A Mini Review on Utilization of Nano Cellulose in Sensing Applications

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A Mini Review on Utilization of Nano Cellulose in Sensing Applications

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Abstract: *Cellulose is the most abundant natural polymer found in the cell walls of plants and bacteria. Nanocellulose can be obtained from cellulose and bacteria. Nanocellulose can be found in different forms such as cellulose nanocrystals (CNC), cellulose nanofibers (CNF), and bacterial nanocellulose (BNC). In modern days, nanocellulose is used in various fields. Sensors are one of the fields where nanocelluloses are widely used. The application of nanocellulose into sensing devices resulted in a notable increase in the sensing power of those devices. In order to detect toxins and other biological components, a wide variety of sensors use various forms of nanocellulose. The addition of nanocellulose into these sensors results in significant improvements to the devices' sensing power as well as their selectivity and sensitivity. In this work, we studied various toxin sensors, biosensors and the use of nanocellulose in these sensors.*

Keywords: Nanocellulose; Sensing; Biosensing; Toxin sensing

1. INTRODUCTION

Several kinds of nano compounds are utilized nowadays for several purposes [1,2]. Sensing is such an application. Nano sized particles are utilized in various sensing techniques. Several sensing techniques include an electrode which is used as transducer element in the presence of an analyte [3]. Potentiometric technique is a commonly used sensing technique. It's used to determined analyte concentration by measuring difference between a reference electrode and a working electrode [4]. There are also other sensing technique like conductometric and amperometric technique. Researchers introduce nanocellulose to these techniques which increased the sensing power [5]. The use of nanocellulose in the sensing techniques has increased the stability, selectivity and sensitivity of the sensors. Nanofiber, nanocrystal is the forms in which nanocellulose can be used. This form helps the sensors to achieve versatility [6]. Nanocellulose can be functionalized by different molecules and applied in specific field. Nanocellulose based electrochemical sensors can detect both biological and nonbiological elements [7]. These detect heavy metals, pollutants, neurotransmitters, pathogen, various toxic elements, glucose, DNA, cholesterol etc. Nanocellulose has high surface area and which makes it an ideal substrate for immobilising enzymes, antibodies, or DNA probes. For the purpose of detecting diclofenac sodium, a non-steroidal anti-inflammatory medication and an electroactive painkiller that is commonly used, hybrid nanocellulose f-MWCNTs were adapted onto a glassy carbon electrode. A substantial increase in the anodic peak current was seen at the modified electrode when tested under ideal conditions [8]. Conductometric sensors are capable of being shrunk, mass-produced, operating at low voltages, and not requiring a reference electrode. In biomedical applications, including healthcare and diagnostics, nanocellulose-based conductometric sensors have shown promise [9]. They can be used to detect biomarkers such as glucose, cholesterol, and proteins, which are significant disease indicators. Nanocellulose's high surface area and biocompatibility make it an ideal substrate for immobilizing biomolecules in biological fluids, enabling sensitive and selective detection [10]. Amperometric is an electrochemical sensing technique that can be used in toxin sensing. It is also used in biomedical diagnostics especially in detecting biomarkers [11]. Specific and precise detection of target molecules is made possible by functionalizing these sensors with immobilized enzymes, antibodies, or DNA probes. Possible uses include the study of neurotransmitters in neurological illnesses, the identification of indicators for cardiovascular disease, and glucose monitoring for the treatment of diabetes [12,13]. Nanocellulose based electrochemical sensors are low in cost and offer sustainability. The abundance of nanocellulose is high in nature therefore the production cost is low. These sensors also have reduced impact on the environment related to sensor disposal [14,15]. In this study, we discussed about sensing techniques and the utilization of nanocellulose in this techniques. The aim is to give an overview about the utilization of nanocelluloses in the sensing purposes.

