SYNTHESIS OF NANOCOMPOSITE HYDROGELS BASED ON POLYACRYLAMIDE AND CELLULOSE NANOCRYSTAL

A thesis submitted in partial fulfillment of the requirement for
the degree of M.Phil. in chemistry

SUBMITTED BY

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DECLARATION BY THE CANDIDATE

I do hereby declare that this thesis work, entitled "**SYNTHESIS OF NANOCOMPOSITE HYDROGELS BASED ON POLYACRYLAMIDE AND CELLULOSE NANOCRYSTAL**" submitted in partial fulfillment for the requirement of M.Phil. Degree in Chemistry to the Department of Chemistry, Bangladesh University of Engineering and Technology (BUET) in April 2017, is genuine work done by me under the supervision of Dr. Md. ShafiulAzam, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET). The thesis or part of it has not been submitted before in any degree or diploma.

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Certification of Thesis
A thesis on
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April, 2017 Md. Jahangir Hossen

Dedicated to

My Honorable supervisor

Abstract

In this research, we employed a mussel-inspired strategy to the synthesis and characterization of nanocomposite hydrogels based on polyacrylamide (PAM) and cellulose nanocrystal. Nanocomposite hydrogel was prepared by freeradical polymerization of acrylamide and dopamine (DOPA) grafted carboxylated cellulose nanocrystal initiated by redox initiator potassium persulfate (KPS) and N, N´-methylene bisacrylamide (MBA) was employed as a crosslinking agent.Dopamine grafted carboxylatedcellulose nanocrystal has been incorporated into the polymer matrix (PAM) to produce a mechanically stable hydrogel. First, cellulose nanocrystal (CNC) was synthesized from a waste sawdust. The synthesized CNC was converted to carboxylated cellulose nanocrystal (CCN) by using selective oxidizing agent 2,2,4,4-tetramethyl-1-oxyalpiperidine (TEMPO) radical. Then we synthesized a CCN-DOPA material. In presence of coupling agent N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), the CCN was modified with dopamine (DOPA) bythe coupling reaction. Finally the synthesized CCN-DOPA was incorporated in cross-linked polyacrylamide (PAM) hydrogels. Incorporated CCN-DOPA in hydrogel produced nanocomposite hydrogel. The morphology of theresulting nanocomposite hydrogels, thermo-sensitive properties, and swelling behavior were investigated. The results indicated that CCN-DOPA-PAM hydrogel exhibited temperature sensitivity. The morphologies observed on the scanning electron microscopy (SEM) images supported that the added CCN-DOPA appeared to be an integral network of the hydrogels, which is responsible for the improved mechanical strength as we expected. In the swelling measurement the hydrogels exhibited appreciable water uptake and were moderately sensitive to temperature.

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Chapter 1

Introduction

1.1 Composite

Composite material has a long history. As early as 3000B.C the accient Egyptians embedded Straw in their mud bricks in order to control shrinkage and improve the tensile strength. After that many more new composite materials are invented and scientists are trying to develop its different propertied. A new dimension added in the field of chemistry when the nanomaterials invented. Composite is a material combined of two or more constituents of different properties which is made significant and unique properties [1]. As an example wood is a natural composite material where long cellulose fiber is matrix and lignin is reinforcement. In fiber-reinforced polymer matrix, fiber is reinforcement and polymer is matrix. Reinforcement enhance the strength and stiffness of composites. The best advantage of composite material is that they are light, corrosion resistance as well as strong. Composite materials are becoming more important day by day being used to aerospace [2,3,4], transportation [5,6], construction [7,8], sporting goods [9,10] and marine goods [11,12,13].

1.2 Nanocomposite

A nanocomposite is a multiphase solid material where one of the phases has a nanoscale dimension less than 100nm [14,15]. Nanocomposite are nanomaterials that incorporate nanosized particles into a matrix of standard material. The result of the addition of nanoparticles is drastic improvement in properties that can include mechanical strength, toughness and electrical or thermal conductivity [16]. Any material with at least one dimension in the 1-100 nm range. Nanocomposites are a class of materials in which one or more phases with nanoscale dimensions (0-D, 1- D, and 2-D) are embedded in a metal, ceramic, or polymer matrix.

1.2.1 Polymer-matrix nanocomposite

Nanoparticle added polymer matrix can improve its performance [17]. Nanoparticle is used as a reinforcement. Sometimes it is called nano-filler. So nanoparticles such as grapheme, carbon nanotubes are used as reinforcement in polymer matrix for developing the strength and stiffness. Polymer and nanoparticles show the unique properties due to interactions. Polymeric nanocomposites are used widely in biomedical applications such as tissue engineering [17], drug delivery and cellular therapies. Starch [18], cellulose [19], collagen, poly vinyl alcohol (PVA) [20], acrylamide (AAm) [21], acrylic acid (AA) [22] are used for polymer matrix .

1.2.2 Metal-matrix nanocomposite

MMC (Metal matrix composites) are metals reinforced with other metal, ceramic or organic compounds [23]. They are made by dispersing the reinforcements in the metal matrix. Reinforcements are usually - allydone to improve the properties of the base metal like strength, stiffness, conductivity, etc.Aluminium and its alloys have attracted most attention as base metal in metal matrix composites [24]. Aluminium MMCs are widely used in aircraft, aerospace, auto- mobiles and various other fields [25]. The reinforcements should be stable in the given working temperature and non-reactive too. The most commonly used reinforcements are Silicon Carbide (SiC) and Aluminium Oxide (Al2O3). SiC reinforcement increases the tensile strength, hardness, density and wear resistance ofAl and its alloys [14]. A metal matrix composite (MMC) is a material with at least two constituent parts of metal. Alloys are one kind of metal matrix nanocomposite. These materials combine metal and ceramic features, i.e., ductility and toughness with high strength and modulus. Metal matrix nanocomposites are suitable for production of materials with high strength in shear/compression processes and high service temperature capabilities. They show an extraordinary potential for application in many areas, such as aerospace and automotive industries and development of structural [26,27].

1.2.3 Ceramic matrix nanocomposite

Ceramic Matrix nanocomposite (CMC) is a material consisting of a ceramic matrix combined with a ceramic oxides, carbides in dispersed phase [28]. Ceramic Matrix Composites are designed to improve toughness of conventional ceramics. Over the past half century ceramics have received significant attention due to its application as structural materials under conditions of high loading rates and high temperature. Ceramic Matrix Composites are reinforced by either continuous fiber. CMC examples are Silicon carbide matrix composites**,** Alumina and alumina-silica (mullite) matrix composites. It has popularity for aerospace [29] and automotive applications.

1.2.2 Application of Nanocomposite

Nanocomposites are currently being used in a number of fields and new applications are being continuously developed. Applications for nanocomposites include:

a. Thin-film capacitors for computer chip
b. Solid polymer electrolyes for batteries.
c. Automotive engine parts and fuel tanks
d. Impellers and blades
e. Oxygen and gas barrier
f. Food packaging
g. Drug delivery systems
h. Anti-corrosion barrier coatings
i. UV protection gels
j. New fire retardant materials
k. New scratch/abrasion resistant materials

1.3 Hydrogel

Hydrogels are hydrophilic, highly crosslinked polymeric networks capable of absorbing large amount of water. Hydrogels contain water solubility groups such as –OH, -COOH, $-NH_2$, $-CONH_2$ and $–SO_3H$.They are insoluble in water and are available in dry or hydrated sheet or gel. It is highly stimuli responsive such as pH [30], temperature [31], electric field and magnatic field. So it is called smart hydrogel. Temperature sensitive hydrogels are also called as thermogels. These stimuli-sensitive hydrogels can display changes in their swelling behaviour of the network structure according to the external environments Hydrogels are also generally highly biocompatible, which may be attributed to the high water content of hydrogels. Hydrogels are gels in which the liquid phase is water. Cross-linking can render these gels insoluble and provide additional mechanical strength. Such gels swell by imbibing small to large quantities of water. These gels are biocompatible. It became soft when absorb water. Hydrogels are generally synthesized by free radical polymerization. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains. Many materials, both naturally occurring and synthetic, fit the definition of hydrogels. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains. It is a polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water

1.3.1 Polyacrylamide based hydrogel

Acrylamide based hydrogels are the most common hydrogels. Polyacrylamide(PAM) hydrogels are cross-linked polymer network synthesised by the polymerization of acrylamide in presence of bifunctional crosslinking agent such as N,N'- methylenebisacrylamide [32] .PAM hydrogels have sufficient hydrofilicity but are low in hydrolytic stability and tensile strength. These hydrogels undergo large volume transition on swelling but they lack hydrolytic stability. Their hydrolytic stability can be increased if substituted acrylamides have alkyl or hydroxyalkyl groups. Polyacrylamide hydrogels are nontoxic, stable, and biocompatible. Poor mechanical properties have limited further development of PAM hydrogel.Polyacrylamide (PAM) based hydrogels are bloodcompatible biomaterials that find applications in coatingof catheters and controlled release devices [33].

Besides the good mechanical performance PAM hydrogels are characterized by high water content, transparency, long-term stability as well as homogeneity. Furthermore, PAM hydrogels demonstrated non-toxicity and biocompatibility. The high cohesive and adhesive properties favor PAM hydrogels as a competent material in tissue engineering [34]. PAM hydrogels also offer broad applications in different technological areas, *e.g.* as materials for contact lenses and protein separation, matrices for cell-encapsulation, and devices for controlled release of proteins and drugs [35]. The PAM hydrogels are widely used in ophthalmic operations, food packaging as well as water purification. These hydrogels have also been used in plastic and aesthetic surgery for more than 20 years [36].

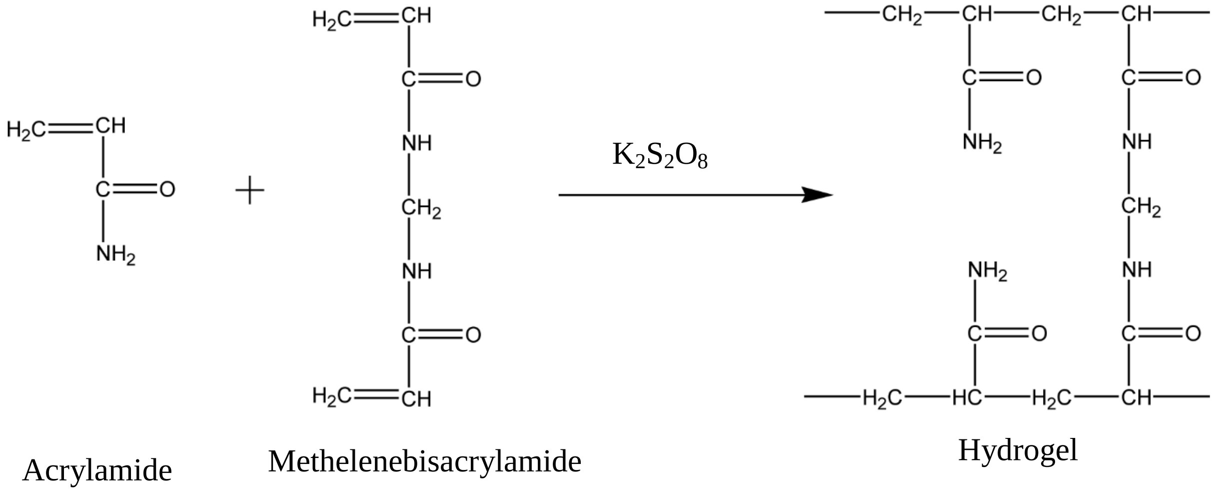

Figure 1.1Polymerization of acrylamide chains with bis cross-linker

1.3.2 Properties of Hydrogel

For any material, the physical, chemical and mechanical properties play an important role in determining if it is suitable for a given application. However, for hydrogels, these properties are highly depended on the environmental conditions as well. Thus, while determining the properties of a hydrogel, mimicking the in situ conditions becomes imperative. Hydrogels have a variety of properties including their absorption capacity, swelling behavior, permeability, surface properties, optical properties and mechanical properties which make them promising materials for a wide variety of applications. The characteristics of the polymer chains and the crosslinking structures in these aqueous solutions play an important role in the outcome of the properties of the hydrogel.

a) Swelling properties: All polymer chains in hydrogels are cross linked to each other. One of the variables that effects capacity of water absorption is the degree of cross linking and the type of cross linking agent used. The amount of the aqueous medium incorporated in a hydrogel is determined gravimetrically and can be expressed by its swelling ratio

$$swelling\ ratio = \frac{w_t - w_0}{w_0}$$

Where, W_t is the weight of hydrogel in swollen state and

W_0 is the weight of hydrogel in dry state. Swelling ratio will be change when solvent pH, temperature, magnetic field are changed.

b) Mechanical properties: Mechanical properties of hydrogels are very important from the pharmaceutical and biomedical point of view. The evaluation of mechanical property is essential in various biomedical applications such as ligament and tendon repair, wound dressing material, matrix for drug delivery, tissue engineering and cartilage replacement material. When nanocomposite material will be incorporated in hydrogel, its mechanical strength will be increased. By changing the degree of crosslinking the desired mechanical property of the hydrogel can be achieved. Increase in the degree of crosslinking, a stronger hydrogel can be obtained through the higher degree of crosslinking.

c) Biocompatibility: Biocompatible property is important for the hydrogels to be biocompatible and nontoxic in order to make it application. Biocompatibility is the ability of a material to perform with an appropriate host response in a specific application.

