Advances in Modern and Applied Sciences

A Collection of Research Reviews on Contemporary Research (Volume 1)

Sujay Pal

Tushar Kanti Biswas

Scientific Research Publishing

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Advances in Modern and Applied Sciences

A Collection of Research Reviews on Contemporary Research

(Volume 1)

Editors
Sujay Pal
Tushar Kanti Biswas

Srikrishna College (Govt. Sponsored)
Affiliated to University of Kalyani
Bagula, Nadia, West Bengal, India 741502

Foreword

It is a great pleasure to write this foreword for the book "Advances in Modern and Applied Sciences, A Collection of Research Reviews on Contemporary Research (Volume 1)". When I heard about publishing a comprehensive book on science from one of the Editors, I was very much excited to see it. At last, the dream came true for Science Departments of Srikrishna College. Indeed, this book contains a wide variety of research topics in modern science presented in a systematic and engrossing way to acquire knowledge without knowing its cutting-edge technologies. The readers can experience the latest developments in the field of computer and material sciences. The field of atmospheric and space Sciences is of growing importance for our future life in view of Sustainable Developments Goals (SDGs). Then the articles regarding Astrophysics, Astronomy, and High Energy Physics attract our curiosity about how our universe works. All the above-mentioned topics are carefully and well documented in four chapters by many experts from their respective fields. This book must be suitable not only for scholars but also for students and researchers working in different research fields to widen their view of science. I am eagerly waiting for the next volume of this book.

With best wishes.

Yasuhide Hobara

Yasuhide Hobara

Professor

Head, Center for Space Science and Radio Engineering

Graduate School of Informatics and Engineering

The University of Electro-Communications, Tokyo, Japan

Preface

This book *Advances in Modern and Applied Science* materializes our long-cherished dream of publishing a series of volumes consisting of review papers on contemporary research fields from a broad spectrum of basic sciences. The present volume, which is our first baby-step towards that fulfilment, includes a collection of twenty-five review articles contributed by about fifty researchers and scientists whose vocations are in diverse fields of science including astrophysics, astronomy, high energy physics, space science, atmospheric sciences, computer sciences to material sciences.

The main objective of this book is to provide an insight into the advances that modern day science has made and bring forth a better understanding of this vast and exhilarating discipline called *science*. Keeping this in mind the contributors have emphasized on the essemplastic power by incorporating both the quantitative and qualitative research outcomes in a very lucid manner that would dulcify the readers with its ineluctable pedagogy as put forward by esteemed personalities mostly through the review articles. We are certain that new graduates, Ph.D. scholars, teachers, and researchers from diverse fields will benefit from this volume, which can be considered as a stock-taking of the new developments in recent day science.

The editors have compiled and edited the articles duly to suit the purpose of the book and at the same time to keep a balance between diverse topics. We have organized our book into four specific chapters. To begin with, *Chapter 1* consists of nine articles from Astrophysics, Astronomy and High Energy Physics. In this section, the reader is provided with a brief overview on various topics focusing on Monte Carlo simulation of black hole imaging in X-ray domain, multi-messenger astronomy, properties of radio galaxies, galaxy rotation curves, neutron stars, radio study of the atmosphere in Saturn's moon and new quantum methods in Krein space. *Chapter 2* is devoted to Atmospheric and Space Sciences comprising eight articles. Articles on recent topics like extraordinary air pollution in New Delhi, atmospheric factors affecting transmission of Covid-19, impact of extreme weather events on agriculture, effects of ionospheric forcing from above and below due to solar flares, seismic events, cyclonic storms, polar stratospheric warming events and their experimental measurement techniques have enriched this Chapter. In *Chapter 3*, researchers have explored advances in modern Computer Science and Mathematics through five articles focusing on recent topics like routing and spectrum allocation scheme in elastic optical networks, Spectrally-spatially elastic optical networks technologies and their challenges considering different types of fibers and Verifiable Visual Cryptography for transmitting secret image over the internet and Alexander-Spanier cohomology theory. Finally, *Chapter 4* contains three articles from Material Sciences giving an overview of the current state of the art focusing on topics like data-based material designing using Machine Learning, thermo-electric devices, and applications of Chitin and Chitosan based composite as promising green energy resources.

The book has been sponsored by Srikrishna College, Bagula, West Bengal, India. In this regard, we take the opportunity to thank Dr. Sukdeb Ghosh, Principal of the College, and Mr. Anup Kumar Bhadra, President of Governing Body for their constant support and encouragement without which it would have been difficult for the book to see the light of day. The book can truly be said to act as a springboard in our endeavours to promote and further advance the culture of research environment in our institution..

We earnestly thank all the authors for their efforts and enthusiasm to submit their contributions to this volume and make this book a successful publication. Our sincere thanks reaches out to all the faculties and staff members of Srikrishna College, especially Dr. Bipul Mandal, Prof. Somnath Chakraborty, Prof. Anamika Chakraborty, Ujjal Kumar Das, Dr. Ankita Indra, Dr. Tushar Kanti Bose, Dr. Pranab Das, Supratick Adhikary, Dr. Paramita Hajra, Dr. Nabadyuti Barman whose constant support and succour made the book a success. Finally, we must thank the Publisher Scientific Research Publishing Inc., USA for agreeing to publish the book in a timely manner.

May, 2022

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Advanced Electronic and Energy Applications of Chitin and Chitosan based Composites

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Abstract Sustainable green energy resources chitin and its derivative chitosan have been considered as promising materials to reach the global energy demand in an environment-friendly way. The inherent properties such as antimicrobial, non-toxic, biocompatibility, biodegradability in addition to ease of fabrication and low-cost availability have made chitin and chitosan a suitable material for green energy harvesting, biological and industrial fields. This review provides a detailed study of chemical structures, extraction routes along with physical and chemical properties of chitin, chitosan and their composites followed by their numerous electronic and energy storage device applications including different sensors, energy harvesting devices, solar cells, fuel cells, super capacitors and Li-ion batteries.

