonic hydrogels. UV-vis spectroscopy was the main method of characterization used to assess the swelling of the hydrogels due to the photonic nature. The hydrogels could be modified to swell at different rates, to be photopatterned, to endure ionic strength changes with little effect and to be sensitive towards pH changes. These characteristics show the versatile nature of the photonic hydrogels, and demonstrate how these gels could be adapted for use in a collection of applications related to sensing. The method used to form the photonic CNC hydrogels is straightforward and uses common hydrogel precursors, along with cellulose, an extremely abundant, non-toxic renewable resource, making these specific hydrogels good candidates for widespread use. However, in order for the hydrogels to be considered useful for sensing applications, they must demonstrate selective responsiveness and higher sensitivity. Additional studies could focus on adapting the gels for selectivity.

Another obstacle limiting the potential of the CNC hydrogels is the variability between CNC samples, leading to slight shifts in the reflected colour of the films. Films produced from the same CNC sample displayed very similar reflectance, but films formed from different CNC samples would exhibit shifted reflectance. These differences may be attributed to trace electrolytes present within the CNC suspensions, or the sonication power the samples were subjected to during their preparation. Both of these factors would influence the pitch of the chiral nematic structure and therefore the reflectance observed.

The presented studies on the responsiveness of the hydrogels described in this chapter provide a good foundation for the potential uses of the photonic hydrogels, and further studies could build upon these towards useful sensors. In addition to improving the sensing properties of the hydrogels, future studies could investigate the formation of co-polymer hydrogels, to produce multi-responsive gels.

Chapter 3 – Hybrid Photonic Structures

3.1 Introduction

Self-Assembly

Self-assembly is the process of components in a medium going from a disordered state to an ordered pattern or structure without external involvement.⁸⁵ This process is based on reversible, local interactions between components that arrange themselves in an attempt to reach equilibrium.⁸⁶ Interactions between components are typically weak and non-covalent; examples of these interactions include van der Waals forces, Coulombic forces and hydrogen bonding.⁸⁷ The size and shape of the components will also influence the self-assembly process, and control over these factors can lead to intelligent design of patterns or structure.⁸⁸ Self-assembly concepts can be applied to components on a number of scales, from the molecular to macromolecular and even planetary.⁸⁷ Of particular interest for this chapter is the self-assembly of macroscopic components, specifically rod-shaped particles and nanospheres.

Onsager was the first to explain how rod-like particles spontaneously form ordered structures at critical concentrations.⁸⁹ Onsager's study found that the balance of orientational entropy and entropy associated with excluded volume, favoring order, determines the phase of rod-like structures at various concentrations. At low concentrations of rods, orientational entropy favoring disorder will dominate, but at higher concentration of the rods, a packed, parallel arrangement associated with a high excluded volume has the lowest entropy and is therefore thermodynamically favoured.⁵⁰ CNCs, one example of rod-shaped particles, exhibit chiral nematic ordering upon reaching a critical concentration, as first reported by Revol *et al.*⁴⁰ Following Onsager's description, below a critical concentration CNCs will form an isotropic, non-ordered phase and above it, a biphasic system consisting of an isotropic region and chiral nematic region will form. When the concentration of CNCs is increased further, the isotropic phase eventually disappears, leading to the formation of a completely chiral nematic CNC phase.⁷⁰

Another example of macroscopic components that can self-assemble into ordered structures is colloidal spheres. This self-assembly process can occur through different pathways including sedimentation,⁹⁰ solvent evaporation causing attractive capillary forces,^{91,92} crystallization in physically confined cells⁹³, or through electrostatic interactions.⁹⁴ Each of these processes has their own advantages and disadvantages, depending on the desired properties of the resulting films. For example, sedimentation procedures are simple but require long waiting periods and typically produce polycrystalline domains.⁹⁵ Vertical deposition through solvent evaporation, on the other hand, can produce large area, high quality colloidal crystals with few defects.⁹⁶ However, the process of vertical evaporation is limited by the solvent evaporation time, which may be slow, and to colloidal particles that sediment at a slower rate than that of the solvent evaporation rate.⁹⁵