1.3.3 Application

Polyacrylamide hydrogels are widely used in drug treatment, food packaging products, and water purification, Hygienic products, Agriculture [38], Drug delivery systems and sealing [39][40], Coal dewatering [41], Artificial snow, Food additives, Pharmaceuticals [42], Biomedical applications, Tissue engineering [43], Regenerative medicines and Diagnostics, Wound dressing, Waste water treatment [44], Separation of biomolecules or cells and Barrier materials to regulate biological adhesions, Biosensor.

1.4 Cellulose nanocrystal based nanomaterials

1.4.1 Nanomaterials

Nanomaterials are generally considered as the materials that have a characteristic dimension (e.g. grain size, diameter of cylindrical cross-section, layer thickness) smaller than 100 nm. Nanomaterials can be metallic, polymeric, ceramic, electronic, or composite.

1.4.2 Cellulose Nanocrystal (CNC) as nanomaterial

Cellulose nanocrystal as a nanomaterial is very smart material. Cellulose nanocrystal is prepared from chemical treatment of cellulose. Cellulose is one of the world’s most abundant, natural and renewable biopolymer resources. It has many unique properties such as high stiffness, high strength, low thermal expansion coefficient and a high aspect ratio. Cellulose is a fibrous, tough, and water-insoluble polymer and it plays an essential role in maintaining the structure of plant cell walls. Moreover, cellulose is a biodegradable, biocompatible, and renewable natural polymer and hence it is considered an alternate to nondegradable fossil fuel-based polymers. Chemical modifications of cellulose were interesting routes for preparing cellulose derivatives with specific properties. By oxidation reaction, especially selective oxidation reaction, new functionalities, such as carboxyl and aldehyde groups can be formed and the oxidized products may have new industrial utilities. Various selective oxidation systems were found. It was reported that primary alcohol groups of cellulose were converted to carboxyl groups by the oxidation of cellulose with TEMPO mediation.

1.5 Properties of CNC based Hydrogel

Hydrogels are soft, wet and cross-linked hydrophilic polymeric materials that are capable of absorbing large amount of water. Hydrogels have been studied for wide range of biomedical, pharmaceutical, tissue engineering and daily-care application. In spite of multiplication it has lack of mechanical strength. Most of polymeric hydrogels are brittle due to polymeric structure. But CNC based hydrogels possess greater tensile strength of hydrogel. It was a good achievement for hydrogel.

1.6 Literature review

Hydrogels and their properties

Back to 1960, the pioneering work of Wichterle and Lim introduced hydrophilic hydrogels for biological uses [45]. During the past decades, hydrogels have gained tremendous interest to the scientist due to their exceptional promise in biomaterial applications. More than 50,000 reports has been published on hydrogel up to now. Hydrogel is a polymeric material which exhibits the ability to swell and retain a significant fraction of water within its structure but it will not dissolve in water. It has existed in nature since the evolution of life. Bacterial biofilms, hydrated living tissues and extracellular matrix components are some examples. A variety of naturally occurring polymers such as collagen, alfinate, agarose and gelatin were also explored in early human history. However the modern history of hydrogels as a class of materials designed for medical uses.

Dates back to the late 1950s, Poly (2-hydroxyethyl methacrylate) commonly known as P-HEMA was the synthetic hydrogel to be synthesized in 1936 by DuPont Scientist, but it was not until 1960 that Wichterle and Lim established the importance of P-HEMA hydrogels as excellent candidates for contact lens applications. This innovation led to the modern field of biomedical hydrogels. This success generated enormous interest in hydrogels and led to the development of smart hydrogels that can change their properties of an external stimulus such pH, temperature, magnetic field, ionic strength or electric field. Hydrogels began to be expanded in various research field such as biomaterials, agriculture, pharmaceuticals and biotechnology. More recently hydrogels have become especially attractive to the field tissue engineering as matrices for repairing and regenerating a widely of tissues and organs.

Hydrogels have a variety of properties including their absorption capacity, swelling behavior, permeability, surface properties, optical properties and mechanical properties which make them promising materials for a wide variety of applications. The characteristics of the polymer chains and the crosslinking structures in these aqueous solutions play an important role in the outcome of the properties of the hydrogel.

1.6.1 Swelling behavior of hydrogels

Hydrogels can be characterized by their degree of swelling. The swelling behavior of hydrogels is an important factor deciding their applications especially in pharmaceutical, biomedical and tissue engineering [46]. The water absorption of hydrogels depends on many factors such as cross-link density (the most important factor), nature of the solution, hydrogels structure (porous or poreless), network parameters. The swelling behavior can be seen as a diffusion process. Highly cross-linked hydrogel network show faster swelling compared to their slightly cross-linked counterparts because of the structure of the hydrogel .Usually the driving force for the absorption is from a balancing of three forces of electrostatic, osmotic and entropy favored dissolution of polymer. The final water content of hydrogels depends on kinetics as well as thermodynamic parameters. Water diffusion into the network structure is rate determining at the beginning of the swelling from the hydrogel. This depends on the molecular weight and temperature of the solvent as well as the extent of porosity within the hydrogel structure. Omidian and park reported that the swelling process of a hydrogel was controlled by three major elements: the crosslinker content, the ionic content and the hydrophilic content.

Ionic content of the system and the surrounding: Swellable hydrogel networks can be classified into two groups: ionic and non-ionic. At a certain amount of elastic forces, swelling of the ionic hydrogels will be a more entropy-favored process compared to their non-ionic counterparts. As the number of ions within the hydrogel network increases, more and more osmotic and electrostatic forces will be induced. Changing the nature of the environment (water) can control the entropy-driven swelling process of the hydrogel. The addition of ions to the environment limits the swelling capacity of an ionic hydrogel.

Hydrophilic content: The hydrophilic content of the hydrogel will influence the intermolecular forces responsible for the diffusion as well as the swelling of the network. As hydrophilicity of the hydrogel increases, the interaction between water and hydrogel will increase too, and thus the water diffusion is facilitated whereby a greater swelling of the hydrogel results.

1.6.2 Mechanical Properties of Hydrogels

The mechanical properties of hydrogels depend on their composition and structure. Because of the high water content of fully swollen hydrogels, they normally have weak mechanical strengths. The mechanical properties of the hydrogel are affected by the co-monomer composition, crosslinking density, polymerization conditions and degree of swelling [47]. The mechanical strength of the hydrogel is often derived entirely from the crosslinks in the system, particularly in the swollen state where physical entanglements are almost nonexistent. The dependence of mechanical properties on crosslink density has been studied intensively by many researchers. However it should be noted that when the crosslinking density is altered, changes to properties other than strength also occur. For example, increasing the crosslinker concentration would make the polymer chains to come closer, thus reducing the diffusivity, release and swelling rates including the maximum degree of swelling. This would mean that these properties will need to be re-measured every time additional crosslinks are added.

The mechanical behavior of hydrogels is best understood by theories of elasticity and viscoelasticity. These theories are based on the time-independent and time-dependent recovery of the chain orientation and structure respectively. Elasticity theory assumes that when a stress is applied to the hydrogel the strain response is instantaneous. However for many biomaterials, including hydrogels and tissues, this is not a valid assumption. For example, if a weight is suspended from a specimen of ligament, the ligament continues to extend even though load is constant. Similarly, if the ligament is elongated to a fixed length, the load drops continuously with time. This is due to creep and stress relaxation respectively and these are the result of viscous flow in the material. Despite this liquid-

1.6.3 Surface Properties of Hydrogels

Biocompatibility is the ability of a hydrogel to reside in the body without inducing significant immune response or toxicity. The important question in biocompatibility is how the hydrogel transduces its structural makeup to direct or influence the response of proteins, cells and organisms. This transduction occurs through the surface properties of the hydrogel, i.e. the body reads the surface structure and responds to it. The surface of a hydrogel can be rough, smooth or stepped; it can be composed of different chemistries or could be highly crystalline, disordered and inhomogeneous. Studies have been performed on the importance of roughness, wettability, surface mobility, chemical composition, crystallinity and heterogeneity, however significant research has not yet been performed on determining which parameters are of utmost importance in understanding biological responses to surfaces. Some of the techniques used for determining the surface property include electron spectroscopy [48], scanning electron microscopy, Fourier transform infrared spectroscopy [49], scanning tunneling microscopy and atomic force microscopy. The information obtained using these methods can be used to monitor contamination, ensure surface reproducibility and explore the interaction of the hydrogels with living systems.

1.6.4 Permeability of Hydrogels

Permeability is the ability of a hydrogel to transmit another substance such as fluids, cells or proteins. Developing hydrogel membranes and coatings of appropriate permeability characteristics is key to the success of a number of bioartificial organ transplantations. The permeability of a hydrogel to water and solutes can be adjusted over a wide range by varying the crosslinker concentration at synthesis or copolymerizing with more hydrophilic or hydrophobic monomers Some of the real life situations where permeability of hydrogels is critical are oxygen permeation for contact lens applications, nutrient and immunological biosubstance transport for immunoisolation and release of drugs and proteins for drug delivery systems.

1.6.5 Stimuli Responsive hydrogels

Responsive hydrogels are called smart or intelligent hydrogel. After the discovery of responsive hydrogels in the late seventies by Tanaka large number of polymers were identified ,responding to all thinkable stimuli. Hydrogels are response to changes in temperature, pH, pressure, electric field, magnatic field, chemical stimuli, light and to irradiation. Small changes can show more significant result. The application and development of temperature-responsive and pH-responsive system have been extensively studied for stimuli – responsive drug delivery.

pH responsive hydrogel

Response to pH is widely found stimulus, that originates from the electrostatic repulsion between charged group within the polymer. At high pH polyacrylates show enhanced swelling, whereas polyamines exhibit the same behavior at low pH.

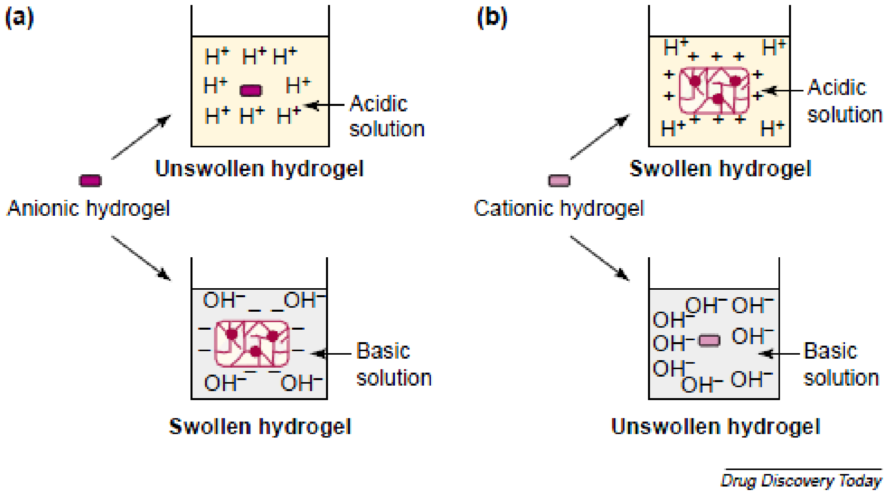

Figure 1.2 The pH-responsive swelling of (a) anionic and (b) cationic hydrogels.