Keywords: *Chitin, Chitosan, Electronics, Energy, Composites*

1. Introduction

Rapid advancements of modern civilization with increasing industrial and technological fields along with growing population, lead to high global demand of energy in daily life. Conventional energy resources like fossil fuels such as coal, natural gas, petroleum and its derivatives are trying to fulfil this huge energy demand. However, these fossil fuels are not unlimited in nature [1] and being exhausted rapidly [2, 3]. On the other hand, its uncontrolled exploitation and combustion also emit various pollutants in the air which are harmful for our environment [4, 5]. Hence, to overcome this energy crisis problems and environmental pollution, many research works are being carried out to find biodegradable and biocompatible sustainable green energy resources [6]. Recently, much interest have been taken on the polysaccharides specifically on chitin and its derivative chitosan by the researchers while exploring new materials for green energy applications [7]. Chitin and chitosan have been considered as attractive material for green energy resources due to their ease of fabrication, low cost, availability, biocompatibility and biodegradability properties [7, 8, 9]. Chitosan is derived from deacetylation of chitin which is the most ubiquitous natural biopolymer after cellulose. Chitosan has better solubility in water and organic solvents which makes it is more suitable than chitin for its applicability in biological fields [10, 11]. Due to its non- toxicity and biodegradability nature, chitosan has been used widely in various fields such as agriculture [12], water treatment [13, 14], food packaging [15-17] and biomedical applications [18, 19]. In recent years, chitin and chitosan based composites have gained utmost importance in electronic and electrical energy storage applications like sensors, energy harvesting devices, solar cells, organic light emitting diodes (OLEDs), supercapacitors, fuel cells, diodes and photoelectrical applications not only because of their high stretchability and better electrical conductivity but also for their non-toxic and biocompatible nature. [20-23]

2. Chitin and Chitosan Structures and Extraction

2.1. Structure of Chitin

 # Somtirtha Kool Banerjee was previously known as Somtirtha Banerjee

Chitin [$(C_8H_{13}O_5N)_n$] is a long chain natural biopolymer with two monomer units (N-acetyl-D-glucosamine and D-glucosamine) linked with β-(1-4) glycosidic bonds as shown in Figure 1 [24].

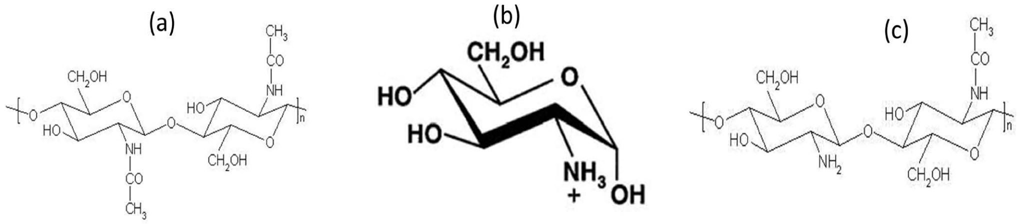

Figure 1. (a) Structure of chitin, (b) Glucosamine and (c) Chitosan. [24]

Natural chitin has three crystalline polymorphic forms namely α, β and γ (Figure 2) chitin having different orientations of microfibrils. The most abundant α-chitin has highest crystallinity with antiparallel alignment of microfibrils and found in crabs, shrimps, insect cuticles, yeast cells marine sponges and other species [25, 26]. The β- crystalline form has parallel orientation and γ-structure has a mixed alignment with two parallel microfibrils followed by one antiparallel one. β-chitin is found in chaetae of certain annelids, squids chrysalides, crustaceous, and fungi whereas γ-Chitin is rare and found in cocoons of moth and stomach of Loligo [27, 28]. These different polymorphs of chitin has different physicochemical properties depending on microstructures.

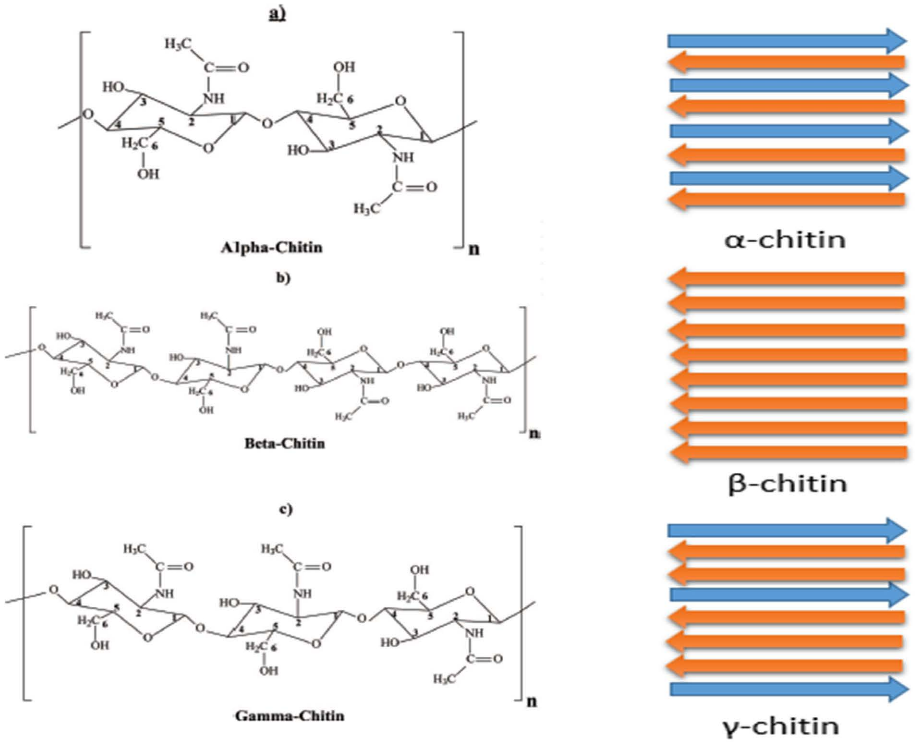

Figure 2. Schematic representation of the three polymorphic forms of chitin. [25]

2.2. Structure of Chitosan

Chitosan has a little compositional difference between the two monomers N-acetyl-D-glucosamine and D-glucosamine compared to the chitin structure. (Figure 1) Chitosan has higher number of D-glucosamine (2-amino-2-deoxy-D-glucose) monomer unit whereas chitin has more N-acetyl-D-glucosamine (N-acetyl 2-amino-2-deoxy-D-glucose) units. Thus, chitosan has a heteropolysaccharide structure with linear β-(1-4) linkage between monomer units and it can be easily obtained from chitin by the process of deacetylation. Chitosan and has better solubility in water and acidic-aqueous solutions compared to chitin due to presence of positive charges by its amino group. Degree of deacetylation highly influence the solubility, conductivity, crystallinity, biocompatibility, biodegradability, flexibility, antioxidant, antimicrobial and other properties of cationic chitosan polymer.