2. SENSING TECHNIQUES

Sensing techniques are methods or procedures that are used to detect, measure, and evaluate a variety of different physical, chemical, or biological phenomena that are present in the surrounding environment. These methods are extremely useful in a wide variety of domains, including engineering, healthcare, environmental monitoring, and a great deal of other areas. Sensing techniques allow us to obtain insights, make educated decisions, and build new solutions. These benefits are achieved through the techniques' ability to capture and understand important data [16]. There is a wide variety of sensing techniques accessible, each of which has its own set of guiding principles and uses. The process of detecting and quantifying the qualities of substances or materials through the utilization of light is known as optical sensing. Methods such as spectroscopy, which examines the interaction of light with materials to identify properties such as composition, concentration, or molecular structure, are examples of these kinds of sensing techniques [17].

Measurements of temperature shifts or heat distribution are among the tasks performed by thermal sensing techniques. Thermocouples, infrared cameras, and thermal imaging systems are all examples of equipment that can be used to accomplish this goal. These imaging systems capture and analyze the thermal energy that is released by an object or environment [18]. In mechanical sensing, the quantification of particular parameters is accomplished through the observation of mechanical changes or responses [19]. Magnetic sensors are capable of detecting and measuring changes in magnetic flux as well as magnetic fields [20]. Techniques of chemical sensing are utilized in order to detect and assess the existence of numerous chemical species inside a sample. This is done by analyzing the concentration of these chemical species. This can be accomplished by the utilization of techniques such as chromatography, mass spectrometry, or gas sensors, all of which are able to recognize and measure particular gases or volatile molecules [21]. Electrochemical sensors make use of the electrical properties of the substances being tested in order to detect and quantify particular analytes. These sensors are dependent on chemical processes that take place at an electrode interface, which results in the production of quantifiable electrical signals that can be connected to the presence or concentration of the target analyte [22]. Potentiometric sensors, Amperometric sensors, conductometric sensors etc. are example of electrochemical sensors. Potentiometric sensors detect analyte concentration by detecting the dissimilarity of potential between a reference electrode and a working electrode [23,24]. A selective membrane separates these components from the rest. Recent research has shown that permeabilized *P. aeruginosa* can alter the potentiometric biosensor that is based on a pH electrode. It was designed specifically for the selective and immediate impact that antibiotics have. The generation of protons near the pH electrode followed the hydrolysis of cephalosporin caused by the microbial layer's enzyme activity. The reaction resulted from a shift in the electric potential differential value between the reference and working electrodes [25]. Conductometric sensors are capable of being downsized, manufactured in vast numbers, without requiring a reference electrode, and operating at low voltages. When conductometric detection is used, the actions that are carried out by enzymes always result in changes to the ionic composition of the reacting solution. These changes are a direct consequence of the conductometric detection [26–28]. Observations made with conductometric sensing equipment have revealed that there has been a modification to the ionic part of the surrounding environment. The antigen–antibody combination coating on the electrode affects the conductivity of the electrolyte in which the immobilized enzyme is submerged, the biocatalytic activity of an enzyme that has been immobilized is reduced. This is due of the mechanism described above. In order to accomplish this, antibodies that have been tagged with enzymes have been adsorbed on the electrode. Then the antibodies were linked to the antigens that were present in the sample solution, as was illustrated above [29]. The sensation of large range of chemicals has accomplished via the use of conductometric biosensors. In comparison to other kinds of transducers, this kind of biosensor offers a number of distinct benefits [30–32]. Amperometric is an electrochemical sensing technique that can be used in toxin sensing [33].