Structural Colour from Ordered Materials

The self-assembly of spheres from a colloidal solution into a close-packed arrangement provides a facile route to produce three-dimensional photonic structures when the size of the spheres are on the order of magnitude of wavelengths of visible light. The self-assembly of polymer-based spheres can occur in the presence of inorganic precursors that will occupy the voids between the spheres to form an opal structure. The spheres can later be removed, for example through heating or etching, to form an inorganic inverse opal structure.⁹⁶ Both opal and inverse opal structures are classified as three-dimensional photonic crystals, where a periodic change in refractive index occurs in all three dimensions within the structure. This arrangement leads to colour production from an otherwise uncoloured system (e.g. silica). Examples of the colour and structures observed from opal and inverse opal films are shown in Figure 3 - 1.



Figure 3 – 1 The colour observed from opal a) and inverse opal c) films is a result of the structural ordering of the films b) and d).

Similar to the self-assembly of spheres, cellulose nanocrystals can self-assemble into a one-dimensional photonic crystal producing structural colour. In this case, the pitch, the distance over which one helical turn of the chiral nematic structure occurs, must be on the order of magnitude of wavelengths of visible light (ca. 400- 800 nm) to produce colour. The self-assembly process of CNCs is compatible with inorganic precursors and can be used as a template to yield inverse, porous photonic structures upon removal of the cellulose (Figure 3 - 2).⁴⁶ These structures can be tuned to control the colour of the resulting films by the addition of salts⁷³, ultrasonication⁹⁷ or drying temperature⁷³ during the assembly process.



Figure 3 – 2 A schematic of the chiral nematic ordering a) shows the helical pitch. The length of the pitch determines the colour observed from the films b). The ordering of the film can be observed with SEM c). Reprinted with permission from Macmillan Publishers Ltd: [Nature] Reference 46 copyright (2010).

These two classes of photonic crystals are interesting due to the ease of formation of structures that can produce colour from colourless components. Both processes can be altered prior to, or during the drying process to produce PCs exhibiting different colours. These properties make opal and chiral nematic films excellent candidates towards potential applications in photonics, for example, as tunable filters or sensors.

This chapter will explore the combined self-assemblies of one-dimensional photonic structures based on cellulose nanocrystals, and three-dimensional photonic structures based on nanospheres. Investigations into the co-assembly of these nanoscale building blocks from a combined starting solution will be presented first. Next, new hybrid photonic structures produced from successively layering these two classes of photonic crystals will be introduced. Both the combined and layered structures were characterized using scanning electron microscopy (SEM). Finally, suggestions for future studies in this work will be put forth; how this project can be continued in order to fully characterize and produce more unique hybrid photonic structures based on CNCs and nanospheres.

3.2 Experimental

Materials

Cellulose nanocrystals (CNCs) were received in a 3.0 wt. % aqueous solution, pH 2.4 from collaborators at FPInnovations. Hydrochloric acid (HCl), sulfuric acid, tetraethyl orthosilicate (TEOS), and tetramethyl orthosilicate (TMOS) were purchased from Sigma Aldrich and used without further purification. Ammonium hydroxide and hydrogen peroxide were purchased from Fisher Scientific and used as received. Sulfate latex spheres, batch 1872, with diameters of 290 nm, were purchased from Invitrogen and used as received.

Preparation of Stöber Silica Spheres

Silica spheres were synthesized following adapted Stöber methods.⁹⁸ Distilled water (10.8 mL), ethanol (73.8 mL) and ammonium hydroxide (9.8 mL) were first combined and stirred at a consistent speed in a round bottom flask. TEOS (5.6 mL) was then added to the solution and the mixture was stirred overnight; altering the stirring times could produce spheres of different diameters. After stirring, the reaction mixture was centrifuged and the resulting precipitate was dispersed in ethanol. The spheres were further centrifuged and dispersed in ethanol an additional three times before centrifuging with Millipore filtered water until the solution pH was neutral. The silica spheres were

then dispersed in ultrapure water at 1.5 wt. % concentrations until used in the synthesis of opal films.