2.3. Extraction of Chitin

The second most abundant natural bio-polymer chitin is mainly extracted from the shells of crabs, mussel shrimps, insect cuticles or squid gladius. Chitin can be extracted from the exoskeletons of these species either by chemical or by biological extraction techniques. The expensive, less efficient and non-ecofriendly chemical technique is primarily used for industrial applications whereas biological method of extraction is used for laboratory purpose with longer processing time though more eco-friendly nature.

Chemical extraction of chitin can be performed by three steps namely demineralization, deproteinization and decolouration. In the demineralization step minerals like calcium carbonate, calcium phosphate are removed using dilute HCl or dilute sodium hypochlorite solution whereas deproteinization or removal of protein can be performed using NaOH solution followed by washing with deionized water for removal of alkaline. Finally for the purpose of obtaining colourless product organic solvents like acetone are used. A schematic diagram for chitin extraction via chemical route is shown in Figure 3.

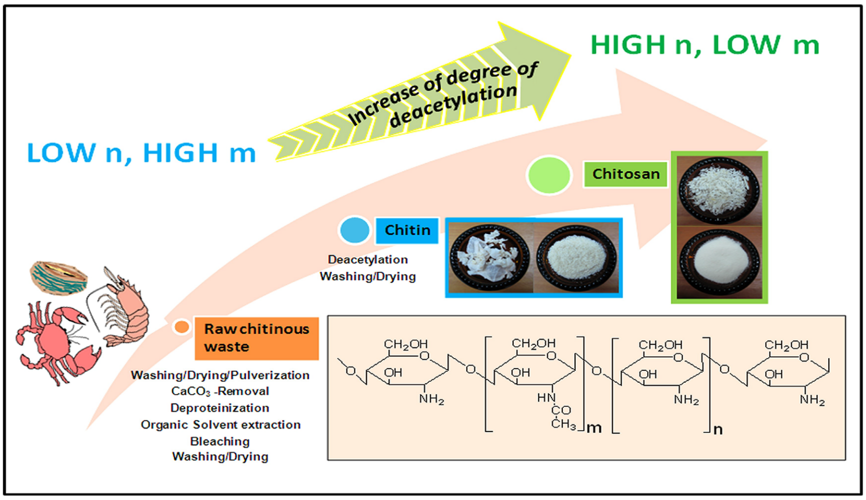

Figure 3. Chemical structures and extraction of chitin and chitosan. [Reprinted (adapted) with permission from [29]. Copyright (2013) American Chemical Society]

On the other hand, in biological extraction process of chitin is less hazardous and energy-consuming compared to the chemical method. In biological method, demineralization step is done with the help of lactic acid forming bacteria because bio-generated lactic acid removes minerals like calcium carbonate by producing calcium lactate which can be easily eliminated by washing. The deproteinization step in biological extraction method is performed by fermentation with the help of bacteria like *Pseudomonas aeruginosa K-187, Bacillus s subtilis, Bacillus cereus etc.* [30].

2.4. Extraction of Chitosan

Chitosan is obtained by the deacetylation of chitin and thus extraction of chitosan comprises of two steps: extraction of chitosan and deacetylation of it. Deacetylation is done by chemical hydrolysis or enzymatic treatment of chitin. Chemical hydrolysis method uses alkaline or acids with alkaline deacetylation having higher efficiency [31]. However, chemical hydrolysis releases many soluble and insoluble products which are harmful for environment. This is why instead of lower production rate, enzymatic treatment is used conventionally for the deacetylation of chitin. Additionally, variety of methods namely photochemical, electrochemical, sonochemical or microwave irradiation techniques have gained attention among the scientists. Deacetylation of chitin by microwave irradiation is especially important as it not only increases the yield but also reduces the reaction time and unnecessary side reactions [32]. However, a suitable combination of chemicals with power controlled microwave irradiation technique can provide controlled deacetylation with better efficiency [33].

3. Physical and Chemical Properties

Chitin is a biodegradable, biocompatible and non-toxic polymer that is a very useful in biological and industrial field due to its unique physicochemical properties [34, 35]. The extraction methods, protein content and sources significantly affect its properties. Due to the presence of two hydroxyl and an acetamide group, chitin shows more crystallinity than chitosan with strong hydrogen bonding [36]. Chitin shows the first step of thermal decomposition due to water evaporation in the temperature range of 50°C-110°C and the second step of thermal decomposition due to degradation and dehydration of saccharide rings in the temperature range of 300°C-400°C [37]. Chitin is insoluble in water and hydrophobic in nature due to presence of larger number of N-acetyl-D-glucosamine monomer units [38]. On the other hand, chitosan is a basic natural polysaccharide with respective to other polysaccharides such as cellulose, dextran, pectin etc. which are neutral or acidic in nature. Chitosan shows hydrophilicity due to presence of large number of amino and hydroxyl groups within its structure as shown in Figure 1 though being insoluble to alkaline aqueous solution in its crystalline form [39]. Presence of amino group makes chitosan to pH sensitive and governs its cationic and solubility [40]. Chitosan shows the first step of thermal decomposition due to dehydration and attains the peak value at a temperature of 168°C. Chitosan shows the main thermal degradation in the temperature range 230°C-400°C and attains the peak value at 273°C [41]. Chitosan has received much attention to the researchers due to its availability, low-cost [42] and hydrophilic nature [43].