Temperature responsive hydrogel

Another important stimulus for causing hydrogel responsiveness is temperature. Polymers, which become insoluble upon heating, have a so-called lower critical solution temperature (LCST). Systems, which become soluble upon heating, have an upper critical solution temperature (UCST) some hydrogels are temperature sensitive as they exhibit a critical solution temperature. Most of them show a decreased solubility in water with rising temperature. Above their lower critical solution temperature, they collapse. Interstingly the reverse behavior exists as well. Few polymers are known to have an upper critical temperature. Temperature sensitive polymers are generally pressure sensitive as well.

1.7 **Cellulose**

Cellulose is the most abundant natural biopolymer available on the earth and it is a structural constituent of the cell wall of various plants. It is important not only for plant growth and development but also for industrial use. Apart from plants, cellulose is also present in a wide variety of living species, such as algae, fungi, bacteria, and even in some sea animals such as tunicates [50]. Cellulose is a fibrous, tough, and water-insoluble polymer and it plays an essential role in maintaining the structure of plant cell walls. Moreover, cellulose is a biodegradable, biocompatible, and renewable natural polymer and hence it is considered an alternate to nondegradable fossil fuel-based polymers. The chemical structure of celluloseshows that the polymer, formed by condensation, consists of monomers joined together by glycosidic oxygen bridges. Cellulose is made of β-1,4-linked glucopyranose units that form a high–molecular-weight linear homopolymer, in which every repeating unit contains three hydroxyl groups – one primary and two secondary hydroxyl groups and is corkscrewed at 180° with respect to its neighbors [51] Hydrogen bonds form between hydroxyl groups and oxygen atoms both within a single repeating unit and between neighboring chains. Together with van der Waals forces, hydrogen bonding aggregates polymer chain together side-by-side and promotes parallel stacking of cellulose microfibrils into crystalline cellulose [52, 53]. Compared to starch, cellulose is also much more crystalline and thermally stable

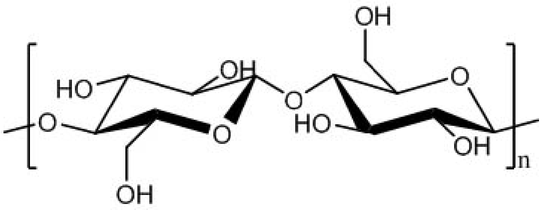

Figure 1.3 Typical structure of cellulose polymer

constituents	% Weight	
	Softwoods	Hardwoods
Cellulose	40-50	40-50
Hemicellulose	20-30	25-40
Lignin	25-35	20-25
Extractives	0-25	0-25

Table 1.2 Constitutent of plant material

Sources of cellulose

The main sources of cellulose are plants; however, algae, bacteria, and some sea animals are also able to produce cellulose in large quantities. A short description about the main sources is as follows.

Cellulose Nanocrystals (CNCs)

cellulose nanocrystal(CNCs) and its modified biodegradable products recently have received increasing interest in nanotechnology due to its advantages of abundance, renewability, and excellent mechanical properties and some potential applications in nanofiller, as reinforcement in matrix nanocomposite, electronics, nanocomposite films, drug delivery, protein immobilization, metallic reaction template, pharmaceuticals, cosmetics, and personal cares [54]. Compared to cellulose fibres, CNC possesses many advantages; such as nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc .These amazing physicochemical properties and wide application prospects have attracted significant interest from both research scientists and industrialists. Among the different methods for the preparation of CNC chemical method like acid hydrolysis is most promising [55]. Acid hydrolysis followed by ultrasonic treatment is also reported for the preparation of transparent aqueous gel of CNC [56]. It is well known that native cellulose consists with amorphous and crystalline regions.

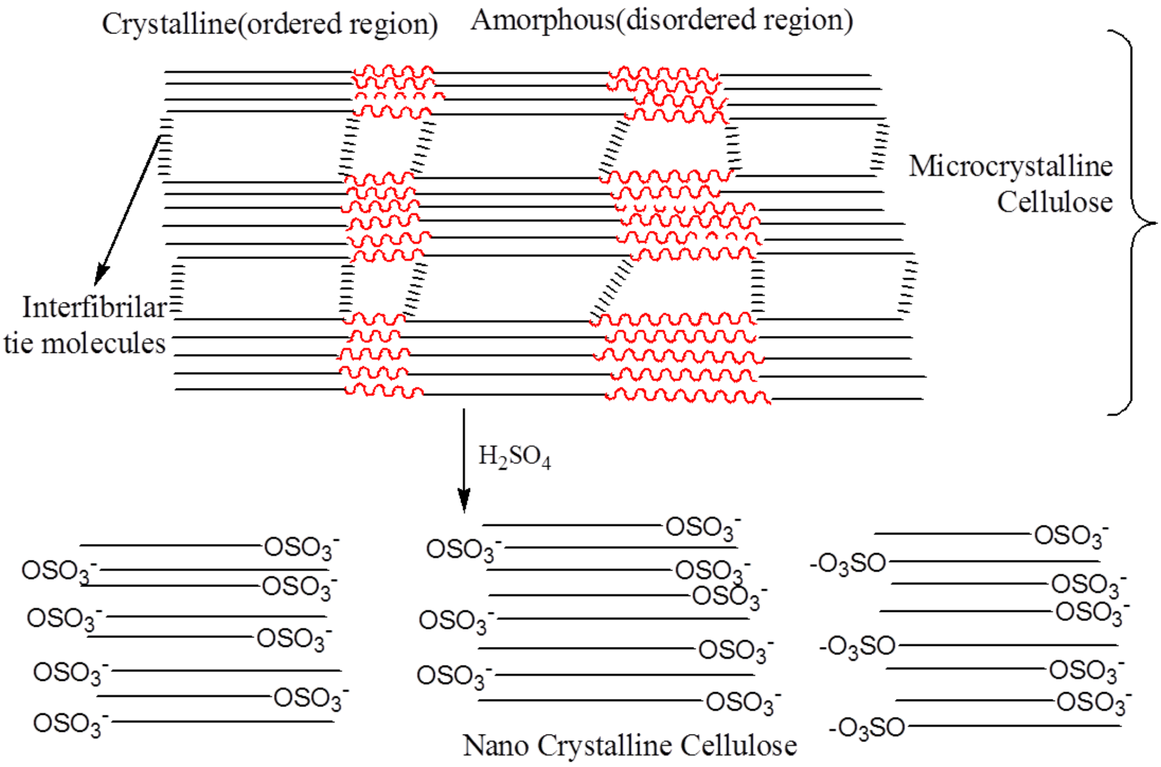

Figure 1.4 Degradation of amorphous region of cellulose by sulfuric acid

When native cellulose is subjected to harsh sulphuric acid treatment, the hydronium ions migrate to the amorphous regions since they have lower density compared to the crystalline regions. The hydronium ions cleave the glycosidic linkages hydrolytically thereby releasing the individual crystallites. Acid hydrolysis is dependent on different parameters, such as acid concentration, time of reaction, temperature of reaction and the specific acid used for the treatment. Another important characteristic of CNCs is that the individual crystallite has negative charges on their surface due to the formation of sulphate ester groups during sulfuric acid treatment. The negatively charged CNCs forms stable aqueous suspensions due to the electrostatic repulsion between the individual crystallites. On the other hand, acid hydrolysis with hydrochloric acid does not produce as many negative surface charges on nanocrystalline cellulose, resulting in less stable NCC suspensions. Nanocrystalline cellulose derived from acid hydrolysis of native cellulose possesses different morphologies depending on the origin and hydrolysis conditions. In order to characterize the morphology of CNC, various types of instruments can be used. The most conventional and common one is the transmission electron microscopy (TEM), which can directly provide high-resolution images. Moreover, scanning electron microscopy (SEM), dynamic light scattering (DLS) were also employed to study the morphology of CNC.

Despite many advantages of NCC, however, these fibers have certain limitations, which consequently hinder their potential applications. For example, they have limited thermal stability during composite processing limited matrix compatibility due to their highly hydrophilic character and high moisture absorption of the fibers that can affect the dimensional and mechanical stability of the final products. Attempts to rectify these shortcomings and make cellulose more conducive for different application means there is thus a great need to modify the cellulose and incorporate different functionality in it to make innovative materials. In the field of cellulose chemistry, numerous studies have been conducted within the last decades that have been aimed at searching for an appropriate application of cellulose for a variety of novel derivatives, or modification of the fibers themselves to provide them with specific properties like compatibility with composite material, hydrophobicity, and decrease in moisture absorption [57].

As described earlier, to improve cellulose processability and to make new cellulose derivatives for specific industrial application, chemical modification of cellulose is a necessity. Cellulose can be derivatized in various ways by modifying its abundant hydroxyl groups. New functional groups can be introduced into cellulose through chemical modification; these functional groups can accordingly introduce new properties to the cellulose without destroying its many desirable intrinsic properties. This derivatization of cellulose would open windows of opportunities, broaden its use. Some of the original properties of cellulose can be altered by these chemical modifications. As cellulose is a carbohydrate polymer made up of repeating β-D-glucopyranoseunits and consists of three hydroxyl groups peranhydroglucose unit (AGU) giving the cellulose molecule a highdegree of functionality. Oxidation is one of the important ways to incorporate new functionality in cellulose chain. However, most of the oxidation reaction is unselective. Depending on the nature of the oxidant and the reaction condition used, these oxidized celluloses may contain carboxylic, aldehyde, and/or ketone functionalities, in addition to the hydroxyl groups. Though most of the chemical modifications of cellulose have been done on the primary hydroxyl groups at C-6 position like esterification, etherification, oxidation, etc., however, periodate can oxidize vicinal hydroxyl groups of cellulose at C-2 and C-3 positions to aldehyde groups, and at the same time cleave the corresponding carbon-carbon bond of the anhydro D-glucopyranose ring to form 2, 3-dialdehyde cellulose.

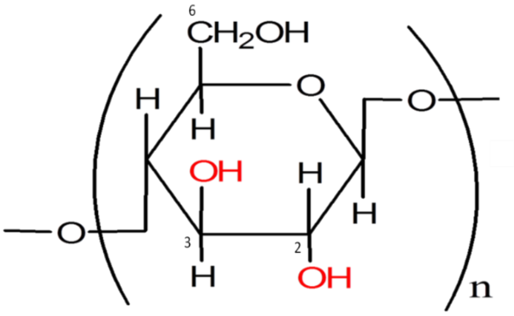

Figure 1.5 Repeating glucose unit of nanocrystalline cellulose

The reaction proceeds under mild conditions and hence the amount of introduced aldehyde can be easily controlled . Generally, amorphous regions are preferred by most chemical oxidations of cellulose in heterogeneous systems. In instances of periodate oxidation, however, crystalline domains are also affected and upon the introduction of aldehyde groups, crystallinity decreases with increasing level of oxidation [58]. Varma *et al*. reported that oxidized cellulose is thermally more stable than unmodified cellulose at higher temperature but less stable at lower temperatures below 25^0 C . Moreover, upon the study of the morphology of the oxidized fibers it was found that the oxidized derivatives of cellulose showed a decreased aspect ratio when the cellulose samples were oxidized at a level of 30% .

Naturally occurring bulk cellulose consists of highly ordered, crystalline regions along with some disordered (amorphous) regions in varying proportions, depending on its source [58]. When these microfibrils are subjected to a proper combination of mechanical, chemical, and enzyme treatments, the highly crystalline regions of the cellulose microfibrils can be extracted, resulting in the formation of cellulose nanocrystals (CNCs). CNCs are stiff rod-like particles consisting of cellulose chain segments in a nearly perfect crystalline structure. These nanocrystals are also referred to as whiskers, nanoparticles, nanofibers, microcrystallites, and so on, but the most widely accepted nomenclature is CNCs. Compared to bulk cellulose, which has greater amorphous fractions, these nanocrystals exhibit high specific strength, modulus, high surface area, and unique liquid crystalline properties.

