PREPARATION AND CHARACTERIZATION OF BIOAEROGEL-BASED FILTERS FOR PARTICULATE MATTER REMOVAL

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by

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LIST OF ABBREVIATIONS

PM	Particulate matter
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
TEMS	Triethoxymethylsilane
CNF	Cellulose Nano Fiber
CS	Chitosan
FTIR	Fourier Transform-Infra-Red
mL	Milliliter
mm	Millimeter
µL	Microliter
µm	Micrometer
3D	3 Dimensions
MPa	Mega Pascal
NCC	Nano Crystalline Cellulose
Nm	Nano Meter

PEMBANGUNAN DAN PENCIRIAN PENAPIS BERASASKAN BIOAEROGEL UNTUK PENYINGKIRAN ZARAH TERAMPAI

ABSTRAK

Kajian ini memfokuskan kepada pembangunan penapis berasaskan bioaerogel untuk penyingkiran zarah terampai (PM) dari udara, dengan menangani cabaran yang timbul dalam keadaan normal dan lembap. Kaedah penapisan udara semasa sering bergantung kepada bahan sintetik yang tidak terbiodegradasi, mahal, dan cenderung kehilangan kecekapan dalam keadaan kelembapan tinggi. Objektif utama kajian ini ialah untuk mensintesis bioaerogel daripada pelbagai campuran gelatin, kitosan dan nanoselulosa serta meningkatkan prestasi penapisan melalui pengubahsuaian permukaan. Bioaerogel yang dihasilkan telah dicirikan dari segi sifat mekanikal, morfologi dan keupayaan penapisan zarah terampai. Pencirian fizikal menunjukkan bahawa bioaerogel dengan nisbah 60/40 nanoselulosa kepada kitosan memberikan keseimbangan terbaik antara kekuatan, kelenturan, dan porositi, dengan kecekapan penyingkiran PM10 yang mengagumkan sebanyak 98.89%. Untuk meningkatkan prestasi dalam persekitaran lembap, pengubahsuaian permukaan telah dilakukan menggunakan Triethoxymethylsilane (TEMS), yang secara signifikan meningkatkan sifat hidrofobik bioaerogel. Sudut sentuhan air meningkat daripada 49.01° kepada 136.21° selepas pengubahsuaian, menunjukkan peningkatan daya tahan terhadap kelembapan. Pengubahsuaian ini penting untuk mengelakkan penyerapan air yang sering menyebabkan keruntuhan liang dalam bioaerogel yang tidak diubah suai. Analisis FTIR mengesahkan kehadiran kumpulan berfungsi baharu, khususnya kumpulan silana daripada TEMS, yang menyumbang kepada peningkatan sifat hidrofobik. Sifat mekanikal bioaerogel yang diubah suai juga menunjukkan

peningkatan yang ketara. Kekuatan mampatan dan daya tahan bioaerogel meningkat dengan ketara selepas pengubahsuaian, memastikan kestabilan struktur semasa operasi penapisan berpanjangan. Kedua-dua bioaerogel yang diubah suai dan tidak diubah suai telah diuji untuk penapisan udara, dan hasilnya menunjukkan prestasi yang sangat baik. Untuk penyingkiran PM_{10} (menggunakan habuk simen), bioaerogel yang diubah suai mencapai kecekapan penapisan melebihi 99% dalam kedua-dua keadaan normal dan lembap. Ini merupakan peningkatan ketara berbanding bioaerogel yang tidak diubah suai, yang menunjukkan penurunan kecekapan kepada kurang daripada 97% dalam kelembapan tinggi akibat penyerapan kelembapan, yang membawa kepada keruntuhan separa dan penyumbatan mikrostruktur bioaerogel. Begitu juga, untuk penyingkiran PM2.5 (menggunakan asap daripada pembakaran kayu gaharu), bioaerogel yang diubah suai menunjukkan kecekapan penyingkiran sebanyak 82% dalam keadaan normal dan mengekalkan kira-kira 80% kecekapan dalam kelembapan tinggi, manakala kecekapan bioaerogel yang tidak diubah suai menurun dengan ketara kepada kurang daripada 70% dalam keadaan lembap. Kajian ini membuktikan bahawa bioaerogel yang diubah suai pada permukaan memberikan penyelesaian yang mampan dan sangat berkesan untuk penapisan udara, serta mampu mengekalkan prestasi tinggi walaupun dalam keadaan persekitaran yang mencabar.