4. Chitin and Chitosan Based Composites for Advanced Electronics Applications

Since the invention of electronic devices, they have played an indispensable role for comfortable human life. However, in present situation, care should be taken about the electronic waste, which have now become the biggest threat to the environment. Therefore, to develop a sustainable future, natural environment-friendly materials should be used for sustainable green electronics growth [44, 45].

4.1. Sensor Applications

Recently, polymer and polymer nanocomposite based materials have gained interest among researchers to develop long-lived, low-cost multi-purpose sensors. Sensor is an electronic device that responds to a signal and convert it into electrical or magnetic form Chitosan has been confirmed as a specific polymer for sensing applications due to its chemical versatility, high adsorption capacity, mechanical robustness, flexibility, biocompatibility, biodegradability, hydrophilicity and gel forming ability along with antimicrobial and anti-oxidative properties. Chitin and chitosan based sensors can be broadly categorized in 3 types namely biosensors which senses biological reactions and convert it into detectable electrical signals, chemical sensors which detects chemical ions or gases and physical sensors which can sense physical movement or mechanical strains. [41,46,47]. The presence of 2 hydroxyls (–CH_3OH) and one acetyl (for chitin) or amino group (for both chitin and chitosan) makes chitin and chitosan suitable for chemical and biological sensing applications as the lone pair in the amino groups show affinity towards metal ions and better compatibility in some aqueous system.

4.1.1. Biosensors

Biosensors act as analytical tools in medical science for clinical detection of bio-chemical moieties [48]. In a typical electrochemical biosensor the biological element which has to be sensed is associated and interfaced with a transducer. Chitosan being biocompatible and having functional groups with possibility of chemical modification can be deposited easily on the surface of transducer forming adhesive films for the immobilization process of the sensing elements. The elements like alcohol, lactate, glutamate, glucose etc. can be detected either directly by means of their oxidation and followed by immobilization of their oxidases on chitosan composites or by the immobilizations of some dehydrogenase enzymes [49] (Figure 4) on chitosan composite films with NAD or FAD as cofactors. Different types of biosensors for detecting variety of biochemical compounds are enlisted in Table 1 with type of chitosan composites used along with immobilized compounds on the film.

TABLE 1: ELECTROCHEMICAL BIOSENSORS BASED ON CHITIN AND CHITOSAN COMPOSITES

Types of Biosensors	Purpose of Sensing	Immobilized Agent	Chitosan composite used	References
Glucose biosensors	Detection of glucose in blood or any other biological system	Glucose oxidase	Chitosan carbon nanotubes	[50]
		Glucose oxidase	Multi layered chitosan biofilms- gold nanoparticles	[51]
		Glucose oxidase	Fe_3O_4 Chitosan nafion	[52]
Lactate biosensor	Food and important medical compounds monitoring	Lactate oxidase	Chitosan-polyvinylimidazole-Os-carbon nanotubes	[53]
Glutamate sensor	Sensing of Glutamate	Glutamate oxidase	Chitosan/graphene oxide-polymerized riboflavin	[54]
Xanthine biosensor	Xanthine detection in biological systems	Xanthine oxidase	Chitosan-polypyrrole-gold nanoparticles	[55]
Galactose biosensor	Galactose detection	Galactose oxidase	Chitosan single walled carbon nanotubes	[56]
Cholesterol biosensor	Detection of cholesterol	Cholesterol oxidase	Multiwalled chitosan carbon nanotubes	[57]
Choline sensor	Detection of choline	Choline oxidase	Chitosan/titanate nanotubes	[58]
Immuno sensor	Monitoring organophosphorus(OP) pesticides chlorolpyriphos	Anti chlorpyriphos monoclonal antibody	Multiwalled carbon nanotube-chitosan-thionine	[59]
	Detection and determinationof organophosphorus(OP) pesticides	OP hydrolase	Chitosan-carbon-nanoparticles-hydroxy-apatite nanocomposite.	[60]
	Detection and monitoring of fungal hepatocarcinogen, aflatoxin B1	Polyclonal anti aflatoxin B1	Chitosan-gold nanoparticles	[61]
	To detect alpha fetoprotein in human serum	Alpha-fetoprotein antigen	Gold nanoparticles/ carbon nanotubes/chitosan nano complex	[62]
	To detect HIV1- related capsid protein P24 in human serum	P24 antigen	Gold free-single walled carbon nanotube chitosan complex	[63]

	To detect carcinoembryonic antigen	Carcinoembryonic c antibodies	Chitosan gold nanoparticles	[64]
	To detect hepatitis B	Hepatitis B antibodies	Chitosan/ferrocene/ gold nanoparticles biofilm	[65]
DNA biosensor	To detect typhoid	*Salmonella typhi* single-stranded(ss) DNA	Chitosan/graphene oxide/ITO nanocomposites	[66]
	Detection of Escherichia coli	*Escherichia coli* stranded(ss) DNA	Chitosan/graphene oxide hybrid nanocomposites	[67]

In addition to the enlisted electrochemical biosensors, some biosensors were fabricated by a group of researchers for the detection and quantification of drugs and neurotransmitters like acetaminophen and mefenamic acid [68], dopamine and morphine [69], paracetamol, 5-hydroxytryptamine and dopamine [70] etc. using chitosan-multi walled carbon nanotube composite films