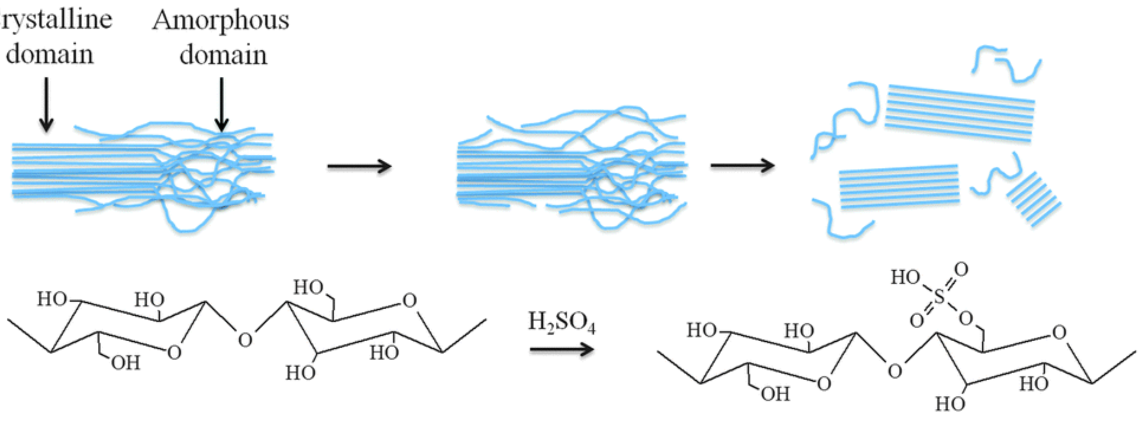

Figure 1.6 Schematic representation of the preparation of CNC

Ehmann, Heike MA, et al. "Design of anticoagulant surfaces based on cellulose nanocrystals." *Chemical Communications* 50.86 (2014): 13070-13072.

Cellulose nanocrystals have been hydrolyzed from many different cellulose sources such as

hardwood pulp, softwood pulp, microcrystalline cellulose (MCC), Sawdust and different sources.

Surface modification of CNCs:

CNCs have very high surface-to-volume ratios and a lot of hydroxyl groups, which make it suitable for many types of surface functionalization. By introducing any chemical functionality on their surface, the type of interactions that the material exhibits with its surroundings can be modified. Generally the surface of CNCs are modified by esterification, etherification, oxidation, amidation, carbamation, nucleophilic substitution, silylation, polymer grafting, etc. Chemical functionalization is done so that it can introduce either negative or positive charge on the surface of CNCs, which ultimately provides better dispersion in any solvent. Oxidation reactions are performed on the surface of cellulose to introduce carboxylic acid or aldehyde functionalities. Recently, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation, periodate−chlorite oxidation, and ammoniumpersulfate (APS) oxidationhave been used to produce carboxylated CNCs.

TEMPO-mediated oxidation of CNs involves a topologically confined reaction sequence, and as a consequence of the 2-fold screw axis of the cellulose chain, only half of the accessible hydroxymethyl groups are available to react, whereas the other half are buried within the crystalline particle .

Tetramethylpiperidin-1-oxyl (TEMPO) radical oxidation of cellulose has become popular both as a surface modification and a bulk technique. Generally, the oxidation is carriedoutwith a catalytic amount of TEMPO with a secondary oxidant such as sodium hypochlorite or sodium chlorite to recycle the TEMPO Sodium bromide is quite often used to increase the rate of oxidation through formation of sodium hypobromite in situ. At $pH < 8$ the reaction proceeds slowly and selectivity between primary and secondary alcohols is not as prominent as at $9 < pH < 11$ where the reaction shows good selectivity to primary

Alcohols [59]. This is backed up by calculations on the energy of various proposed mechanisms that show a hindered transition state in alkaline conditions. This hindered transition state means that complex formation is significantly more favourable for primary alcohols than secondary alcohols and in basic conditions, primary alcohols can be oxidized by this faster pathway [60]. Surface carboxylated CNCs with different sizes and degrees of oxidation were prepared by TEMPO-mediated oxidation of cellulose [61,62].

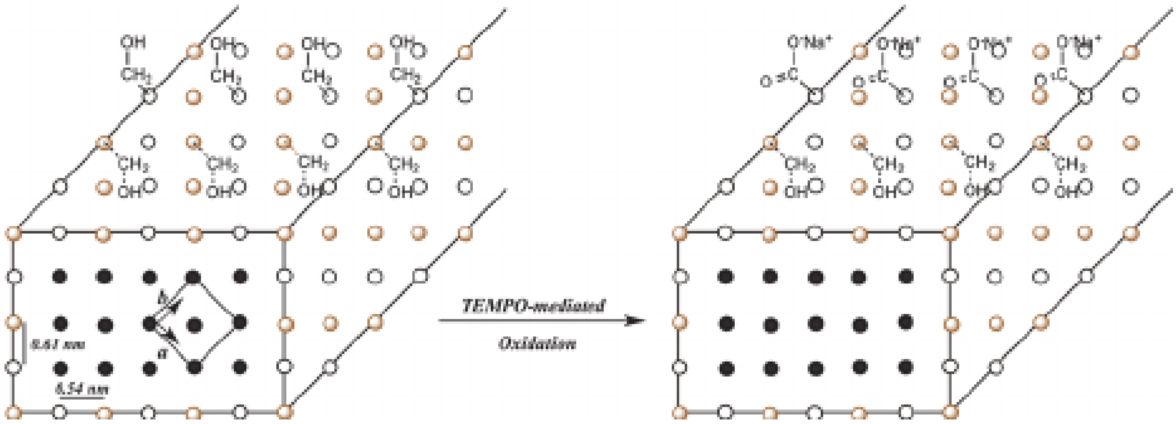

Figure 1.10 Schematic representation of carboxylated cellulose nanocrystal

Habibi, Youssef, Lucian A. Lucia, and Orlando J. Rojas. "Cellulose nanocrystals: chemistry, self-assembly, and applications." *Chemical reviews* 110.6 (2010): 3479-3500.

1.8 The aim of the current research

The main goals in this research was the following:

- to synthesis a nanocomposite hydrogel using Dopamine grafted Cellulose nanocrystal.
- to ensure high mechanical sterength
- to know swelling behavior
- to perform stimuli-responsiveness of synthesized nanocomposite.

Hydrogels are superabsorbent. When it absorb large amount of water, it goes break. The mechanical strength is poor. But hydrogels has a large area of application. Due to brittleness, uses of hydrogels are pain sometimes. So we have tried to improve mechanical strength. From literature review we see scientist has synthesized the nanocomposite hydrogel with a polymer particle, carbon nanotube, super magnetic iron oxide, nano clay as a inforcement. We see it was toxic to human body and low swelling. So we plan to synthesis cellulose nanocrystal and it was grafted with dopamine. Mainly CCN-DOPA is the main component to enhance the mechanical strength. Becase CNC has a high stiffness and Dopamine plays like the nature’s glue. The synthesized nanocomposite was charactrised by Scanning electron microscopy, FTIR, mechanical strength, swelling behavior and temperature responsiveness. The mechanical strength proves that the synthesized nanocomposite hysrogel may be used in biomedical and pharmaceuticals and in many applications.

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Chapter 2

Experimental

2.1 Materials and instruments

2.1.1 Chemicals and reagents

i. Ethanol (Merck, Germany)
ii. Toluene (Merck, Germany)
iii. Sodium chlorite (BDH)
iv. Sodium hydroxide (Merck, Germany)
v. Sodium hypochlorite (Merck, Germany)
vi. Sodium bromide (Loba, India)
vii. Potassium hydroxide (Merck, India)
viii. Potassium per sulfate (BDH)
ix. Sulfuric acid (Merck, Germany)
x. Hydrochloric acid (analytical grade)
xi. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)
xii. Acetone (analytical grade)
xiii. Ammonia solution (25%)
xiv. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) (Sigma Aldrich)
xv. Dopamine (Sigma Aldrich)
xvi Acrylamide (Sigma Aldrich)

2.1.2 Instruments

Analysis of the samples was performed using the following instruments:

i. Fourier Transform Infrared Spectrophotometer (SHIMADZU FTIR-8400)
ii. Field Emission Scanning Electron Microscopy (JSM-7600F, Tokyo, Japan)
iii. Centrifuge machine (Hettich, Universal 16A)
iv. pH meter (Hanna, HI 8424, Romania)
v. Digital Balance (AB 265/S/SACT METTLER, Toleto, Switzerland)

vi. Conductometer (Mettler Toledo Conductivity meter USA)
vii. Freeze dryer (Heto, FD3)
viii. Shaker machine(Stuart, orbital shaker, SSL1)
ix. Oven machine (lab tech,LDO-030E)

2.2 Methods of preparation

2.2.1 Extraction of Cellulose Nanocrystal (CNC)

Cellulose nanocrystal was synthesized from sawdust. First sawdust was dried in sunlight and oven at 80ºC over night. Then cellulose was treated with the mixture solvent of 2:1(v/v) of toluene and ethanol for removing the dewax material using soxhlet apparatus. After that, delignification was carried out using an acidified sodium chlorite ($NaClO_2$) solution at 75^0C for 1h and repeated six to seven times until products become white. Next, blended product was treated with 5% KOH at 90^0C for 2h. This process was also repeated more than 2 times for removing hemicellulose, pectin and got chemically purified cellulose (CPC). This chemically purified cellulose was further blended 10 min and then subjected to acid hydrolysis using concentrated sulfuric acid (64% H_2SO_4) to get cellulose nanocrystal [1,2]. The reaction was carried out at 45°C under vigorous mechanical stirring for 60 min. The hydrolysis reaction was terminated after 60 min by placing the product in an ice cool water bath. The suspension was then washed with distilled water and centrifuged at 5000 rpm for 15 min. The centrifugation process is repeated until constant pH was obtained. It is then placed into dialysis tube and dialyzed against distilled water until pH was neutral (pH 6 -7). After this dialysis process the suspension was again centrifuged at 4000 rpm for 15 min followed by sonication for 10 min in ice bath. Then the resultant concentrated aqueous suspension of cellulose nanocrystal was stored in refrigerator at 4^0C for further use.

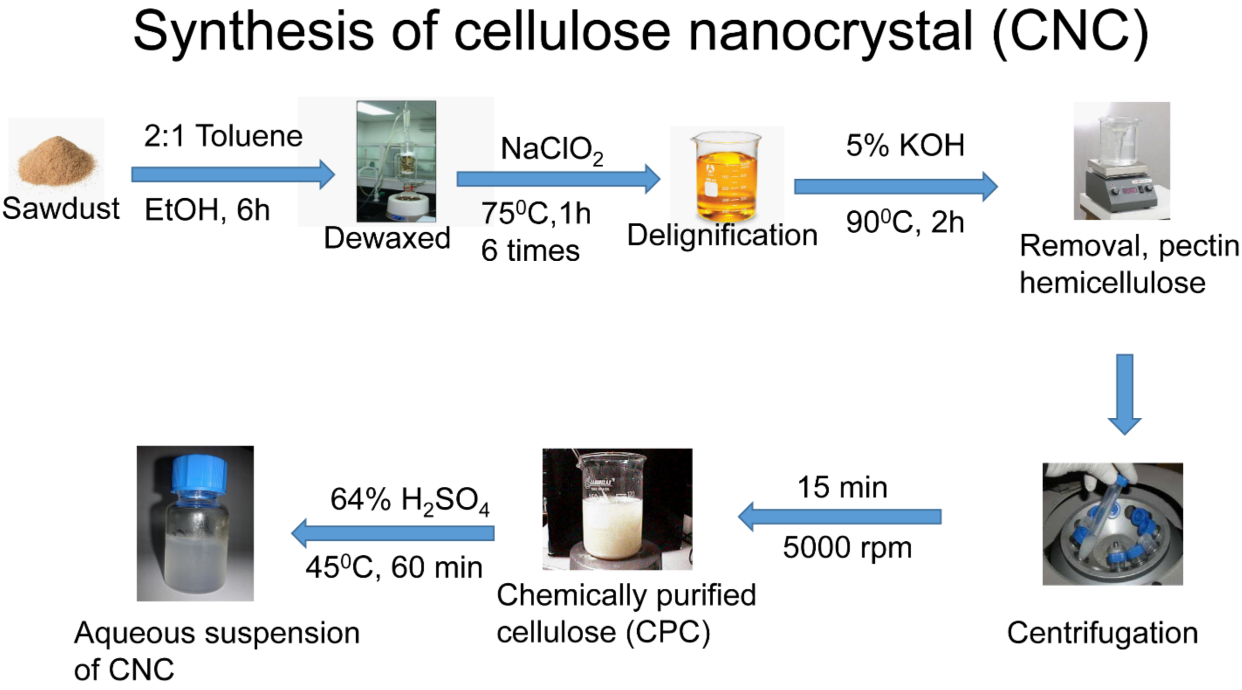

Figure 2.1 Schematic representation of extraction of cellulose nanocrystal from sawdust

(Kumar et al. J. Mater. Physic. Chem., 2014, 2 (1), 1.)