Preparation of One-Dimensional Photonic Crystals from CNC

Chiral nematic silica films were prepared following procedures described by Shopsowitz⁴⁶ and Kelly⁹⁹. The films were prepared by first sonicating 5 mL of a 3 % aqueous solution of CNCs with 200 µL of TMOS for fifteen minutes. The solution was then stirred for one hour at room temperature before casting into a polystyrene Petri dish to dry. Once dry, pyrolysis of the cellulose was initiated by heating the film at a rate of 120 °C/h up to 100 °C and held at that temperature for two hours. The film was then further heated at 120 °C/h up to 540 °C and held for 6 hours. Finally, the film was cooled to room temperature to yield chiral nematic mesoporous silica films. To produce crack-free silica films, the same procedure was followed, but with the addition of 2 mL of a 4.3 wt. % glucose solution to the initial mixture.

Preparation of Three-Dimensional Photonic Crystals from Opals

Opal and inverse opal films were prepared following the method described by Hatton et al.⁹⁶ Latex opal films were prepared via evaporation from an aqueous solution containing 300 nm latex spheres, tetraethyl orthosilicate, 0.1 M HCl solution and ethanol. The films were formed on a glass substrate placed vertically in a beaker containing the latex opal solution, and left to evaporate at 65 °C. This produced a coloured opal film. The opal structure was then sintered at 500 °C for 2 hours to remove the latex spheres, creating a silica inverse opal structure. A similar procedure was followed to make opal films using Stöber silica particles, with only distilled water used as the solvent. The glass substrates used for opal formation were cleaned prior to use in a 3:1 concentrated sulfuric acid to hydrogen peroxide solution.

Characterization Techniques

Scanning electron microscopy (SEM) was performed using a Hitachi S4700; samples were sputter coated with gold or gold/palladium prior to imaging. Ultravioletvisible light spectroscopy was carried out using a Cary 5000UV/Vis/NIR spectrophotometer; transmission spectra were collected with the films mounted normal to the beam path. Polarized optical microscopy was performed on an Olympus BX41 microscope and all images were taken with the polarizers in a perpendicular (crossed) arrangement.

3.3 Results and Discussion

Co-assembly of nanoscale building blocks

Cellulose nanocrystals and micro- or nanospheres are examples of building blocks that, upon reaching an appropriate concentration under the right conditions, will selfassemble into a well-ordered phase.^{40,88} These phases can produce photonic structures when the distance of the periodic change of refractive index within the structures is on the order of magnitude of visible light.^{13,46,100} Based on the relatively simple methods required to produce photonic structures from these nanoscale building blocks, we were interested in investigating how these building blocks would assemble when combined. Potentially, a hybrid of one-dimensional and three-dimensional photonic structures could be formed, or perhaps layers of each building block would assemble intermittently.

Initial experiments for this project included combining synthesized silica nanospheres with cellulose nanocrystals, letting self-assembly occur via evaporation of solvent with a vertically oriented substrate, and investigating the resulting films using SEM.



Figure 3 - 3 SEM images of close packed silica spheres a) and the packing of the spheres disrupted by the addition of CNCs b).

As seen in Figure 3 - 3, when no CNCs were added to the solution mixture the silica spheres self-assembled into a close packed arrangement with minimal disorder. However, upon the addition of CNCs into the solution mixture, the assembly of the spheres into an ordered arrangement was highly disrupted.

This finding led to an interest in investigating the co-assembly of latex nanospheres with CNCs in varying ratios. Additionally, we wanted to investigate whether the evaporation procedure used would affect co-assembly. The self-assembly of CNCs to give chiral nematic films occurs in a petri dish, where the substrate is oriented parallel to the solution surface. To allow self-assembly of the nanospheres into ordered opal films, a vertical evaporation procedure was followed, where the substrate is placed vertically in a solution, perpendicular to the solution surface. As the solution evaporates, the meniscus formed along the substrate acts as a capillary force to 'pull' the spheres together to produce an ordered structure. Spheres have also been shown to self-assemble through horizontal evaporation methods⁹⁰, but the vertical evaporation procedure proved to be most consistent in producing iridescent coloured films, and we wanted to maintain that. Electron microscopy proved indispensible to study the structures formed by these assemblies.