4.1.2. Chemical Sensors

Chemical sensors have broad range of applications in the food industry along with environmental monitoring due to their capability of sensing toxic elements, ions or gases present in food, water or air. Some chemical compounds like ethanol, nitrite, hydrogen peroxide etc. can be detected in a mechanism similar to that of electrochemical biosensors as discussed in the previous section. A sensor for sensing ethanol was fabricated by Wen et al. 2007 [71] using chitosan-eggshell film via immobilization of alcohol oxidase. This sensor is effective to study the reduction in oxygen level with respect to the ethanol concentration. Quan and Shin in 2010 [72] prepared nitrite sensor via the immobilization of Cu-containing nitrite reductase on the vilogen-chitosan film which catalyzes the nitrite reduction. For the purpose of detection of phenolic compounds Liu et al.[73] developed a sensor with horseradish pentoxide being immobilized on alumina-chitosan nanocomposite. Yang et al. in 2012 [74] devised a sensor for detecting catechol and other phenolic compounds by immobilizing tyrosinase on chitosan-nickel nanocomposite film. On the other hand laccase immobilized on ZnO-chitosan nanocomposite for sensing chlorophenol was fabricated by Mendes et al. [75] Sensors for detection of hydrogen peroxide via electrocatalytic reduction of it were developed by Akhter et al. [76] using graphene oxide-polypyrrole-chitosan film with screen-printed carbon electrodes and by Dong et al. [77] using immobilization of catalase on chitosan-β-cyclodextrin via electrocatalytic reduction of hydrogen peroxide. Teepoo et al. in 2017 devised hydrogen peroxide sensor and detector by utilizing horseradish peroxide immobilized on chitin-gelatin nanofiber composite. On the other hand Abu-Hani et al. [78] developed a high-sensitive low temperature H_2S gas sensor using glycerol ionic liquid blended conductive, transparent and flexible chitosan film. The mechanism of detection is based on the proton transfer between H_2S gas and basic amino groups from chitosan chains. This type of device is very sensitive due to large extent of H-bonding for the presence of excess OH groups coming from glycerol. This sensor can operate at a temperature of 20 ^{o}C at as low as 15 ppm level of gas with around 15 second response time. In addition to these sensors, many chemical sensors were developed by the researchers based on chitosan nanocomposites for the detection of trace amounts of toxic and carcinogenic metal ions. Sugunan et al in 2005 [79] and Borgohain et al. [80] developed Cu(II) and Zn(II) ion sensors using chitosan-gold nanocomposites and chitosan capped ZnS quantum dot composites respectively. In other research works, Cd(II) and Hg(II) were sensed using chitosan-carbon nanotube composite by Janegitz et al.[81] whereas Ahmed and Fekry [82] devised a Ni(II), As(II) and Pb(II) sensor using chitosan-α-Fe_2O_3 nanocomposites.

4.1.3. Physical Sensors

The field of advanced electronics of lightweight and wearable devices especially pressure sensing devices are growing fast for their various applications such as electronic skin [83,84,85], flexible touch displays [86,87], soft robotics and energy harvesting devices [88,89,90]. A piezoresistive sensor based on conducting flexible aerogel comprised of chitotsan, polyaniline and bacterial cellulose has been developed by Huang et al. [91]. In addition to piezoresistive sensor, some strain sensors have also been developed by scientists. Liu et al. [92] fabricated a high sensitive strain sensor using chitosan-carbon black conducting aerogels for sensing human activities like breathing or joint bending and another strain sensor based on spiral natural rubber, latex with carbon black and chitin nanocrystal [93]. The second sensor has high strain sensitivity and can be used efficiently to monitor human activities like movement of fingers (Figure 4) or pronunciation.

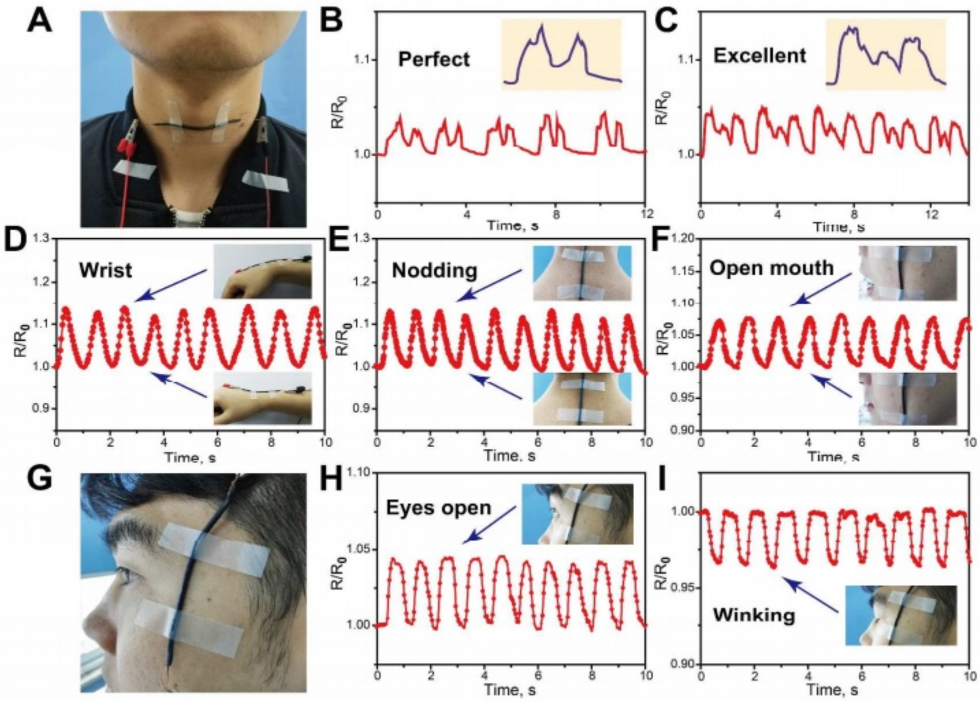

Figure 4. High-sensitive strain sensor attached to throat and cheek (A, G) along with the current signals from the sensor attached to the throat while speaking different words (B, C) and making different movements (D-F) and recorded current patterns from the sensor attached to the cheek while conducting different eye movements (H,I) [Reprinted (adapted) with permission from [93]. Copyright (2018) American Chemical Society].