2.2.2 Synthesis of carboxylated cellulose nanocrystals (CCN)

The primary hydroxyl groups on the surface of CNC were oxidized to carboxyl groups using TEMPO-reagent in the presence of sodium bromide (NaBr) and sodium hypochlorite (NaClO). The reaction conditions were adjusted by the previous studies [3,4]. 1g CNC was dispersed in 100mL distilled water. After vigorous mixing, sonication was performed for 10 min in an ice bath to get a homogeneous dispersion of CNC. 16mg TEMPO and 100mg NaBr was weighed and dissolved separately. After that mixed with CNC suspension and stirred 10 min at room temperature. This was then further sonicated for 15min. The oxidation was initiated with the addition of 3.5 mL of 4-14% NaClO solution to the CNC suspension by dropwise. The pH of the solution was maintained constant at 10 by adding 0.1M NaOH solution until no more variation was observed, indicating that the reaction was finished. Then the solution was continuously stirred for 12 h. Finally, 5mL of ethanol was added to stop the oxidation. Then the solution was washed with distilled water several times and finally obtained concentrated suspension which was sonicated for 2 min and stored at 4^0C.

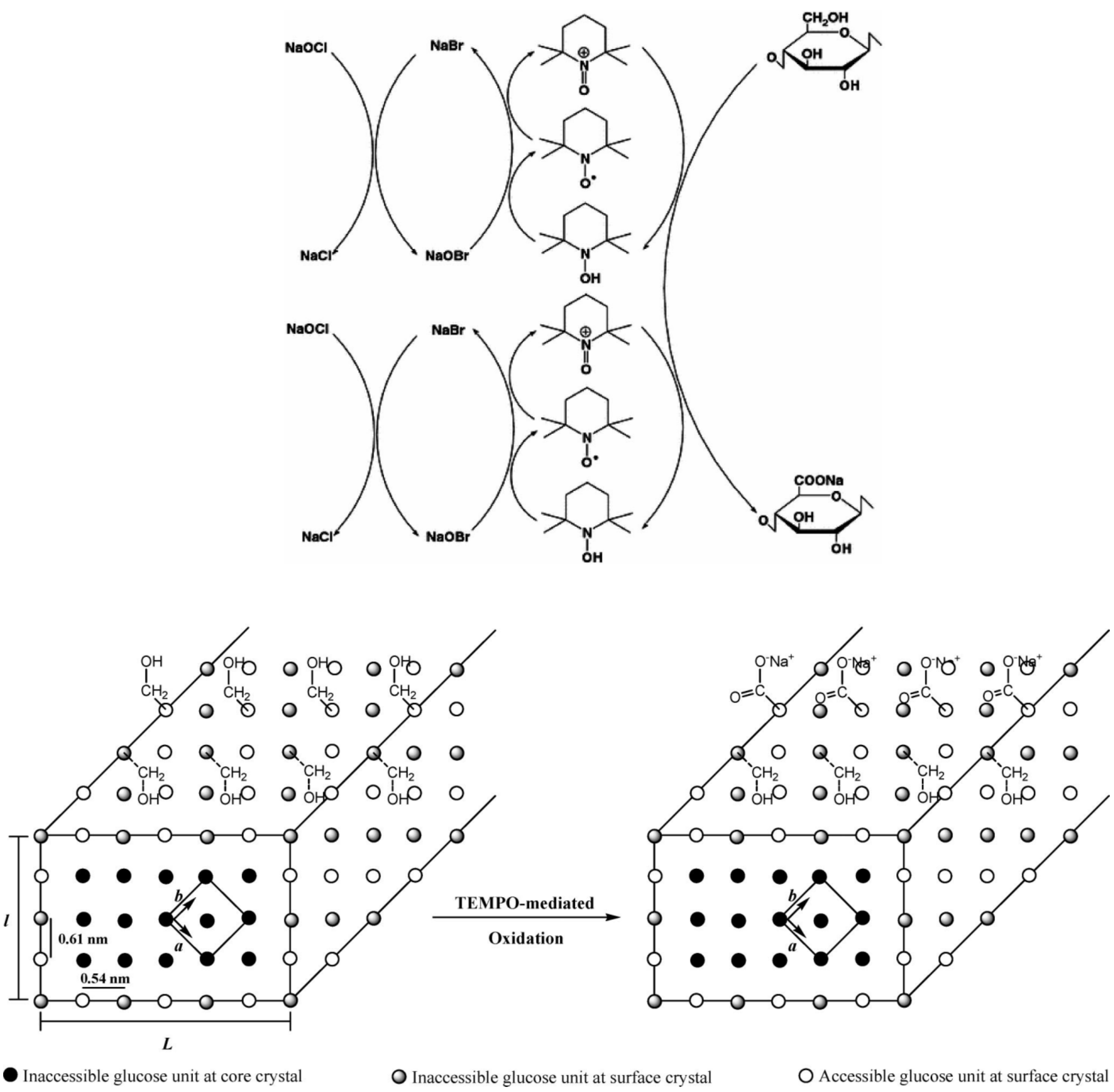

Figure 2.2 schematic representation of carboxylated cellulose nanocrystal

2.2.3 Synthesis of DOPA grafted CCN

A 100 ml amount of 1.4gL^{-1} CNC dispersion was mixed with 100 ml of PBS Buffer, and the pH of mixture was adjusted to pH=5 by adding 0.1 M HCl. To this mixture, 0.06 mmole of DOPA, 0.1 mmole of N-(3-dimethylaminopropyl)-N´-ethylcarbodiimide hydrochloride (EDC) were added, and the pH was maintained at pH=5 while the mixture was stirred vigorously for 6 h. The mixture was dialyzed for 24h in PBS buffer and then five days in distil water. After dialysis, the amount of the DOPA-grafed CNC dispersion was stored in freeze.

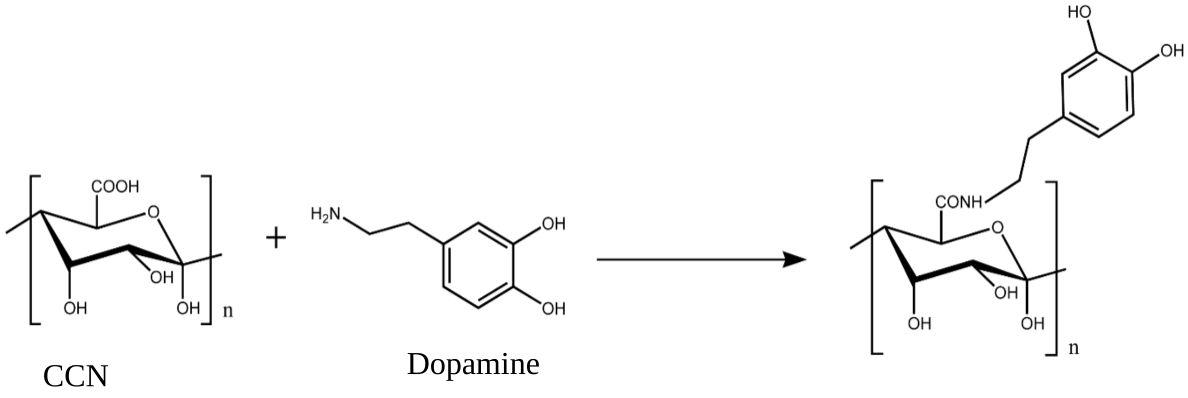

Figure 3.3 Schematic representation of CCN-DOPA

2.2.4 Synthesis of nanocomposite hydrogels

The CNC-DOPA based nanocomposite hydrogel were prepared by the free radical crosslinking polymerization of AM in CNC-DOPA suspension[6,7]. First, the aqueous solutions of the hydrophilic AM were prepared in distil water. Different amoumts of CCN-DOPA were added to AM solution Table1 describes the different formulation used in this work.Free radical polymerization of hydrogels were carried in glass tubes at 65ºC for 3h, using KPS as initiator. The crosslinking of AM hydrogels was carried out by MBA.

After polymerization, hydrogels were removed from glass tubes carefully broken and the hydrogels obtained in long cylindrical shapes were cut into pieces of approximately 1 cm length. Polymer samples were immersed in distil water and the water was refreshed every several hours in order to allow the unreacted chemicals to leach out.

Table 1. Composition of nanocomposite hydrogel

Code	CCN-DOPA(mg)	AM (g)	MBA (mg)	H_2O (ml)	KPS (mg)
CNC(0)	00	2.5	0.01	8	0.01
CNC(20)	50	2.5	0.01	8	0.01
CNC(40)	100	2.5	0.01	8	0.01
CNC(80)	200	2.5	0.01	8	0.01

acrylamide (AM), methelenebis acrylamide (MBA) and potassium persulphate (KPS) are dissolved in water separately. A required amount of CCN-DOPA was taken in and mixed with acrylamide (AM), methelenebis acrylamide (MBA).Then potassium persulphate (KPS) was dropping in mixture.at 35ºC the polymerization reaction was occurred with 24 Hours.

2.3 Conductometric titration

The carboxyl content of cellulose nanocrystals was determined by conductometric titration. Typically 40mg of TEMPO oxidized cellulose nanocrystals were suspended into 50mL of distilled water. After 10 min stirring, titration was performed using 0.01M solution of NaOH (solution was standardized against oxalic acid) and the conductivity was monitored with a Mettler Toledo Conductivity meter USA).

2.4 Fourier Transform Infrared analysis (FTIR)

The infrared spectra of the cellulose nanocrystal, carboxylated cellulose nanocrystal and CCN-DOPA samples were recorded on an FTIR spectrometer in the region of 4000 – 400 cm^{-1}. A small portion of cellulose nanocrystal(CNC),carboxylated (CCN) and CCN-DOPA was taken into vial and oven dried at 80^0C. After that it was cut as much as possible small sized pieces and then grinded as much as possible.

2.5 Field Emission Scanning Electron Microscopy (SEM)

The surface morphology of the synthesized CNC, CCN, hydrogel and nanocomposite hydrogel was adopted using Field Emission Scanning Electron Microscopy (FE-SEM). The completely air dried samples were glued on a conducting carbon strip. The sample loaded strip was then mounted to a chamber that evacuated to ~ 10^{-3} to 10^{-4} tor and then a very thin platinum layer (few nanometers thick) were sputtered on the sample to ensure the conductivity of the sample surface. The sample was then placed in the main FESEM chamber to view its surface. The microscope was operated at an accelerating voltage of 5.0 kV. The system was computer interfaced and thus provides recording of the surface images in the computer file for its use as hard copy.