3. NANOCELLULOSE FOR ENVIRONMENTAL TOXIN SENSING

CNF, CNC, and BNC are dissimilar from one another in terms of their form, size, and chemical make-up. There are significant variations in the morphologies of CNC, CNF, and BNC. Nanocelluloses plant based encompass CNF and CNC, while BNC comes from microbes and thus it is defined as microbial-based nanocellulose [34]. Bacteria, including *Acetobacter xylinum* and *Pseudomonas*, are responsible for the production of BNCs through the process of cellular respiration fermentation in synthetic and nonsynthetic conditions. BNCs are constructed from intricate networks of nanofibrils consisting of pure cellulose that are in the shape of ribbons. The sizes of these are less than 100 nanometers. These nanofibrils have dimensions of 2-4 nm each and are assembled from either a large number of nanofibrils with 2-4 nm diameters together [14]. The usage of these natural nano polymers as substrates or even as components of the sensor active layer has been the primary focus of researchers. These natural polymers are just one of many materials which could be used in the fabrication of sensors. These kinds of materials can make a contribution to sustainability by lowering the amount of nonrenewable and toxic or hazardous components that are used. In some circumstances, these can also lend biocompatibility to the sensors that are eventually manufactured. CNF anisotropy, which can be reached through controlled self-assembly CNC suspensions, has the potential to produce materials with optical birefringence and bright iridescence. So, these particles can be utilized in colorimetric sensors. In both liquid-phase and solid-phase sensors, the CNC trait of becoming entrenched has been the subject of investigation. The optically active arrangement that is present in these sensors is housed in either a polymer matrix or a CNF film [35]. Because of its vast surface area, high aspect ratio, high and unique stiffness and strength, and apparent absence of toxicity, CNC has emerged as one of the most promising biocompatible matrices for the immobilization of biomolecules. By using these CNC, analytic diffusion is sped up, which both increases the test's sensitivity and shortens the amount of time necessary to get a result. Nano cellulose crystals (NCC) are a hydrophilic polymer that does not conduct electricity and dissolves easily in water. To achieve their goal of making NCC more electrically conductive, researchers have investigated a wide range of innovative methods that can transform an insulating material into a highly conductive one. In order for NCC to be utilized in a wider variety of biosensors, it has to be changed by the addition of a hydrophobic cationic surfactant such as cetyltriammonium bromide (CTAB) [36]Metal ions such like mercury, lead, cadmium and arsenic are also some of the examples that can be found in the contaminated water that will be used in agriculture, the food sector, and for drinking water. Mercury is a hazardous metal ion, and being handled to this poisonous metal ion can resulting in a host of serious health issues, including dysfunction in the brain and kidneys, as well as metabolic abnormalities [37].

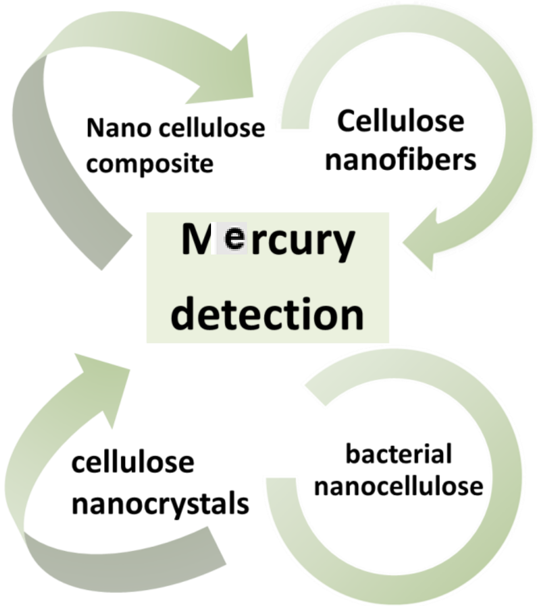

Fig. 1. Several types of nanocelluloses that are utilized in various sensors for Mercury detection.