4.2. Energy Harvesting Electronic Device Applications

Harvesting ambient waste energies into electricity has become very popular not only due to the huge energy crisis of modern society but also due to the recyclability and ease of access. However, some energy harvesting devices release harmful materials to the environment during the fabrication or decomposition. For the purpose of overcoming this limitation, biocompatible energy harvesting devices have gained utmost importance in the energy research field. [94,95,96] An innovative green electrical energy generation device using water vapour cell and chitosan film has been developed by Balyan et al. [97] The amine groups of chitosan acts as the active sites for the conversion of water vapour into electrical energy. The generation starts at 78% relative humidity with highest power generation of 120.13 µW at 4% chitosan concentration and this power is maintained at 90% relative humidity level. Li et al. [98] also generated electricity from chitin nanofibrils. In addition to harvesting water vapour into electricity, many researches are focused on the generation of electrical energy, harvesting ambient mechanical energy based on chitin and chitosan composites which is realised by means of the piezo- and tribo-electric properties of those composites. Hänninen et al [99] compared the piezoelectric response of pure chitosan film, pure cellulose nanofiber films and their blends. They interestingly found the best piezoelectric sensitivity (4 pC/N) for the plain chitosan film which also has the highest elongation during its break making it most flexible among others. Hoque et al. [100] extracted chitin from the waste crab shells and fabricated pure chitin based along with chitin doped poly-vinylidene fluoride (PVDF) based piezoelectric nanogenerators. Only chitin based generator showed an open circuit voltage (V_{oc}) of ~22 V and short circuit current (I_{sc}) of ~0.12 µA whereas PVDF-chitin composite film showed ~49 V of V_{oc} and 1.9 µA of I_{sc}. On the other hand, sustainable power sources for harvesting mechanical energy by means of triboelectric power generation using pulse laser processed surface modified chitosan films have been developed by Wang et al. in 2018. [101] In a recent work, Eom et al. [102] got promising output current from the triboelectric nanogenerator using epitaxially grown PVDF-TrFE (polyvinylidene fluoride tetrafluoroethylene) on chitosan with perpendicular orientation of PVDF-TrFE having best performance (Figure 5).

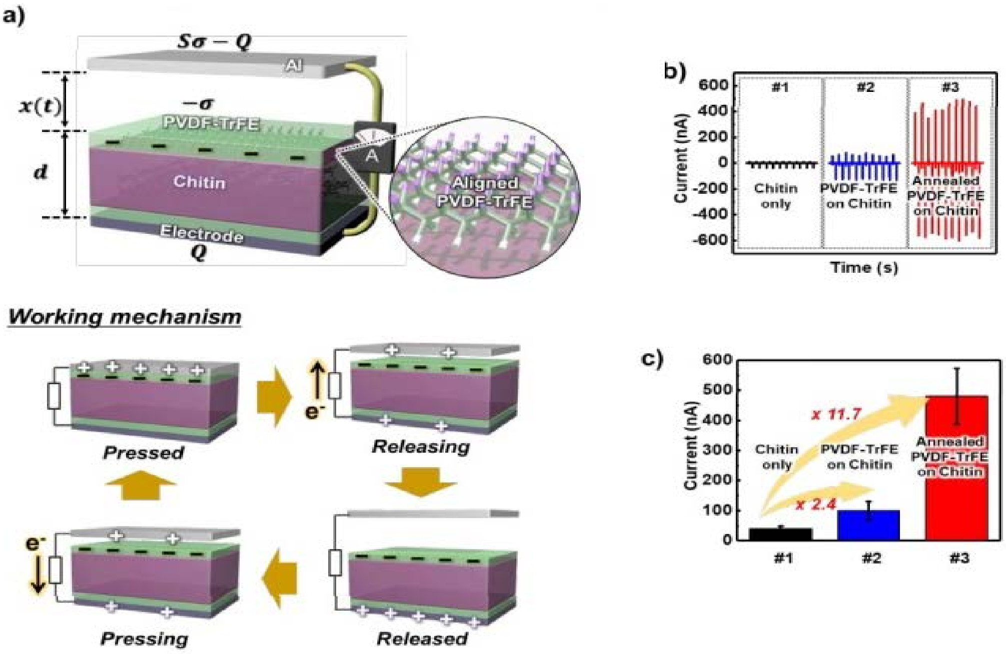

Figure 5. (a) Structure and Working output performance of PVDF-TrFE/chitin triboelectric nanogenerator, (b, c) Triboelectric output current as a function of time with different film-based sensors [Reprinted (adapted) with permission from {102}. Copyright (2020) American Chemical Society].

Kim et al. [103] developed an unconventional diatom frustule embedded chitosan based triboelectric nanogenerator (TENG) with output voltage reached upto 150 V for 0.1% diatom frustule embedded chitosan. In a latest work, Pongampai et al. [104] fabricated triboelectric-piezoelectric hybrid nanogenerator using chitosan-barium titanate ($BaTiO_3$) nanocomposites with enhanced performance by means of self-powered charge pumping mechanism.

4.3. Other Electronic Applications

There are other miscellaneous electronic applications of chitin and chitosan composites including organic light emitting diodes, Schottky diodes, solar cells etc. Lian et al. [105] fabricated organic light emitting diode (OLED) using Cu nanowire/chitosan composite as the anode and obtained the current density and luminance to be higher than the ITO device. Uzun et al. [106] prepared diodes using Al as metal and p-Si as semiconductor with 5-(2,4-dichlorophenyl)-2-furoic acid (C524D2FA) and anthraquinone-2-carboxylic (CA2CA) blended chitosan as interface layers. Al/CA2CA/p-Si diode is found to be more ideal than Al/C524D2FA/p-Si diode and most of other diodes that uses Al and p-Si as metal and semiconductor respectively both in dark and illumination of 100 mW/cm^2. Du et al. [107] prepared flexible organic thin film transistor (OTFT) using Y_2O_3/chitosan thin film as the dielectric gate of flexible OTFT where a P-type semiconductor, poly (3-hexylthiophene) (P3HT) was used as the semiconductor layer on polyimide substrate. In this thin film transistor on/off current ratio was found to be 100 times increased along with the improvement of dielectric properties and low leakage current.

5. Energy Storage Applications

Chitin and chitosan nanocomposites based electrochemical energy storage devices such as solar cells, fuel cells, Lithium-ion batteries, and super capacitors have revealed the applications of chitin and chitosan as a potential materials for sustainable green energy storage devices [108-113].