2.6 Swelling kinetics of the hydrogel

0.20 g of freeze dried hydrogel was placed in 250 ml beaker and 150 ml distil water was added. The swollen samples were remove from water and weighted before blotting off the remaining water on the sample surface with a filter paper. The swelling ratio was defined as the weight ratio of the net liquid uptake to the dried hydrogel. The swelling ratio (SR) was calculated using

$$swelling\ ratio = \frac{wt - wo}{wo}$$

Where wt is weted hydrogel and wo is dry hydrogel

2.7 Temperature dependence of the equilibrium swelling ratio (ESR) of the hydrogels

The classical gravimetric method was used to measure the ESR of the hydrogel. For the temperature dependence of the ESR study, the hydrogel samples were equilibrated in water at a predetermined temperature ranging from 20 to 50ºC . The freeze dried hydrogel sample (about 0.10 g) was soaked in an excessive amount of distilled water at each predetermined temperature for 24h to reach the swelling equilibrium.

2.8 Dynamic light scattering experiments

Dynamic light scattering (DLS) experiments werecarried out with a Malvern NanoZS instrument at25ºC and with a detection angle of 173º. The intensitysize distribution was obtained from the analysis of the correlation function using the multiple narrow mode algorithm.

2.9 Mechanical propertise of hydrogel

Mechanical strength determination was carried out with a hand pressure. 0.30g hydrogels was taken in a Petridis. Then it was taken in under equeal hand pressure.

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Chapter 3

Results and discussion

3.1 Synthesis of nanocomposite hydrogel

Nanocomposite hydrogels are synthesized at 35ºC by free radical polymerization of acrylamide (AM) with the potassium persulphate (KPS) as a initiator, methelenenbisacrylamide (MBA) as crosslinker and carboxylated cellulose nanocrystal-dopamine (CCN-DOPA) suspension [1,2]. CCN-DOPA was synthesized before. Acrylamide, potassium persulphate (KPS) and methelenebisacrylamide (MBA) are dissolved in water separately as a required amount. Then in presence of potassium persulphate (KPS) the reaction was occurred and we got nanocomposite hydrogel.

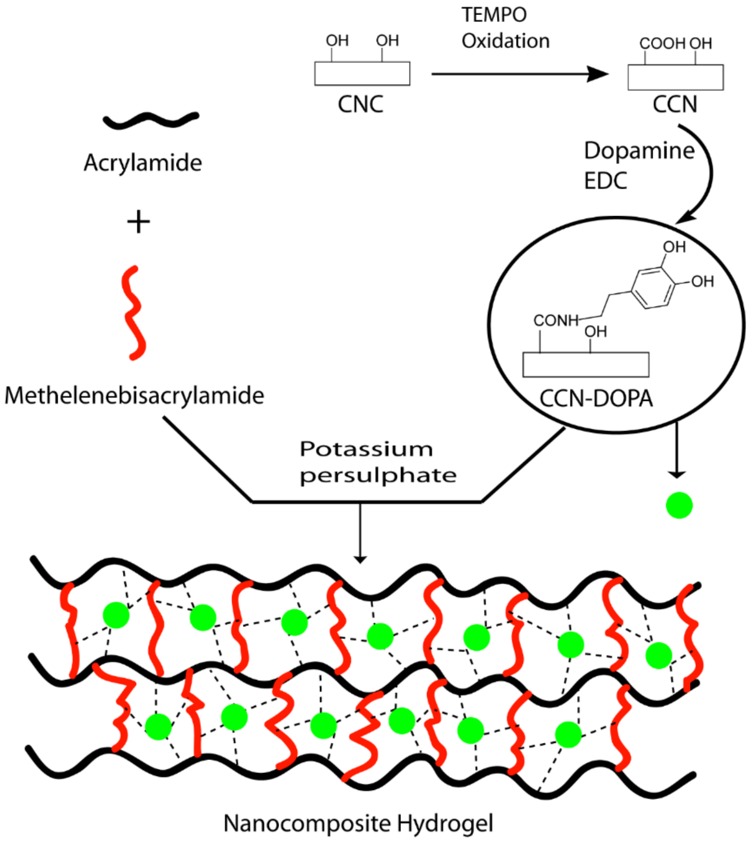


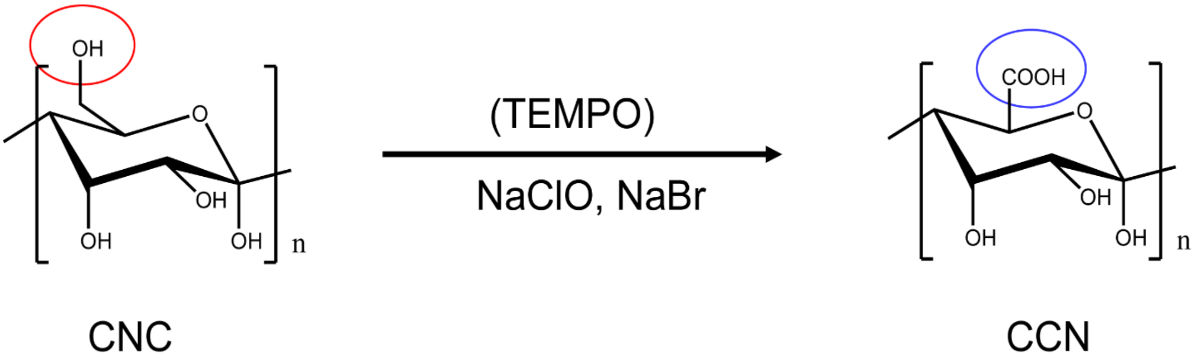
Figure 3.1 Schematic representation of nanocomposite hydrogel

3.2 Synthesis the cellulose nanocrystal (CNC)

Cellulose nanocrystals were synthesized from sawdust. Sawdust is available, abundant and a new source for CNC.CNCs extraction from sawdust creates a new dimension. Synthesized CNC is highly dispersive. A wide range of hydroxyl groups on the surface of CNC are responsible for the tightly hydrogen bonded networks [3].Cellulose Nanocrystals (CNC) have several notable chemical, optical and electrical properties. Their size, shape lead to unique behavior in solutions [4,5]. Its surface is highly chemical reactive. It is very stable in high temperature.Synthesized nanoparticle are determined with dynamic light scattering analysis.

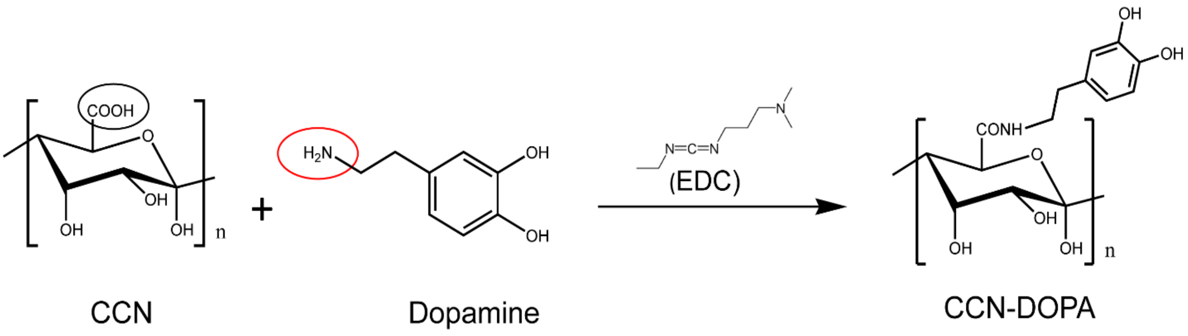
3.3 Carboxylated cellulose nanocrystal (CCN) preparation

Carboxylated cellulose nanocrystal was prepared with a TEMPO mediation.CCN is highly dispersive in water. The primary hydroxyl group was converted to carboxyl group with TEMPO compound[6,7,8].



3.4 Dopamine grafted CCN

Dopamine is called a nature’s glue. It is bio-inspired protein. Dopamine works like mussel strategy. It has adhesive and sticky property. When in presence of EDC as a coupling agent, the coupling reaction is occurred we get CCN-DOPA solution. The amino(-NH_2) group of dopamine and the carboxyl(-COOH) group of CCN are react and produce amide (-CONH)group.This CCN-DOPA incorporated in PAM polymer matrix and it hardens the polymer chain.So the synthesized nanocomposite we got more strong in mechanically and tough.



3.5 Dynamic light scattering (DLS) study

DLS experiments were performed with the CNC suspensions prepared from the cellulose sources. The resulting size distributions are shown inbelow.Since DLS measures the diffusion coefficient of the particles, which is then converted into a hydrodynamic radius from the Stokes Einstein equation, the size given by this technique is therefore the radius of asphere having the same diffusion coefficient as the rod like CNCs [9]. Results in the case of nano rods can therefore only be considered as an indication of the possible presence of aggregates and as an evaluation of the size polydisparity. Size distribution centered around 80 nm for sawdust was obtained in each case, revealing the successful production of nanoparticles without aggregates.

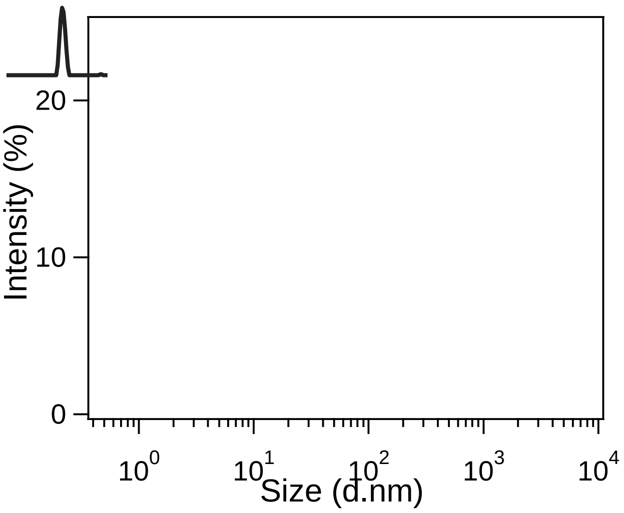


Figure 3.2 Dynamic light scattering of Cellulose nanocrystal

3.6Functional group analysis using Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectroscopy analysis

The FTIR spectra of CCN, and CNC are illustrated. The similar peaks in the CNC and CCN represent chemical structures as follows. The broad bands near to 3,400 cm^{-1} are O–H stretching vibrations and the peaks at 2,900 cm^{-1} are assigned to C–H stretching vibrations. The absorption at1,640 cm^{-1} is related to the adsorbed water due to the presence of abundant hydrophilic hydroxide radical in the cellulose [10]. A peak at 1,382 cm^{-1} corresponds to C–H asymmetric deformations. The sharp absorption peaks at around 1,058 cm^{-1} are due to C–O stretching vibrations [11]. These spectra confirm that the chemical structure of CNC and CCN remains the same. The spectral bands observed at 1427 cm^{-1} and 897 cm^{-1} shows significant cellulose content. In case of CNCs, spectral band at 1375 cm^{-1} was very strong while spectral band at 1335, 1315 cm^{-1} overlap and diffused and other spectral band 1278-1285 cm^{-1} is weak and diffused. On comparing these spectral data which revealed that CNCs are composed of crystalline cellulose. On the other hand, the CCN absorption patterns maintain the peak at 1,734 cm^{-1} due to the presence of carboxylic acid groups.