PREPARATION AND CHARACTERIZATION OF BIOAEROGEL-BASED FILTERS FOR PARTICULATE MATTER REMOVAL

ABSTRACT

This study focuses on the development of bioaerogel-based filters for the removal of particulate matter (PM) from the air, addressing the challenges posed by both normal and humid conditions. Current air filtration methods often rely on synthetic materials that are non-biodegradable, expensive, and prone to performance loss under high humidity. The primary objective was to synthesize bioaerogels from different blends of Gelatin, Chitosan, and nanocellulose, and to enhance their filtration performance through surface modification. The bioaerogels were characterized in terms of their mechanical, morphological, and PM filtration properties. Physical characterization revealed that bioaerogels with a 60/40 ratio of nanocellulose to Chitosan provided the best balance between strength, flexibility, and porosity, exhibiting an impressive PM10 removal efficiency of 98.89%. To improve performance in humid environments, surface modifications were applied using Triethoxymethylsilane (TEMS), significantly increasing the hydrophobicity of the aerogels. The water contact angle of the aerogels increased from 49.01° to 136.21° after modification, indicating enhanced moisture resistance. This modification was crucial in preventing water absorption, which often leads to pore collapse in unmodified bioaerogels. FTIR analysis confirmed the introduction of new functional groups, particularly silane groups from TEMS, contributing to the enhanced hydrophobicity. The mechanical properties of the modified bioaerogels were also significantly improved. The compressive strength and resilience of the aerogels increased notably after modification, ensuring their structural stability during extended

filtration operations. Both modified and unmodified bioaerogels were tested for air filtration, and the results demonstrated excellent performance. Both modified and unmodified bioaerogels were tested for air filtration, and the results were outstanding. For PM10 removal (using cement dust), the modified aerogels achieved an impressive filtration efficiency of over 99% under both normal and humid conditions. This was a significant improvement over the unmodified aerogels, which showed a decrease in efficiency to below 97% in high humidity due to moisture absorption, leading to partial collapse and clogging of the aerogel's microstructures. Similarly, for PM2.5 removal (using smoke from burning smudge sticks), the modified aerogels demonstrated a removal efficiency of 82% under normal conditions and maintained approximately 80% efficiency in high humidity, while the efficiency of the unmodified aerogels dropped dramatically to less than 70% in humid conditions. This study demonstrates that surface-modified bioaerogels provide a sustainable, highly effective solution for air filtration, capable of maintaining high performance even under challenging environmental conditions.

CHAPTER 1

INTRODUCTION

1.1 Research background

Air pollution is any chemical, physical or biological contamination that occur in the indoor or outdoor environment, which alter the natural characteristics of the atmosphere (Martins et al., 2020). This global problem was originated as a result of the natural phenomenon such as volcanic eruption, forest fires, and soil erosion. On the other hand, the human anthropogenic activities such as emissions from burning fossil fuel, industrial wastes, and exhausts gases that contributed significantly in the contamination (Xiao et al., 2021). The expanding air pollution resulted in serious issues related to the environment and human health. Deterioration of human health comes from the pollutants that being consumed by human.

Particulate matter is one of the hazardous pollutants that inhaled by human and causes series health issues (Deng et al., 2019). PM is the tiny matters that are resulted from natural and anthropogenic sources that pollute the atmosphere (Thangavel et al., 2022). Conventionally, PM is classified into two types. The first one is that PM with diameter size below 2.5 μm which known as PM 2.5. The other one is with diameter size between 2.5 to 10 μm which known as PM 10 (Martins et al., 2020). The potential danger of both PM 2.5 and PM 10 comes from the very tiny size which is undetectable by naked eye. So, they are sneaked easily into the human lungs causing respiratory problems. In addition to the respiratory sicknesses, the tiniest parts of PM 2.5 have the ability to penetrate the circular system of human being leading to mortality (Durga et al., 2014).