The first method investigated was vertical evaporation whereby nanospheres and CNCs were combined in solution at specific weight ratios. As the solvent evaporated, a film formed onto a vertically placed glass slide. The weight ratios used for this method were 1:3, 1:1 and 3:1 of nanospheres: CNCs, respectively. Figure 3 - 4 shows that the nanospheres prefer to self-assemble, or at least aggregate, in each of the samples. The 1:3 sample was mostly a disordered combination of CNCs and nanospheres, but in some

areas, regions of close-packed spheres could be found. The formation of areas with packed spheres indicates that spheres in close proximity prefer to arrange in a closepacked manner, and that the abundance of CNCs packed around these areas. Through SEM characterization, there was no evidence of a chiral nematic formation by the CNCs.

The sample containing a 1:1 weight ratio of CNCs to nanospheres was composed of regions of clusters of nanospheres throughout the sample, with little evidence of an organized structure. This implies that the CNCs and spheres work well to hinder the self-assembly of one another. The 3:1 sample, however, showed a gradient of sphere ordering, as can be viewed in images c) and d) of Figure 3 - 4. At one edge of the film the spheres formed a very well ordered structure, while at the other edge, random clusters can be seen.



Figure 3 – 4 SEM images of vertically assembled nanospheres and CNCs at varying weight ratios. Weight ratios were varied from 1:3 a), to 1:1 b) to 3:1 c) and d), for nanospheres: CNCs, respectively.

Next the structures formed from the horizontal evaporation of solutions of nanosphere and CNCs were investigated. The first weight ratio investigated was a 1:1 CNCs to nanosphere solution. Figure 3 - 5 a) and b) show the structure that was observed using SEM; very well ordered nanospheres hardly affected by the presence of CNCs. From what could be observed through these images among others, it seemed that the majority of the spheres self-assembled into a well-ordered pattern near the centre of the film, while other areas showed agglomeration. As solvents evaporate from solutions containing macroscopic components, a 'coffee stain effect' can be observed whereby the centre of the solution dries the fastest, pushing the components to the edge of the drying 'droplet'. In this case, it would seem the CNCs experiences more of a 'coffee stain effect' than the spheres, which could explain the agglomeration at the edges.

At this stage we were interested in determining whether the CNCs would self assemble into a chiral nematic phase at all with nanospheres present, so the weight ratios were varied to heavily favour CNCs. At 50:1 and 200:1 ratios of CNC: nanospheres, the CNC concentration was high enough to form a chiral nematic structure, as can be observed in c) and d) of Figure 3 - 5. Lone nanospheres are visible in these images, and due to the low concentration of spheres in the solution prior to evaporation, it is presumed no assembly of the spheres occurred. As co-assembly of the building blocks together proved to not be viable, we decided to try a different route to produce interesting hybrid photonic structures.


Figure 3 – 5 SEM images of horizontally assembled nanospheres and CNCs at varying weight ratios. Weight ratios were varied from 1:1 a) and b) to 50:1 c) and 200:1 d) for CNCs: nanospheres, respectively.

Self-assembly of CNCs on Opal/Inverse Opal Substrates

One interesting avenue to explore with regards to self-assembling photonic structures was to use one photonic crystal as a substrate to form a second photonic crystal, thereby creating a hybrid photonic structure. Layered photonic systems could provide a route to limit a number of select wavelengths from being transmitted through a material. This system could be useful in optics, for example as a type of filter. In this section, we were interested in forming a novel photonic structure based on two classes of photonic crystals formed via self-assembling processes, one-dimensional chiral nematic photonic crystals and three-dimensional opal/inverse opal photonic crystals.

The first process investigated was the assembly of CNCs into a chiral nematic phase using an opal film or an inverse opal film as a substrate. The chiral nematic phase of the CNC self-assembly can be affected by the choice of substrate¹⁰¹, so the first characterization performed was to observe the chiral nematic ordering of a CNC/TMOS solution on opal and inverse opal films using polarized optical microscopy. Visible in the POM images in Figure 3 - 6 are fingerprint structures indicative of the chiral nematic ordering of the CNCs on both the opal and inverse opal films, indicating that layered hybrid structures could be formed. The fingerprints formed are a result of the nematic layers of CNCs stacking together to eventually produce a chiral nematic structure.