CNC [38], BNC [39], CNF [40] can detect Mercury (see Fig. 1). CNC can also detect lead [41]. The performance of the sensing layer is improved by incorporating the conductive polymer known as poly(3,4-ethylenedioxythiophene) (PEDOT) with NCC. In comparison with other conducting polymers, this polymer has excellent features, including high conductivity, high transparency, and good chemical and electrochemical properties. Subsequently, it is helpful to add these benefits to use in optical sensors [42]. Because of the importance of correctly identifying potentially harmful organisms within biological and environmental systems, there is a significant demand for fluorescence sensors that are compact, user-friendly, sensitive, selective, and versatile. Researchers were able to create a fluorescence sensor with a "switch-on" capability by using pyrene-modified nanocrystalline cellulose and the Schiff base reaction. Because of this, it became possible for the very first time to test samples of black tea, rice, and soil for the presence of cadmium in a way that was simple, sensitive, quick, and selective. As a sensing platform and a fluorophore, respectively, nanocrystalline cellulose and pyrene are incorporated into this particular process of creation. Nanocrystalline cellulose has many great qualities, such as being easy to get, cheap, having a lot of hydroxyl groups, a large surface area, and being strong. These qualities, along with the improved photophysical properties of its pyrene groups, make it useful and commercially viable in the long term. The first-ever Cd^{2+} detection on real materials was done using a new type of cellulose called hybrid nanocrystalline cellulose. Using a method called "spike/recovery" and ICP-MS, the best fluorescence parameters for sensing cadmium were found. Based on the results, a newly made platform is a strong candidate for detecting Cd^{2+} fluorescence in samples of food and soil. The way the nanoparticles interact with Cd^{2+} in tests showed that the nanocellulose "turn on" fluorescence response to Cd^{2+} could be used to detect quercetin as a "turn off, on, off" signal with static quenching. The "turn-off-on-off" fluorescence signal response of nanoparticles could be used to do this. Changes were made to the surface using the C=N Schiff base reaction (CHEF). With the help of photo-induced electron transfer (PET) and chelation enhanced fluorescence, the C=N bond could be used to control how a proposed fluorescent sensor can "switch off" and "switch on". Synergistic excimer emission of pyrene moieties with PET and CHEF processes led to a big "turn-on" of fluorescence at 453 nm [43]. In modern years, magnetic hybrid materials have been formed by adding CNCs with cobalt-iron oxide particles into a composite material [44]. When poisonous gases like NO_2 are identified early on, and it might be possible to take prompt action to successfully avert the adverse effects of these gases. In recent years, CNF have been commonly used in the manufacture of ammonia gas sensors [45,46]. A novel kind of heterocyclic-ligands/Nanocellulose/Co_3O_4/carbon-nanotube was created in the lab and its properties were analyzed by the researchers. This sensor was built as a novel sensor platform for the ultra-trace impedimetric direct detection of cadmium ions in samples taken from municipal water supplies. With a lower detection limit (LOD) of 1.5 x 10-13 M (S/N = 7), and an R2 value of 0.99, the researchers were able to obtain great sensitivity as well as a broad linear range across the concentrations (10-13 M to 10-2 M). When the sensor was put to use for actual sample analysis (on tap water), it was possible to get a high recovery percentage of between 96 and 120% [47]. Researchers have begun research on a unique nanocellulose-based hydrogel (NBH) that is dependent on silver nanoclusters. This NBH is being developed for the goal of sensitive detection and removal of Cr(VI). The NBH displayed excellent selectivity and sensitivity to Cr(VI), with a detection limit of only 0.43 g/L. They made the discovery that the cost of removing Cr(VI) ions with NBH was approximately six times lower than the expense of doing so with commercial activated carbon [48]. When it comes to the removal of Cr(VI) ions, one of the most exciting developments in the field of functional hydrogel sal activated carbon is the application of CNF to fluorescent hydrogels. The CNF possesses excellent hydrophilicity, biocompatibility, a large specific surface area, and the capacity to biodegrade. Nanofibers derived from cellulose also exhibit exceptional biodegradability. Researchers have developed a fluorescent hydrogel based on CNF that is capable of detecting mercury ions [49]. Scientists have developed a novel luminous nanocellulose hydrogel (NH) that is based on cellulose nanocrystals and gold nanoclusters. This NH possesses a distinctive fluorescent quality. This NH has a high sensor sensitivity and selectivity for Hg(II), in addition to a powerful adsorption ability with a maximum adsorption capacity of 95.7 mg/g for Hg(II). [50].