Treatment of PM is crucial to have clean and safe atmospheric environment. In the early periods of air industrial revolution, filters have been used to purify the atmosphere from PM. Different materials like cotton, wool, jute, and cellulose were used to manufacture air filters (Martins et al., 2020). Jute fiber was used as raw materials for PM filters by (Mandal & Srimani, 1987). The air filters were developed rapidly during the last period of time. Nanoscale polyacrylonitrile fiber was used by (Liu et al., 2020) to create a filter with efficient removal of PM reached 99.996%. Besides, wastes of expanded polystyrene was utilized by (Rajak et al., 2020) to synthesize nanofibrous membranes filters that proved efficiency to remove 99.99% of PM 2.5. Recently, Invention of nanofiber with charged fibres was introduced to capture aerosols with diameter of 100 nm that are considered similar to covid_19 virus (Leung & Sun, 2020). Regardless the efficient results obtained by conventional air filters, there are some limitations related to the toxicity of raw materials and the final fate of air pollutants still concern the researchers (Cusidó & Cremades, 2012).

Aerogel filtration was introduced as a new concept to purify atmosphere that can overcome the limitations. It is a 3D composite that has the ability to capture the PM pollutants since it has unique porous structure. For this reason, it was widely used in synthesizing filters (Zhao et al., 2020). Biomass is usually used as a raw material to composite the aerogel. In this regard, two syntheses methods were reported in literature. The first one is the supercritical drying method which is not preferrable due to the complexity procedures and high costs (Zhao et al., 2020). The other one is widely used since it is affordable and safer which is the freeze-drying method. This method is based on the sublimation principle in which the biomass materials are converted into gel under low temperature and high vacuum depending on the biomass materials (Błaszczyński et al., 2013).

Wide spectrum of biomass materials has been used as raw materials for aerogels preparation in pure and composite formulation. Most of biopolymers are hydrophilic in nature, which require chemical modification before they can be used. Herein, the current research aims to fabricate modified biopolymer nanostructured aerogel able to resist moisture and remove particular matter from the air (Abdul Khalil et al., 2020). Green and cost-effective fabrication and modification processes will be used to ensure the sustainable development goals.

1.2 Problem Statement

The increased population accompanied by the huge development in the civilized industry led to high levels of air pollution. Particle pollution or PM is the pollution made up of particles (tiny pieces) of solids that are in the air (Ysebaert et al., 2021). PM have been reported to form a real danger to the human health since they have the ability to penetrate the human body through respiratory system. Exposure to fine particles can cause short-term health effects such as eye, nose, throat and lung irritation, coughing, sneezing, runny nose and shortness of breath (Kim et al., 2015). Accordingly, removal of PM, or at least reduction, is a necessity for safe environment (Vithanage et al., 2022). For this reason, air filters have been used to capture the PM10 and PM2.5. However, the toxicity of synthetic materials filters still concerns the researchers (Ni et al., 2022). In addition, the management and final disposal of collected PM from air filtration systems present a continuing environmental challenge, as these trapped pollutants often accumulate in the filter media without appropriate treatment or safe disposal protocols. If not properly handled, the retained PM composed of toxic metals, organic compounds, and other hazardous substances can be

reintroduced into the environment, posing risks to soil, water, and air quality, and potentially reversing the intended benefits of the filtration process (Tian et al., 2022).