Figure 3 – 6 Fingerprints indicative of the chiral nematic ordering can be seen in POM images of CNC solution on opal film a) and inverse opal film b).

The chiral nematic ordering of CNCs on the opal and inverse opal substrates was a good indication towards hybrid structures. The next facet to study was the use of CNCs as a template for chiral nematic silica structures on opal and inverse opal substrates. This would produce more stable hybrid structures, and could lead to a dual inverse photonic structure composed only of silica. The compatibility of silica precursors (namely TMOS) and CNCs allowed for facile templating of the chiral nematic structure. However, it was found that upon complete evaporation of the CNC/TMOS solution on the inverse opal structure, the resulting films would crack into small fragments, Figure 3 - 7. The cracking of the film was not a major issue in terms of characterizing via SEM; in fact, in some cases the bottom inverse opal structure would adhere to the chiral nematic silica and could be peeled from the glass substrate. This allowed for viewing of the structure from the 'bottom' (viewing the inverse opal structure on top of the chiral nematic) as seen in Figure 3 - 12. Notwithstanding, the cracking of the chiral nematic layer could be an obstacle for other characterization methods, and would be a barrier to producing useful hybrid photonic structures for any applications. For this reason, later samples followed a method to produce crack free chiral nematic silica films⁹⁹, by adding glucose to the CNC/TMOS solution. Additionally, for the rest of the experiments in this chapter, focus was placed on latex opal and silica inverse opal films that were prepared by combining latex nanospheres with TEOS, a silica precursor, to form an opal structure space filled with silica. The latex opals were then removed through calcination to produce silica inverse opal films. The latex spheres in combination with TEOS consistently formed reproducible, coloured films, which made them ideal for use in these experiments. Examples of the typical colours and structures of opal and inverse opals films produced can be seen in Figure 3 - 1.



Figure 3 – 7 Photo of the cracking observed for silica chiral nematic structure formed on an inverse opal substrate.

Once formed, the layered chiral nematic-opal and –inverse opal films were characterized using SEM to investigate the ordering within the bilayer photonic structures, and UV-vis spectroscopy to examine the optical properties of the films.



Figure 3 – 8 SEM images of the chiral nematic structure formed on top of an opal film.



Figure 3 – 9 SEM image of the CNC-templated chiral nematic structure on an opal substrate.

Figures 3 - 8 and 3 - 9 show the ordered structures produced by the self-assembly of the opals and then cellulose nanocrystals. Figure 3 - 8 clearly shows the two layers of this bi-layer structure. The top image has the chiral nematic structure in focus, while the bottom image focuses on the ordered opal structure. It can be seen in this image that the opal layer remains well intact after the chiral nematic layer is formed on top, a positive result towards hybrid structures. In Figure 3 - 9, the periodic structure of the chiral nematic phase can be observed in the foreground of the image, while the ordered opal structure can be observed near the edges of a crack in the film. In order to image the layers within this hybrid structure, it was necessary to fracture the film and attempt to image at these fracture points.



Figure 3 - 10 Transmission spectra of opal structure, and hybrid chiral nematic-opal structure with and without the addition of glucose.

The transmission spectra of the chiral nematic structures on opal films are plotted in Figure 3 - 10. The relative transmission through these films is interesting, as the transmission intensity decreases as the chiral nematic layer is added to the opal structure. This result is attributed to variations within the films, most likely due to differences in sample thickness. The addition of the chiral nematic layer increases the reflected wavelength region, as would be expected as the thickness of the film is increased and due to two photonic structures contributing to reflecting certain wavelengths of light. The successful formation of the chiral nematic structure on the opals then led into formation of the chiral nematic structure.

The chiral nematic structures formed very well on inverse opal structures, as can be seen in Figure 3 – 11 and 3 – 12. Figure 3 – 11 clearly shows the ordered chiral nematic structure on top of an inverse opal structure that is visible along the edge. Figure 3 - 12 better shows that these two structures are adhered, and that free-standing hybrid photonic structures can be produced.



Figure 3 – 11 SEM image of an ordered chiral nematic structure on an inverse opal structure.