5.1. Solar Cells

To overcome global energy crisis and huge environmental issues of conventional fossil energy resources, solar energy may be the alternative of fossil energy resources due to its no cost and renewability. As long as sun, there is no problem of harvesting energy from solar energy. To replace silicon based solar cell for its high manufacturing cost and environmental issues, a low cost, stable dye-sensitized based solar cell (DSSC) was developed by researchers.

Buraidah et al. [114] fabricated polymer electrolyte based on chitosan blended with polyethylene oxide powder (PEO) for dye-sensitized solar cells applications. A fixed amount of ammonium iodide (NH_4I) was mixed with chitosan blend. For 16.5 wt% of chitosan, 38.5 wt% of PEO and 45wt% of NH_4I showed highest ionic conductivity of 3.66×10^{-6} S/cm with current density Jsc of 2.71mA/cm^2, open circuit voltage Voc of 0.58V and efficiency 0.78%. Lojpur et al. [115] fabricated a novel electrolyte blend based on Sb_2S_3 with chitosan and polyethylene glycol (PEG).The fabricated electrolyte based solar cell offered efficiencies of 23.1%, 2.9%, 0.75% respectively at intensities of 5%, 35% and 100% Sunlight. Zhang et al. [116] developed efficient cathode interlayer film instead of substrate materials in organic solar cells (OSCs) using chitosan derivatives obtained by electrostatic layer-by-layer self-assemble technique. The film as a cathode interlayer exhibited a power conversion efficiency of 9.34%. Zulkifli et al. prepared phthaloyl chitosan (PhCh) based gel polymer electrolytes (GPE) using dimethyl formamide (DMF), ethylcarbonate (EC) and a mixed composition of potassium iodide (KI) with iodine (I_2) [117]. The maximum ionic conductivity 4.94×10^{-2} S/cm of PhCh based GPE was achieved for the 0.0012 mol of KI: I_2. When the gel polymer electrolyte sample I_2 applied to dye-sensitized solar cells (DSSCs) it showed conversion efficiency of 3.57% with ionic conductivity of 2.08×10^{-2} S/cm, a short circuit current density (J_{sc}) of 20.33 mA/cm^2, open circuit voltage Voc of 0.37 V and fill factor (FF) of 0.65. In another work, Ratan et al. [118] prepared bio-polymer based electrolyte by incorporating succinonitrile (SN) in N-Phthaloyl chitosan. The electrolyte was obtained by using dimethyl formamide (DMF), chitosan, phthalic anhydride, polyethylene oxide (PEO), ethylene carbonate (EC), tetra propyl ammonium iodide (TPAI), iodine and succinonitrile. The incorporation of succinonitrile enhanced conductivity value of 1.30×10^{-2} S/cm at 2 wt% of SN as compared to 7.84×0^{-3} S/cm at 0 wt% of SN at 25°C. The formed GPE showed an overall efficiency of 4.82% with open circuit voltage (Voc) of 0.63 V in dye-sensitized solar cells (DSSCs) applications.

5.2. Fuel Cells

Fuel cells are electrochemical devices which convert electrochemical energy into electrical energy. Proton conducting membrane based fuel cell is a promising alternative to conventional power sources. Chitin and chitosan has been extensively investigated and found as a novel material for primarily microbial fuel cell applications. Dashtimogadam et al. [119] developed a low cost, biodegradable polyelectrolyte membrane by modified chitosan structure by various amount of sulfo succinic acid/glutaraldehyde as a crosslinking agent. The formed membrane showed proton conductivity of 0.04525 S/cm and methanol permeability of 9.6×10^{-7} cm^2 /sec showing a favourable power density of 17 mW/ cm^2 at 30° C and 41 mW/ cm^2 at 60° C in 2M methanol feed. Xiang et al. [120] fabricated polymer electrolyte membrane by crosslinking sulfonic groups of chitosan sulfate with amido groups of pure chitosan monomers. The obtained membrane exhibited the conductivity of 0.03 S/cm at 80°C and observed much lower methanol permeability than Nafion 112. A proton exchange membrane by modifying chitosan were fabricated by Binsu et al. [121] by introducing phosphonic acid group with it and its composite membranes were also formed with variable compositions of polyvinyl alcohol. The obtained membrane showed good proton transport number, conductivity and higher selectivity, lower methanal permeability than Nafion 117. In another research work Hasani-Sadrabadi et al. [122] developed a low-cost, triple layer proton exchange membranes for direct methanol fuel cells applications (DMFCs). The membranes were formed by modifying structure and showed output power density of 68.10 mW/cm^2 at 5M methanol with improved proton transport conductivity and methanol permeability. He et al. [123] architectured a bioanode material with hierarchically porous chitosan and vacuum stripped graphene (CHI/VSG) for high performance microbial fuel cell applications. The formed material showed a maximum power density of 1530 mW/cm^2. Liu et al. [124] on the other hand, prepared a promising proton exchange membrane by chitosan (CS) with silica coated carbon nanotubes (SCNTs). The composite membrane showed higher mechanical properties, proton exchange conductivity than pure chitosan membrane. In another work a chitosan/polyvinyl alcohol based composite membranes with intercalated glycine betaine layered double hydroxides (LDHs) for direct methanol fuel cell applications has been developed by Hu et al. [125].The membrane with 5 wt% LDHs showed ionic conductivity of ~35.7 mS/cm at 80°C and power density of 97.8 mW/ cm^2. Gong et al. [126] developed an anion exchange membrane using modified chitosan/polyvinyl alcohol with layer double hydroxides (LDHs) carbon nanotube which has been considered as a promising membrane material for direct methanol fuel cells. This membranes showed a conductivity of 47 mS/cm with 1 wt% of LDH@CNTs and maximum power density of 107.2 mW/cm^2 with 2M methanol and 5M KOH at 80°C. Li et al. [127] degradated chitin anaerobically by electroactive Aeromonas hydrophila bacteria for energy recovery and used effectively in microbial fuel cells (MFCs) for its faster degradation than fermentation system whereas Vijayalekshmi et al. [128] developed chitosan based electrolyte membrane by doping methanosulphonic acid (MSA) and sodium salt of dodecylbenzene sulfonic acid (SDBS) with crosslinked chitosan. The membranes with 15 wt% MSA showed proton conductivity of 2.86×10^{-4} S/cm at 100°C and conductivity of 4.67×10^{-4} S/cm with 10 wt% of SDBS at 100°C.