PM filters industry has tremendous progression. Even though some concerns and challenges are still exited. First of all, the technology that has been used for the existing PM filters is lacking eco-friaerogelendly characteristics since remarkable amounts of solvents and toxic materials are used for electrospinning process that would result in negative influence on human health and surrounding environment (Lv et al., 2019). Moreover, the accumulating discarded filters with high volumes of trapped PM constitute a direct threat for the environment. Beside the toxicity, those PM filters were designed to capture the PM at a small range of concentration which is 1,000 mg within the size of cubic centimeter. In this case, those filters are facing a great challenge to capture PM within the high polluted environments. So, the efficiency of normal filters is questionable (Zhao et al., 2017). Due to its excellent performance, is considered to be a promising new material that can solve many issue associated with the conventional air filtration. Despite the promising advances in filtration materials, a significant gap remains in their practical application, particularly in distinguishing between industrial Air Pollution Control Systems (APCS) and indoor air filtration contexts. Many commercial filters are tailored for limited concentration ranges and controlled environments, making them unsuitable for harsh industrial conditions characterized by high PM loads, fluctuating humidity, and chemical exposure. On the other hand, indoor filters often prioritize breathability and aesthetic form over long-term durability and high-efficiency PM capture. Therefore, it is crucial to develop a bioaerogel-based filter that not only demonstrates high PM removal efficiency but is also adaptable to both APCS in industrial settings and indoor applications. This study

aims to bridge that gap by producing a sustainable, high-performance filter with potential for dual-use in environments with diverse pollution profiles.

Aerogels manufactured using biopolymers, which is a renewable, biocompatible, nontoxic and biodegradable natural materials known to have various advantages over the synthetic based materials such as regeneration, biocompatibility, biodegradability, low density, high porosity, and large specific surface area (Yahya et al., 2021). Currently, there is growing interest in finding inexpensive, abundant, and effective materials as effective air filtration with much focus on natural organic polymers mainly from agriculture. Although natural-based materials are low cost, abundant, eco-friendly, and support proper utilization of waste, their high water and moisture absorption is inferior compared to the efficiency of synthetic materials (Zhao et al., 2020). Their main disadvantages stem from their poor oleophilic/hydrophobic properties.

Aerogel filters are recent approach as a multi-layered porous material to remove the PM pollutants from the surrounding atmosphere. Aerogels were synthesized from natural biomass to have an eco-friendly property but the hydrophilic nature of biomass and most of biopolymers are still a great challenge. Most of prepared biomass aerogels including white protein (Selmer et al., 2015), whey protein (Buggy et al., 2018), starch (Ubeyitogullari & Ciftci, 2016), Arabic gum (Wang et al., 2016), Chitosan (Yin et al., 2020), alginate (Zhuang et al., 2020) and pectin (Groult et al., 2021) are lacking the hydrophobicity, which make the aerogel loos its architecture in high humid conditions. Several researchers aimed to improve the stability and mechanical properties of the biopolymers aerogels by using different chemical modification but this will raise the cost of production and produce non-eco-friendly

material. The current research aims to fabricate aerogel-based filter for PM removal by using biopolymers as precursor materials.

The aerogel will be specifically engineered to possess a pore size of less than 1 μm, a critical structural feature to effectively capture fine particulate matter such as $PM_{2.5}$. By tailoring the pore architecture at the micro- and nanoscale, the aerogel ensures physical entrapment and enhanced surface interactions with airborne particles, thereby improving its filtration performance against ultrafine pollutants commonly found in urban and industrial environments. Eco-friendly modification approach will be applied to the fabrication to increase its moisture resistance and enhance its stability in humid conditions. Multi-layered aerogel filter differs than the conventional mono-layered filters, which can even eliminate the ultra-fine PM along with the fine ones. The entire fabrication approach will be eco-friendly and cost-effective, using biomass as precursor materials.

1.3 Objectives

1) To prepare and characterize bioaerogels utilizing various blends of three selected biopolymers, including gelatin, chitosan, and nanocellulose.

2) To assess the effectiveness of the prepared bioaerogels in the air filtration process, focusing on cement dust particulate matter removal.

3) To modify the hydrophilicity of the bioaerogels through surface chemical modifications to improve their moisture resistance and mechanical properties.

4) To assess the effectiveness of the modified bioaerogel in the air filtration process, focusing on fine particulate matter removal in normal and humid conditions.