4. NANOCELLULOSE FOR BIOSENSING

The identification of target molecules through the use of the same fundamental principles utilized by biological systems such as the immune system is known as biosensing. When attempting to carry out biosensing, detection specificity and sensitivity are two essential characteristics to take into account. Labeling the target molecules is a tried-and-true method that is required for achieving the desired level of specificity [51–53]. Biosensing is a technique which is used to detect biomolecules with the help of biosensors. Biosensor is an analytical device. Biological components such as sweat, saliva or other vital bodily fluids can be combined with a physicochemical detector by biosensors. Biosensors are portable, small or even heavy machinery. Biosensors also can be wearable devices. The time needed for sensing is very little with these devices [54]. BNC has become a good option to surfaces that keep boats from getting dirty. To make BNC more useful as a biosensing device, it could help keep certain chemicals from moving around [55].

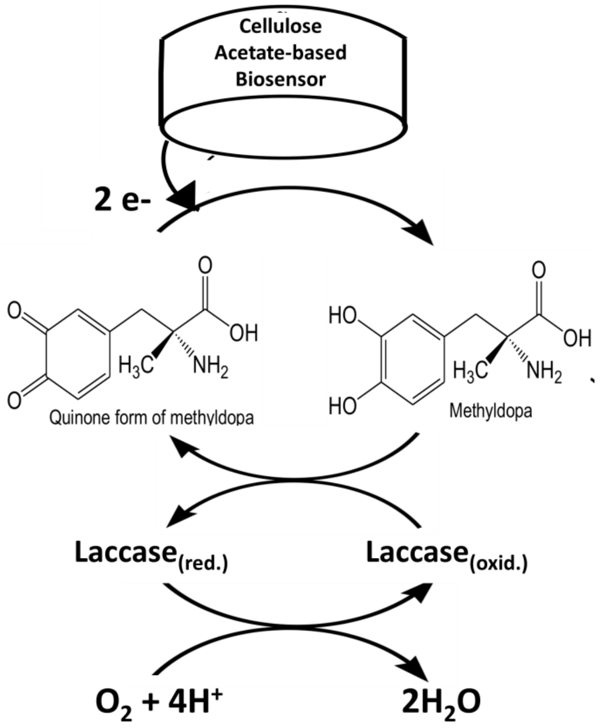

Fig. 2. The laccase-catalyzed oxidation of methyldopa followed by an electrochemical reduction process [5].

Immobilization of laccase from Aspergillus oryzae onto activated cellulose acetate that had been combined with ionic liquids such as 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide was the method that was utilized in the preparation of a methyldopa biosensor. The methyldopa biosensor had good linearity when evaluated using square wave voltammetry. Additionally, the biosensor had a detection limit of around 5.5 M. It demonstrated reusability, excellent anti-interference, and reproducibility, in addition to a stability that was sufficient for around sixty days. In addition to this, it demonstrated a high level of accuracy when testing pharmaceutical samples for the presence of methyldopa. After beginning with 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and cellulose acetate as an ionic liquid, the process of preparing the laccase-based biosensor was carried out. The methyldopa was oxidized to quinone in the presence of laccase, which acted as a catalyst for the reaction. The quinone was then electrochemically reduced on the surface of the biosensor back to methyldopa at a potential of +0.07 V vs. Ag/AgCl (see Fig. 2) [5].