Figure 3 - 12 SEM image viewing the inverse opal structure attached to the chiral nematic structure that was formed on top of the inverse structure.



Figure 3 – 13 Transmission spectra of inverse opal structure and hybrid chiral nematic structure on inverse opal structure.

The transmission spectra of the chiral nematic structures on inverse opals, Figure 3 - 13, reflect more what was expected to observe for the hybrid structures. The range of wavelengths not being transmitted through the inverse opal film, the dark blue trace in Figure 3 - 13, broadens as the chiral nematic layer is added to the structure, the light blue trace. This is congruent with the photonic crystal layers combining to reflect more wavelengths of light as a hybrid structure than the inverse opals do on their own. The hybrid sample with the addition of glucose shows a similar trace to the hybrid sample without glucose, with the % transmission being the main difference between the two, indicating that only minor changes in optical properties occur for glucose samples. These results show that the hybrid inverse opal-chiral nematic structures could have potential as optical filters within the visible region of the electromagnetic spectrum. Presumably, alterations to the structures could lead to optical filters for different regions of the visible spectrum.

Self-assembly of Opals using a Chiral Nematic Substrate

The next step in producing hybrid photonic structures was to investigate the assembly of opals on a chiral nematic-silica substrate formed from CNC templating. As with the chiral nematic assembly of CNCs, the assembly of colloidal crystals can also be affected by the choice of substrate.¹⁰² Ideally, hybrid photonic structures could be formed by self-assembling either class of photonic structure using another photonic structure as a substrate. This flexibility would be necessary to produce multi-layered structures, and would display the versatile nature of these methods.

Self-assembling opals on a chiral nematic silica film was technically a bit more challenging than the reverse self-assembly, as the chiral nematic silica films are quite thin and brittle. In order to form substrates large enough for opal self-assembly, it was necessary to use the crack-free CNC/glucose method for templating chiral nematic silica structures. Following vertical evaporation methods, the opal were self-assembled on a chiral nematic silica film, and then heated to thermally decompose the nanospheres to yield a hybrid silica chiral nematic-inverse opal structure. Figures 3 - 14 and 3 - 15 show ordered spheres and an inverse opal structure formed on a chiral nematic silica substrate, respectively. The inset image in Figure 3 - 14 clearly shows the periodicity of the chiral nematic structure before the opals were formed on the film. The successful formation of these structures indicates that these hybrid photonic structure systems are versatile, and can be produced through different routes.



Figure 3 – 14 SEM image of latex nanospheres assembled on a chiral nematic silica substrate, inset shows the periodicity of the chiral nematic film before opal assembly.



Figure 3 – 15 SEM image of silica inverse opal structure formed on a chiral nematic silica structure.

Multi-layer Photonic Structures

Upon being able to successfully form each class of photonic structure in this chapter using another one as a substrate, the next step was to produce multi-layer structures. For these structures, a chiral nematic silica structure was used as a substrate for the opal films. Next, as with the bi-layer structures, vertical evaporation was used to layer opals on the chiral nematic silica structure. Then finally, another layer of the chiral nematic silica structure was formed as the final layer. The SEM images in Figure 3 - 16 are taken from a fracture area within the same sample. The image on the left shows an inverse opal structure on top of the chiral nematic structure, while the image on the right shows that the formation of a multi-layered hybrid photonic structure is possible. These novel hybrid structures could be useful for optical applications and investigation into the optical properties, such as reflectance would provide insight as to what uses would be most ideal.



Figure 3 – 16 SEM images of tri-layered photonic structure consisting of chiral nematic silica structures composing the top and bottom, with a silica inverse opal structure in the middle.

3.4 Conclusions and Future Work

This chapter showed that new, multi-dimensional, hybrid photonic structures can be produced from self-assembling nanoscale building blocks. While co-assembly of the blocks led to preferential assembly of one form, or resulted in no self-assembly, systematic layering of the structures was proved possible by alternating assembly processes one at a time. It was shown that the chiral nematic structure of CNCs would form on both opal and inverse opal substrates to produce bi-layer structures. Conversely, opal structures can be formed using chiral nematic silica structures as a substrate for vertical evaporation methods. Also shown was the ability to form multi-layered structures when a bi-layer film is used as a substrate for self-assembly. This method could potentially be used to build up more successive layers. All of the structures presented have been characterized using electron microscopy, and only a few of the structures were characterized optically. Future studies should fully investigate the optical properties of these films. One restriction to investigating the optical properties of these films was the difficulty in maintaining sizable films upon forming bi-layer structures, due to the brittleness of the silica films. The ability to develop large scale bi-layer films would be the first step towards adequate optical characterization.