1.4 Scope of research

This research consists of two major sections, which are biopolymeric aerogel preparation and particulate matter removal. Firstly, different biopolymers will be used in different concentrations and different combinations for the fabrication of aerogels. The effect of type, concentration of materials and preparation approach on the aerogel properties will be investigated in term of porosity, pore size and pore shape. The aerogels with the desired properties will be selected and echo-friendly modification will be applied to enhance its moisture resistance and underwater stability. Modification process will be limited to the selected aerogel samples, which then will be furtherly investigated for the PM removal. The modified bioaerogel will be investigated for their ability of 2.5 PM removal from a burning smudge stick. Other sources of PM having different sizes will be also tested using transparent chamber.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Air filtration biomaterials have recently become a research hotspot on account of the increasing attention paid to the global air quality problem (Lu et al., 2021). PM is the pollution made up of particles (tiny pieces) of solids that are in the air that may include finely divided solids or liquids such as dust, fly ash, soot, smoke, aerosols, fumes, mists and condensing vapours that can be suspended in the air for extended periods of time (Mack et al., 2019). PM air pollutants result from both natural and anthropogenic sources. Increased concentration of PM on the surrounding atmospheric environment devastates the human health (Almetwally et al., 2020).

Particulate matter has been divided into three different groups; the first group is PM10, which include coarse particles or the relatively large particles. PM10 mostly describes inhalable particles, including those particles with less than 10 micro-meters in diameters (Alfano et al., 2020). The second group is fine particle matter (PM2. 5), which include tiny particles that can cause haziness to the air upon its elevation. PM 2.5 are able to travel deeply into the respiratory tract, reaching the lungs (Thangavel et al., 2022). Exposure to fine particles can cause short-term health effects such as eye, nose, throat and lung irritation, coughing, sneezing, runny nose and shortness of breath (Ćurić et al., 2022). The third group is ultrafine particles (PM0. 1), which have an aerodynamic diameter of around to 0.1 μm (Hachem et al., 2021). Figure 2.1 presents Classification of particulate matter and sources of particles. All the three groups of PMs form a real danger to the human health since they have the ability to penetrate the human body through respiratory system. Therefore, the removal of PM, or at least reduction, has become necessity for safe environment.