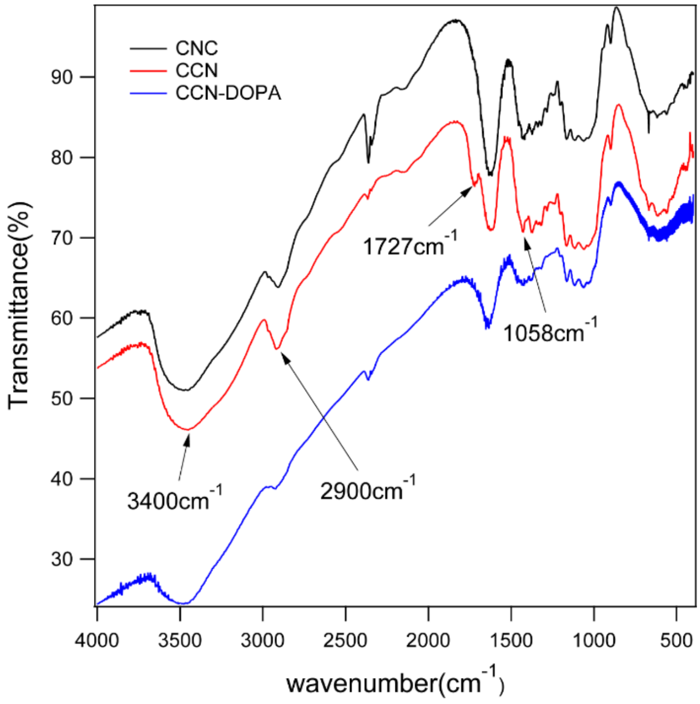


Figure 3.3 FTIR spectra of CNC, CCN and CCN-DOPA

The peak at 850-1500 cm^{-1} region is sensitive to crystal structure of the cellulosic material. The peak at 1250 cm^{-1} for assymetrical S=O vibration which shows the presence of sulfate ester groups on the surface of CNC. According to ref. [12] 850-1500 cm^{-1}region is sensitive to crystal structure

Table 3.1 characteristic IR band of CNC,CCN and CCN-DOPA

Wavenumber(cm^{-1})	interpretation
2905	C-H stretching
2360	Sp3 C-H stretching
1634	For water absorption from by cellulose material
1422	C-H bending
1377	C-H bending
1317	CH_2 wagging
1245	C-O out of plane stretching
1110	C-O-C glycosidic ether band
1054	C-O-C pyranose ring stretching vibration
898	CH_2 bending

of the cellulosic material. Spectral bands at 1420-1430 cm^{-1} and 893-897 cm^{-1} are very important to elucidate to the crystal structure of cellulosic material and its (1420/893 cm^{-1}) spectral ratio and (1375/2900 cm^{-1}) spectral ratio show index of crystallinity [13].

3.7Conductometric titration for CCN

The carboxyl content of oxidized cellulose samples canalso be determined by conductometric titrations. In mostalkalimetric methods, the metallic cations bound to the carboxyl groups are exchanged by hydrogen ions through treatment with acid in excess [14]. We carried out a direct titrationwith alkali and the titration curves show the presence of a strong acid, corresponding to the excess of HCl and a weak acid, corresponding to the carboxyl content, as shown in figure

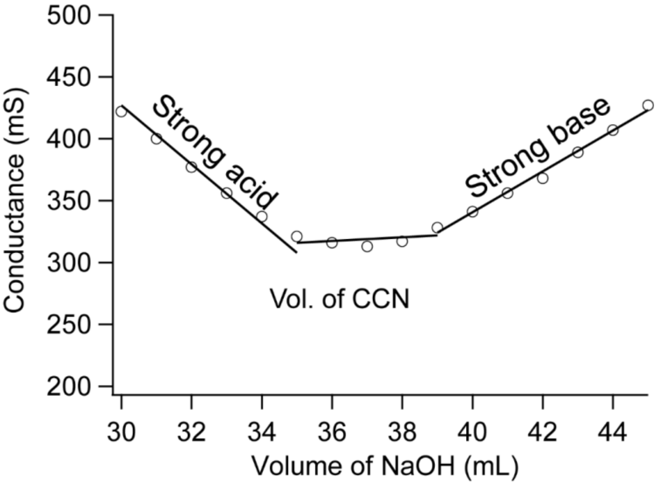


Figure 3.4 Conductrometric titration of a mixture of a strong acid (HCl) and a weak acid (CCN) vs a strong base(NaOH)

The carboxyl groups content or degree of oxidation (DO) is given by the following equation:
$DO=162(V2-V1)c[w-36(V2-V1)c]^{-1}$
where V1 and V2 are the amount of NaOH (in L) as shownin Figure 3.4, *c* is the NaOH concentration (mol/L), and *w* is the weight of sample (g).
We have obtained very reproducible results, both on water-soluble andwater-insoluble cellulose oxidized samples.

3.8 Surface morphology study using Scanning electron microscope

The surface morphology of synthesized CNC,CCN, PAM hydrogel and composite hydrogels were studied by FE-SEM.

Fig. 3.5 shows the FESEM micrograph of CNC prepared through sulphuric acid hydrolysis from chemically purified cellulose (CPC). It is clear that the 64% H_2SO_4 acid also produced ‘cross-linked fiber’ crystallites however, which are in micro-scale with a diameter 100 to 200 nm and length 10 to 20 nm [15]. This result indicates that the crystallites are almost transformed to nano-sclae. So, it can be assumed that if the sulphuricacid concentration, reaction time and temperature to be maintained with proper condition CPC would be converted into CNC.

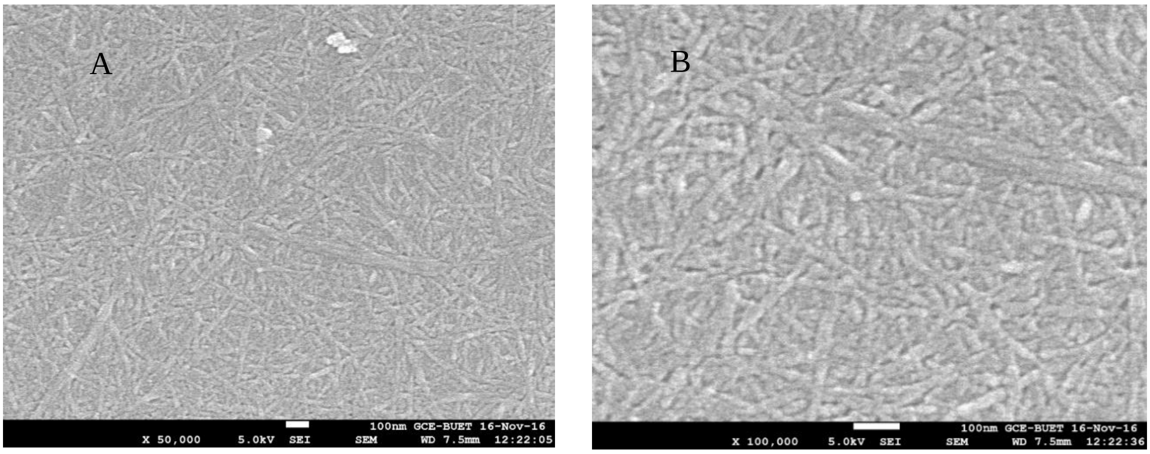


Figure 3.5 SEM image of CNC (A) Magnification x 50000 (B) Magnification x 100000

According the figures, CNC particles display a regular short rod-like structure with the length ranging from 80 - 120 nm and width 10 -20 nm. As CNC was prepared by sulfuric acid hydrolysis and amorphous region was remove from long chain of cellulose. It was found that the strong H-bonding among CNC led to the formation of agglomeration. The cellulose nanocrystal was reported in the forms of spherical.

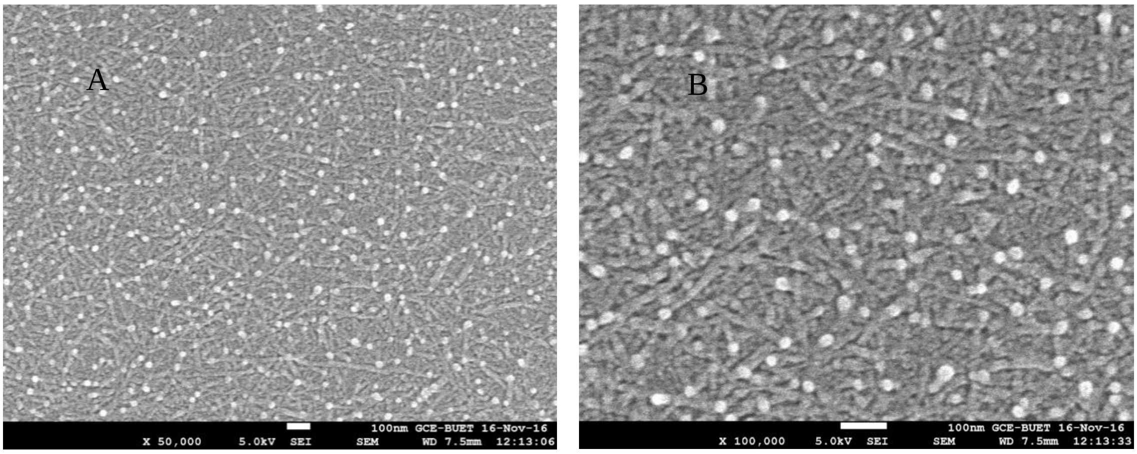


Figure 3.6 SEM image of CCN (A) Magnification x 50000 (B) Magnification x 100000

Figure shows the C_6-OH convertion to –COOH. The CNC was oxidized with TEMPO oxidation. From figure we see CCN appearance is spherical and its length is 60 to 90 nm and width 10-20 nm.

The cross-sectional view of the freeze-dried PAM hydrogel reveals porous nature of the matrix.

The freeze-drying technique has been used extensively in characterizing surface morphology of hydrogels. The SEM images of freeze-dried gels are given in fig (A-D) shows the surface morphology of dry PAM and PAM-CCN-DOPA gels at the 30000 magnification level, respectively. From fig. It can be seen that all gels have had large number of pores. The pore sizes of different ratio PAM-CCN-DOPA were smaller than these of pure PAM, supporting the fact that composite gels have a lower swelling ratio due to the correlation between water content and pore size[16,17]. In addition, the pore distribution of the PAM-CCN-DOPA gels was more regular than that of other gels, suggesting that the PAM-CCN-DOPA had more well defined polymer network, which limited the developments or irregular pores during freeze drying process.

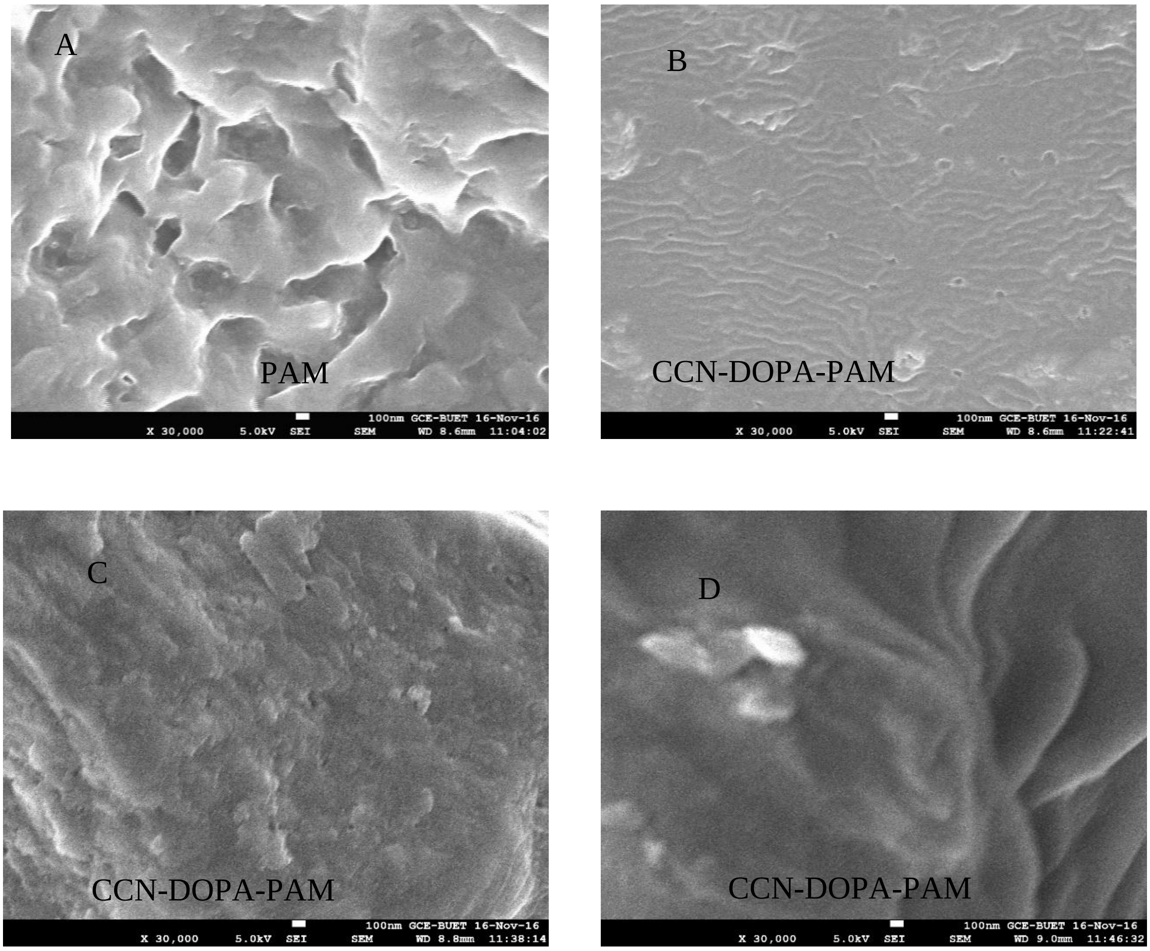


Figure 3.7 SEM image of PAMhydrogel(A) and Nanocomposite hydrogel (B-D), the weight of PAM and CCN-DOPA:(A)1:0, (B)1:25, (C) 1:50, (D) 1:100

(A-D)Magnification: x30000,

3.9 Swelling kinetics of hydrogel

The swelling behavior is the main characteristic parameter for any hydrogel and is depending on the nature of the polymers and the environmental conditions (pH and temperature of the medium). When a polymer network is in contact with an aqueous solution, the network starts to swell due to the thermodynamic compatibility of the polymer chains and water.