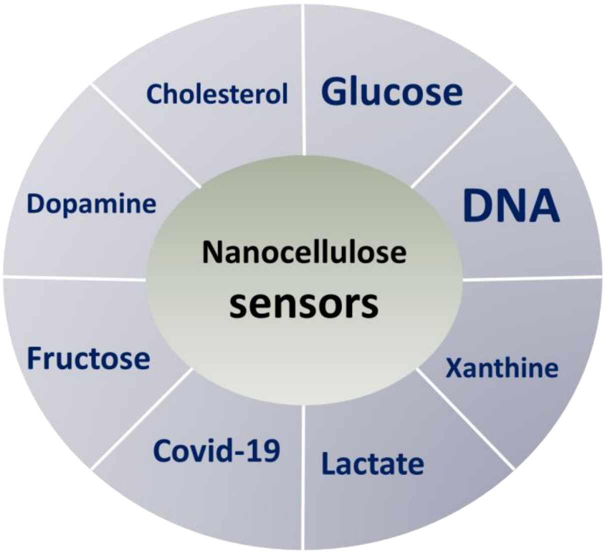

Fig. 3. Nanocellulose based sensors in sensing various biological components in several researches.

Nanocellulose has been utilized in detection of glucose [56], xanthine [57], cholesterol [58], DNA [45], dopamine [59] , Fructose [60] , COVID-19 [61], lactate [55] etc. *(see Fig. 3) biological compounds*. Carboxyl nanocellulose is a useful material for biosensing devices to detect glucose colorimetrically. Glucose is used as a substrate, glucose oxidase (GOx) acts as an enzyme to selective oxidation of glucose. Peroxidase and ABTS are employed colorimetric system to detect signal from oxidation of glucose indirectly [62]. CNC possesses high specific strength and modulus, low density, and high surface area. These properties of CNC will improve the electron transfer properties of sensors as a result performance of biosensor was enhanced. Polyaniline (PANI) was utilized to fabricate The PANI/CNC/IL/GLU nanocomposite which was used to improve the performance of biosensors to detect cholesterol. In order to identify cholesterol, cholesterol oxidase (ChOx), this composite was immobilized on a modified electrode where was aided by glutaraldehyde and served as the crosslinking agent. As a consequence of a chemical interaction that took place between the enzyme and the cholesterol, the PANI/CNC/IL/GLU/ChOx modified electrode demonstrated a significant rise in the number of redox peaks, which was followed by the optimum formation of hydrogen peroxide. The range within which cholesterol can be detected by the PANI/CNC/IL/GLU/ChOx modified electrode is 0.001-12 mM. High sensitivity and fast response was also observed [63]. Researchers successfully construct a peptide nuclide acid (PNA) biosensor which is based on TEMPO-nanocrystalline cellulose (TNCC) to detect *M.Tuberculosis*. This biosensor shows a good selectivity toward different types of *M.Tuberculosis* [64]. For detection of glucose researchers found another biosensor based on polypyrrole-cellulose nanocrystal (PPy-CNC) with glucose oxidase (GOx). This composite enhanced biosensor performance. This biosensor detects glucose ranging from 1.0 to 20 mM. It also shows a high sensitivity. This sensor can exclude interfering species like cholesterol, ascorbic acid, uric acid etc. Reproducibility and stability over time is also acceptable [65]. In order to facilitate the creation of cotton cellulose nanocrystals (DCNCs), a deep eutectic solvent (DES) was used. These nanocrystals were then put to use in the process of producing a peptide-cellulose conjugate to act as a protease sensor of human neutrophil elastase. Because the DCNCs-based colorimetric sensor has a sensitivity of less than 0.005 U/mL, it might offer an easy-to-use, sensitive sensor that could be used to enhance colorimetric point-of-care protease biomarker detection. Biosensors can transform biochemical signals into measurable signals. It works based on a physical-chemical transducer, a biological recognition system and an electronic system that processes and displays to show signal. BNC based biosensors possess high catalytic selectivity. BNC based biosensors have significant electronic and optical transduction characteristics. BNC-Au can also detect glucose. Biosensors based on BNC-Au nanocomposite shows amperometric response even when the concentration of glucose is low [66]. Utilizing the percolated conductive network in polyvinyl alcohol (PVA), a team of researchers has developed a versatile composite film that can be used as a flexible strain biosensor. The material was developed on CNC-PANI composites. High sensitivity and easy water-induced self-healing capabilities were displayed by the composite electronic skin, which also exhibited extraordinary mechanical strength of 50.62 MPa [67]. In order to detect xanthine and establish an electrochemical biosensor for fish spoilage monitoring, nanocellulose was fabricated from raw cotton by the use of acid hydrolysis. This nanocellulose acts as an immobilization matrix for xanthine oxidase (XO), which allows for the detection of xanthine. Differential pulse voltammetry (DPV) was used to determine that the linear range of detection for xanthine. The enzyme's high affinity for xanthine was confirmed by the Michaelis-Menten constant value, which was an exceptionally low 12.2 M [57]. CNF, graphite (Gr), and silver nanoparticles (AgNPs) were utilized in the development of a voltammetric biosensor by the research team in order to determine ascorbic acid (AA), dopamine (DA), and paracetamol (PA). The Gr/CNF-AgNPS nanocomposite electrode had a wide surface area, strong selectivity, broad linear responses, and extremely low analytical and determination limits for AA, DA, and PA. An extremely high level of interference resistance was demonstrated by the newly developed electrode. In addition to this, the sensor is able to precisely determine the concentrations of AA, DA, and PA that are found in human urine as well as blood serum [68]. The sensing of the cyanobacterial biomolecule C-phycocyanin (CPC) was improved by using genetically engineered bacteria, and CNF films were used as a carrier material for the improved sensing. Following this, CPC–CNF films were shown to be capable of detecting free copper ions in human blood serum, and heavy metal sensitive fluorescence emission was detected. CNFs in aerogels can also be attached to an immobilized antigen or antibody, which can then conjugate to an enzyme or fluorophore label, which can then be used to identify a specific antibody or antigen (see Fig. 4) [69].