Photonic crystals can be used to restrict the wavelengths of light that are able to pass through them.¹⁰³ Multi-layered hybrid photonic structures could lead to precise control of wavelengths allowed or disallowed to pass through the material. Theoretically, each photonic layer would prohibit certain wavelengths from being transmitted, thereby allowing greater control over the total transmittance. The hybrid structure produced using

an inverse opal as a substrate for a chiral nematic assembly displays this, as shown by the transmission spectra of the films, as an initial proof of concept for prohibiting wavelengths within the visible region from passing through. Materials like these would be very valuable for applications such as filters or waveguides.

The photonics of the structures formed in this chapter could be manipulated in many different ways to produce a family of photonic hybrid structures. First, the colour of both classes of photonic structures can be tuned by changing the size of the spheres, or the size of the chiral nematic pitch. Multiple different hybrid structures could be formed by systematically adjusting the colour of each layer to tune the transmittance as desired. Investigation into controlling the colour of each layer could prove interesting, and would show the versatility in producing multiple types of filters from these materials.

Another interesting avenue to explore would be to look at how the optical properties can be manipulated by the addition of solvents. The chiral nematic silica and the inverse opal structures are both porous, and the introduction of solvents into the pores can eliminate the structural colour that is produced by eliminating refractive index contrasts. Potentially, solvents or molecules could be made to enter the pores of one layer, but not the other, thereby controlling the nature of these hybrid materials.

These novel hybrid photonic systems demonstrate how self-assembly processes can be used to form interesting structures based on photonic crystals. The studies in this chapter lay the foundation for future investigation into the properties of these unique materials, and how they can be modified for use in optical applications.

Chapter 4 – Conclusions and Final Remarks

The notable strength and remarkable ability of cellulose nanocrystals to arrange into a chiral nematic photonic structure has led to much interest into exploring the integration of these properties into new materials. The development of CNCs as a template to produce photonic mesoporous silica, and other inorganic films, is an interesting area that can still be expanded upon. The ability to incorporate the chiral nematic structure formed by CNCs into hydrogel materials to create strong photonic materials that can undergo colour changes in response to stimuli holds promise for different types of sensing applications. Combining chiral nematic silica films with other photonic crystals can lead to unique hybrid structures that could prove useful for optical filters and waveguides.

Reported is the successful integration of CNCs with several different monomers to create a family of photonic hydrogels. It was shown that the reflection from these gels can be modified by changing the polymer used to create the films, through swelling in various solvents, and through controlled crosslinking within the hydrogels. These films can be tuned to respond to specific stimuli, indicating there is potential for the films to be useful as sensors. Additionally, these photonic hydrogels were shown to have high tensile strength as dry films, in comparison to reports of other CNC-containing hydrogels, further showing how the integration of CNCs into hydrogels can not only introduce colour, but also improve gel properties. In order for the gels to realistically be useful as sensing materials, sensitivity and specificity studies would need to be conducted. The formation of novel, hybrid photonic structures composed of silica was reported in this thesis. These structures were characterized using electron microscopy, to show the periodic ordering of both classes of photonic structure, as well as how the structures were adhered together. These studies focused on how hybrid structures could be produced using self-assembly, and maintaining periodic structures. Future investigations into optical properties of the films as layers as produced would indicate how useful these films could be as optical filters. Additionally, as the final silica structures were composed of two sets of porous material, chiral nematic silica, and inverse opal silica, these films could have sensing abilities based on solvent entry into the pores.

Together, the CNC-hydrogel films and hybrid photonic structures display our ability to use CNC as a template, and component in polymer films to produce photonic structures. Flexible, responsive hydrogels can be produced, as well as rigid silica films that take advantage of the chiral nematic structure formed by the self-assembly of CNC.

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