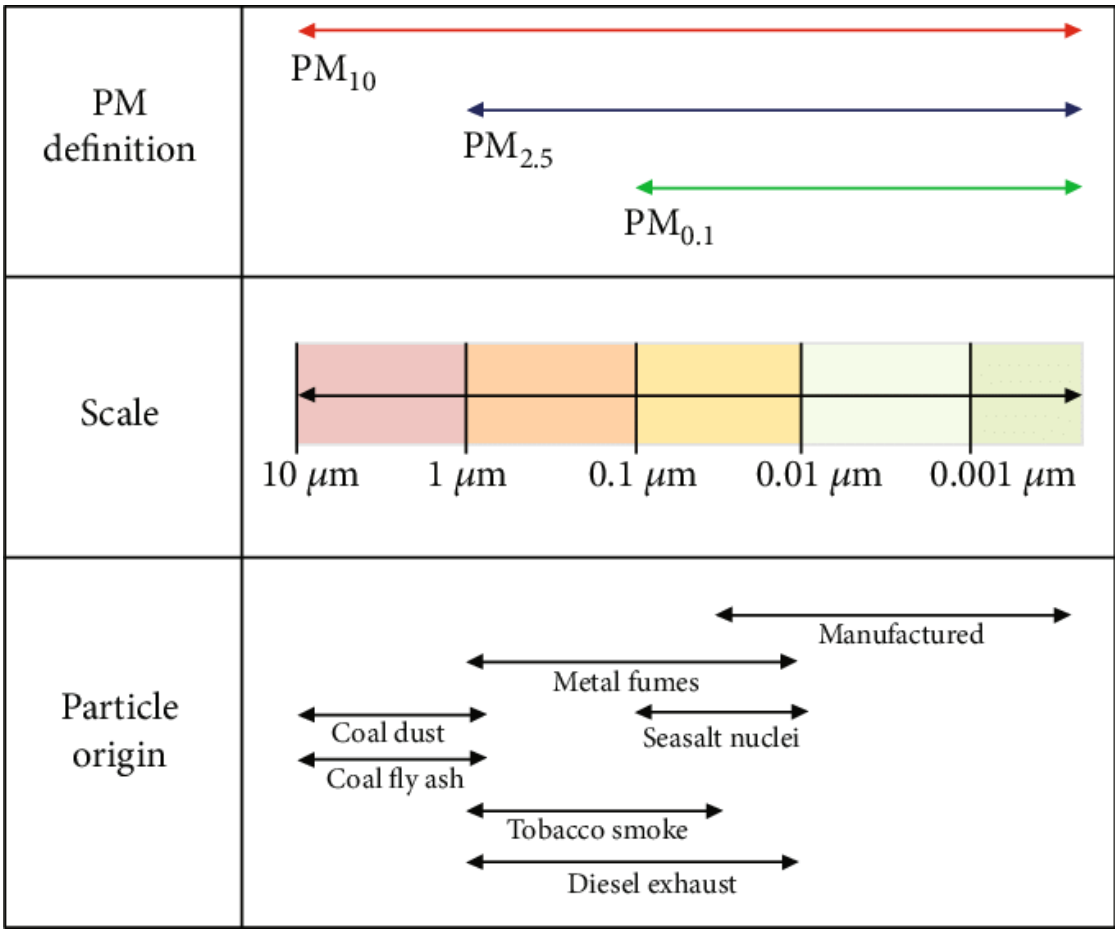

Figure 2.1 Classification of particulate matter and sources of particles. Adapted with permission from (Nurcahyanto et al., 2022)

Air filters have been used to capture different types of PM including PM10 and PM2.5, this industry have tremendous progression in the past few years (Usman et al., 2022). However, the technology that has been used for the existing PM filters is lacking eco-friendly characteristics since remarkable amounts of solvents and toxic materials are used for electrospinning process that would result in negative influence on human health and surrounding environment (Cui et al., 2021). Thus, biopolymer-based aerogels have been proposed for PM filtration as an eco-friendly and sustainable functional materials (Xie et al., 2021a). Bioaerogels are known to have various advantages over the synthetic based materials such as regeneration, biocompatibility, biodegradability, low density, high porosity, and large specific surface area. In the early

periods of air industrial revolution, filters have been proposed to purify the atmosphere from the particulate matter (Tian et al., 2019).

2.2 Biopolymers-based aerogels as functional materials

Biopolymer-based aerogels represent a class of advanced materials derived from natural polymers, characterized by their lightweight, porous structure, and remarkable properties such as high surface area, low density, and excellent thermal insulation (Radwan et al., 2024). These aerogels are synthesized from biopolymers such as nanocellulose, chitosan, and gelatin, which are renewable, biodegradable, and environmentally friendly (Jeong et al., 2024). Due to their biocompatibility and tunable mechanical properties, biopolymer-based aerogels have garnered significant attention for a wide range of applications, including environmental remediation, biomedical devices, energy storage, and filtration (Jeong et al., 2024). By leveraging the inherent characteristics of biopolymers, these aerogels offer a sustainable alternative to traditional synthetic aerogels, with the added benefit of reduced environmental impact. Table 2.1 presents a simple comparison of biopolymer-based aerogel with other inorganic aerogels in terms of the general properties of aerogels.