Figure shows the swelling ratio (SR) as a function of time for the PAM and CCN-DOPA nanocomposite hydrogels in distil water at 25ºC. Initially the rates of swelling increased rapidly. The increased slowed down at 22 min and started level off at 200min. the equilibrium swelling was achieved at about 24h. It can be seen that the swelling ratios of the pure PAM was higher than the nanocomposite hydrogel. The swelling ratio of nanocomposite hydrogel was decreased increansing the CCN-DOPA content [18,19]. This is due to the cross-linking with polymer chain and pore size of hydrogel[20,21,22].This result support that the pore of hydrogel is filled with CCN-DOPA. When the cross-link increase, the swelling ratio decrease. Besides, nanocomposite hydrogel can't absorb water more.

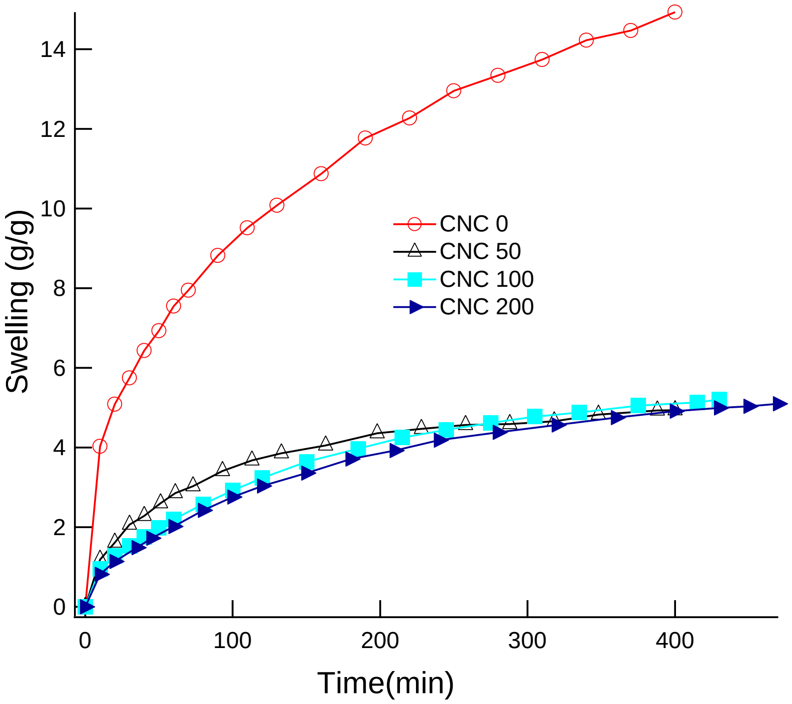
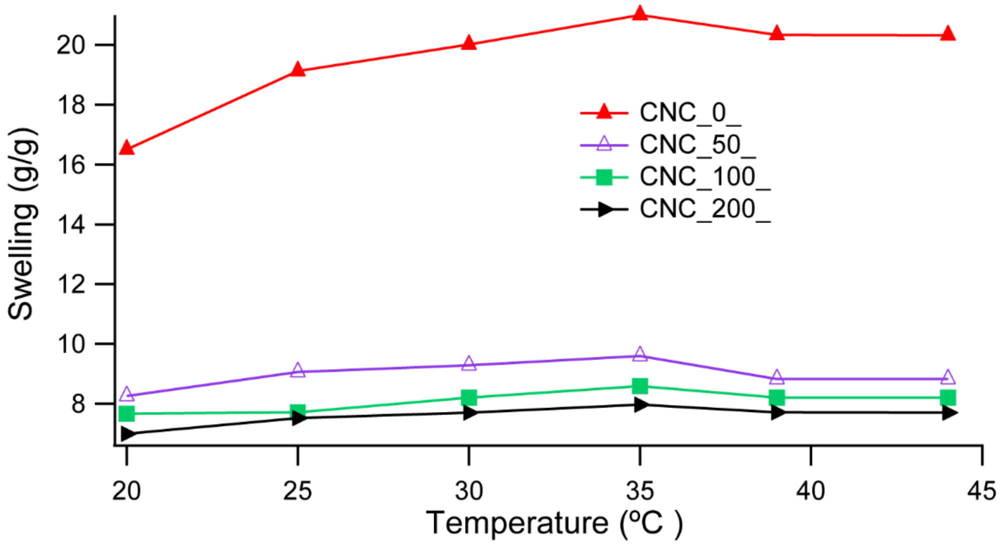


Figure 3.8 Swelling kinetics of PAM and nanocomposite hydrogel

3.10 Temperature effect on swelling

Similar to pure PAM hydrogel, the CCN-DOPA-PAM hydrogel shows the volume phase transition (VPT) behavior responsive to a temperature change, due to the PAM polymer chain. The VPT behavior stemmed from the LCST characteristic of hydrogels. The LCST of hydrogel is the lower critical solution temperature at which phase change is observed for the hydrogel. Below the LCST, the PAM polymer chains tend to form a random coil conformation, causing the hydrogel to swell. When the temperature is increased above the LCST, the random PAM polymer coils collapse, causing the hydrogel to shrink. At a low temperature (<28 ◦C) the swollen hydrogels were homogeneous and transparent. At a high temperature (>40 ◦C), the hydrogels shrank and became cloudy, indicating the occurrence of the volume phase transition. The shrunk hydrogels can be re-swollen in water and became transparent again when they were below the LCST[23,24]. The equilibrium swelling ratio (ESR) is one of the most important parameters for evaluating hydrogels because it can illustrate the temperature-sensitive properties of hydrogels.

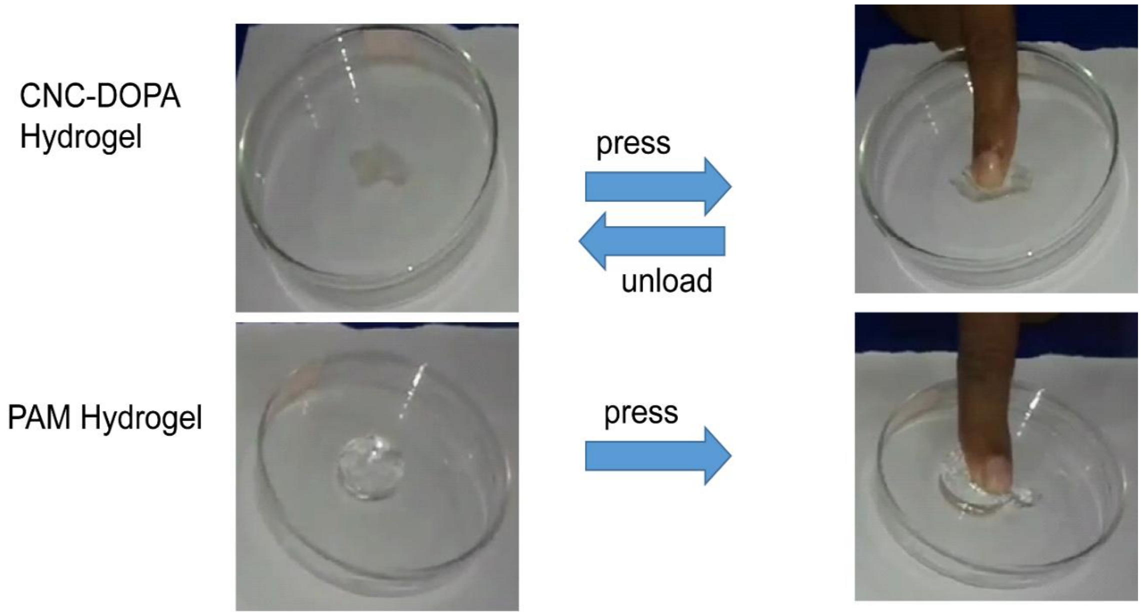
The swelling behavior of the prepared hydrogels in distilled water at different temperatures was determined and the results are shown in. All of the CCN-DOPA-PAM hydrogels



demonstrated similar thermo-responsive profiles. Below the LCST, the hydrogels exhibited swollen states with high swelling ratios. As the external temperature increased, the swelling ratios of the hydrogels decreased, due to the shrinking of hydrogel, resulting from the collapse of the PAM polymer coils. Moreover, at the same temperature (below the LCST), the ESR increases with the all hydrogels. But above the LCST all hydrogel deswell and it decreses with the increase CNC-DOPA[25,] . These results indicate that the water holding space is filled with CCN-DOPA and CCN-DOPA form more H-bond with polymer chain. Temperature can’t break the polymer chain and it’sdeswelling is lowest.

3.11 Mechanical properties of hydrogel

The obtained CCN-DOPAloaded hydrogel displayed high performance under pressure.Thenanocompositehydrogel is tough enough to withstand high deformations in compression without obvious damage. As shown below CNC-DOPA loaded hydrogel was not damaged under pressure [26]. Afterremoving of the force, the nanocompositehydrogel quickly recovers its original shape. In contrast, the counterpart without the introduction of CNC-DOPA hydrogel was broken due to its brittleness as shown in below.



Photographs of hydrogels under pressure.

Figure 3.10 photographs of PAM and CCN-DOPA-PAM hydrogels under pressure

3.12 Conclusion

Successfully we have synthesized a nanocomposite hydrogel based on acrylamide and cellulose nanocrystal. Functional group analysis was carried out using FTIR study. The size was determined by using dynamic light scattering analysis. DLS shows the clear evidence about the cellulose nanoparticle. Carboxylic group was determined by conductometric titration. Conductometric titration display the satisfactory carboxylic group in carboxylated cellulose nanocrystal. The surface morphology of the synthesized nanocomposite hydrogel was characterized by scanning electron microscopy(SEM). From the SEM image it is clear that the size of the particles are in nanoscale dimension and also found that particle is about in uniform size.The swelling kinetics studies were also investigated and the results indicated that the transport mechanism was of a non-Fickian diffusion behavior. Moreover, the swelling behaviors of thenanocomposite hydrogels were greatly related to the content of CCN-DOPA. Effect of temperature on swelling is also investigated. The result shows acrylamide based nanocomposite hydrogels are stimuli responsive. Comparing to pure acrylamide hydrogel and CCN-DOPA nanocomposite hydrogel, nanocomposite hydrogel shows better mechanical strength than pure hydrogel.It is concluded that swelling of polymeric networks is affected by composition of the CCN-DOPA nanomaterial. The overall results suggested thatconsidering its high strength and favorable biocompatibility, it is anticipated that this nanocomposite hydrogel may be used in drug delivery system and bioengineering.

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