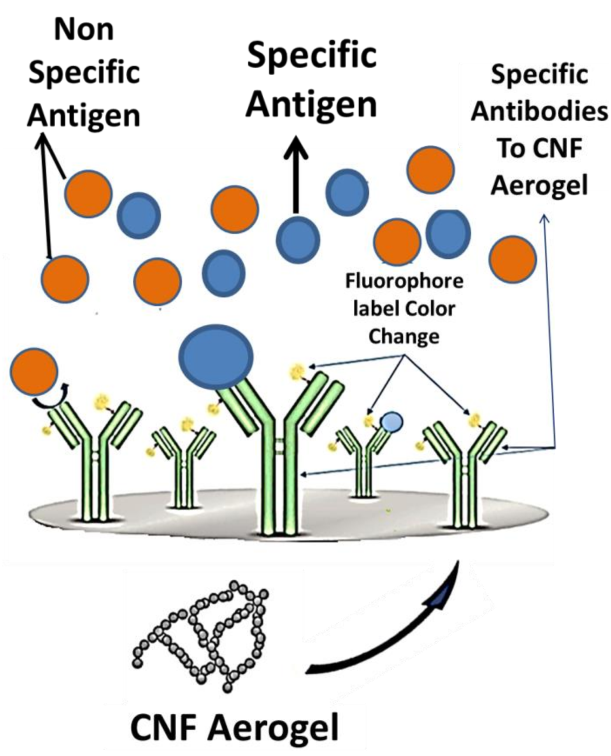

Fig. 4. The possible application of CNF aerogel as a diagnostic tool for specific antigens [69].

5. CONCLUSION

In the conclusion nanocellulose based sensors are one of the most important discoveries by which detection of pollutant, hazardous elements, heavy metals, and biological compounds is possible. After being modified by nanocellulose, these sensors selectivity, sensitivity, rigidity, and sensing power increased much more. Although there are some issues while modifying sensors with nanocellulose, these modified sensors have a wide range of applications. If researchers can overcome those challenges, a great future is waiting for this field, as sensor based on nanocellulose can modify electrochemical sensors and other biosensors.

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