5.3. Supercapacitors

Supercapacitors are considered as a dominant components of energy storage devices due to their high charging and discharging rates, high power density and long life [129]. For safety aspects, supercapacitors require biocompatibility along with high power density and high energy density. Chitin and chitosan based supercapacitors have been widely reported recently [130-139]. Zhang et al. [130] prepared hierarchically porous carbon microspheres (HCM) with chitin/chitosan used as a forming agent. The HCM displayed specific surface area of 1450 m^2/g and polyaniline (PANI) were deposited on HCM nanocluster to use it as an electrode material for supercapacitors. In a different work, Zhang et al. [131] prepared nitrogen enriched (N-enriched) carbon nanofiber aerogels (NCNAs) by using Chitin nanofiber aerogels as the precusor. The NCNAs showed high surface area of (490-1597) m^2/g, specific capacitance 221 F/g at a current density 1A/g and high cycling stability with 92% capacitance retentivity after 8000 cycles. In another research paper, Zhang et al. [132] reported the development of 3D nitrogen doped grapheme aerogels (NGAs) by using graphene oxide (GO) and chitosan via a self-assembly process. Furthermore, the NGAs carbonized at different temperature and NGA-900 showed excellent electrochemical performance with a high specific capacitance 244.4 F/g at a current density of 0.2 A/g and excellent cycling stability with 96.2% capacitance retentivity after 5000 cycles. Sunnetha et al. [133] developed Zn doped chitosan nanocomposites modified electrode which exhibited good capacitance and has been considered as a potential candidate for supercapacitor applications. Ba et al. [134] developed nitrogen doped hierarchical porous carbon (NHPC) materials by using chitosan and polyethelene glycol (PEG). The sample obtained (3:2 chitosan, PEG) exhibits high surface area of 2269 m^2/g and optimized pore structure. It exhibits high capacitance of 356 F/g at a current density 1A/g in 1M H_2SO_4 and 271 F/g at a current density 1 A/g in 2M KOH electrolytes. The cycling stability with 94% in 1M H_2SO_4 and 97% in 2M KOH retention after 10000 cycles 1 A/g.

5.4. Li-Ion Battery

Presence of nitrogen within chitin and chitosan structure results in an increase in their conductivity. Between the two, chitosan has been studied extensively for the use as a membrane material for lithium ion battery [140]. Some studies admitted that chitin and chitosan with other materials can be used as a potential binder and also can be used as electrodes, separators and electrolytes for Li/Na ion batteries [141-148]. Zhang et al. [141] prepared advanced sustainable separators for Li/Na ion batteries from chitin nanofiber. However, this separator shows limited performance and applications. To overcome their complicated pore forming process, low ionic conductivity and low mechanical strength, cyanoethyl groups is grafted on the surface of chitin nanofibers [149]. Wu et al. in a different work [144] developed alginate-carboxymethyl chitosan composite as a water soluble binder for Li-ion batteries. This binder exhibits excellent cycling stability with a capacity of 750 mAh/g remaining after 100 cycles. Sustainable 3D crosslinked chitosan-poly (ethylene glycol) diglycidyl ether (PEGGE) based electrolyte gel were developed by Wen et al. [142]. The obtained gel shows excellent Li-ion transportation for Li-ion batteries with mechanical strength 5.5MPa, lithium ion conductivity of 2.74×10^{-4} S/cm and an initial discharge capacity of 146.8 mAh/g with capacitance retentivity 88.49% after 360 cycles. Lee et al. [143] prepared chitosan binder with $LiFePO_4$ electrode and obtained high electrical conductivity with higher discharge capacity of 159.4 mAh/g compared to 127.9 mAh/g (for PVDF binder). The prepared binder also shows higher capacity retention ratio of 98.38% compared to 85.13% (for PVDF binder). Tang et al. [145] developed water based chitosan-oligosaccharide (COS) binder for lithium ion batteries. This binder shows initial discharge capacity of 225.6 mAh/g and 66.1 mAh/g can be obtained after 1000 cycles. Some others reported about cross-linked chitosan with silicon/graphite and cross-linked chitosan with glutaraldehyde for Li-ion batteries [146]. Recently, N-rich biochars via pyrolysis of chitosan in the temperature range 284°C-540°C has been prepared by Nistico et al. [150] The obtained biochars showed a good homogeneity, good capacity retention and improved coulombic efficiency.

6. Conclusions

Chitin and chitosan being 2nd most abundant polysaccharide and having unique combination of properties like biocompatibility, biodegradability, presence of amine and hydroxyl groups, aqueous solubility etc. have become very popular among researchers not only regarding their bio-medical and biochemical applications, but also for advanced electronics and energy storage device applications. Due to the acetyl deficiency, chitosan is a better functional material as compared to chitin. Chitin can be extracted from the exoskeletons of different natural species via demineralization and deproteinization steps which can be performed either by chemical or biological routes. Numerous biosensors for the detection of biomolecules have been developed by the scientists using composites containing chitin or chitosan. In addition to the biosensors various chemical sensors for tracing the toxic chemicals and physical sensors for sensing body movements have been developed by group of researchers using chitin or chitosan composites. On the other hand, energy harvesting devices using chitin and chitosan composites have utter significance in green energy research. In addition to these advanced electronic device applications, energy storage devices like solar cells, fuel cells, supercapacitors or Li-ion batteries have revealed the suitability and better efficiency of composites of chitin and chitosan. Thus, in summary electronic and energy storage devices based on chitin and chitosan composites are ubiquitous, easy to fabricate, cost-effective and environmentally benign in nature for which chitinous composites have become best suited material for green energy and electronic applications.

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