Table 2.1 Illustration of the general properties of different aerogel prepared from conventional materials

Property	Preparation Method	Mechanical Strength	Key Features	Porosity (%)	Density (kg/m^3)	Surface Area (m^2/g)	Thermal Conductivity (W/mK)	Ref.
Silica Aerogel	Sol-gel process followed by supercritical drying	Low to moderate (fragile without modification)	High thermal insulator, fragile, hydrophobicity can be modified	90-99.8	100-500	500-1000	0.01-0.02	(Chen et al., 2022b; Mazrouei-Sebdani et al., 2021; Zhao et al., 2020b)
Carbon Aerogel	Resorcinol-formaldehyde polymerization followed by supercritical drying	Moderate to high (depends on pore structure and carbonization degree)	Good electrical conductivity, thermal stability, and mechanical strength	80-99	200-800	400-1000	0.01-0.05	(Chang et al., 2023; Lv et al., 2023; Shen et al., 2023)
Polymeric Aerogel	Polymerization of organic monomers followed by supercritical or freeze drying	Low to high (highly dependent on polymer type and crosslinking density)	Flexible, can be made hydrophobic or hydrophilic, diverse chemical functionality	85-99.5	50-300	200-800	0.02-0.03	(Shang et al., 2023; Wang et al., 2023a; Yao et al., 2023; Zhao et al., 2023)
Biopolymeric Aerogel	Gelation of biopolymers followed by supercritical or freeze drying	Low to moderate (depends on biopolymer and crosslinking agent)	Biodegradable, biocompatible, can be used for drug delivery and tissue engineering	80-99	100-600	100-800	0.03-0.05	(Abdul Khalil et al., 2023a; Bakhori et al., 2023; Han et al., 2023; Hu et al., 2023)

2.2.1 Chronological development of aerogels and biopolymers-based aerogels

The development of aerogels began in 1931, when Samuel Kistler, an American scientist, first coined the term "aerogel" and developed the first aerogels through a pioneering process (Abdusalamov et al., 2023). Kistler's goal was to create a solid material with the lowest possible density by replacing the liquid component of a gel with air, without causing the gel structure to collapse (Griffin et al., 2023). He achieved this by inventing a supercritical drying method, which allowed the liquid in the gel to be removed under specific conditions where the liquid could transform directly into gas without passing through a liquid-gas interface (Griffin et al., 2023). This process resulted in a highly porous, lightweight material that retained the gel's original framework, marking the birth of the first silica-based aerogels.

For several decades, the primary focus remained on silica aerogels due to their remarkable properties, including their ultra-low density, high surface area, and exceptional thermal insulation (Li et al., 2023). Silica aerogels found applications in various fields, including insulation for space suits and spacecraft, as well as in scientific research for capturing cosmic dust particles (Karamikamkar et al., 2020; Lin et al., 2021). However, despite their impressive characteristics, silica aerogels had limitations, such as fragility and brittleness, which restricted their broader application (Karamikamkar et al., 2020). During the mid-20th century, researchers began to explore alternative materials and methods to overcome these limitations, leading to the development of aerogels made from other inorganic materials, such as alumina and titania (Liu et al., 2024b). These efforts expanded the potential uses of aerogels, but challenges related to mechanical strength and production costs persisted.

The late 20th century witnessed a paradigm shift with the advent of organic and hybrid aerogels, which combined organic polymers with traditional inorganic materials

(Sheng et al., 2023). This development was driven by the need to enhance the mechanical properties of aerogels while maintaining their desirable low-density and porous structure. The introduction of polymeric aerogels, particularly those based on resorcinol-formaldehyde and polyurethanes, provided a more flexible and mechanically robust alternative to purely inorganic aerogels (Koçyigit, 2023). These materials retained the thermal and acoustic insulation properties of traditional aerogels while offering greater durability and processability, making them suitable for a wider range of industrial applications.

As the 21st century dawned, the focus of aerogel research began to increasingly shift towards sustainability and environmental impact, leading to the emergence of biopolymeric aerogels (Abdul Khalil et al., 2020). Biopolymeric aerogels are derived from natural polymers such as cellulose, chitosan, gelatin, alginate, and starch, which are abundant, renewable, and biodegradable. The development of biopolymeric aerogels represents a convergence of material science and environmental consciousness, aiming to create materials that not only exhibit the superior properties of traditional aerogels but also align with the principles of green chemistry and sustainability (Yahya et al., 2020). This shift was motivated by growing concerns about the environmental footprint of synthetic polymers and the desire to reduce reliance on non-renewable resources. Table 2.2 presents an illustration of the chronological development of aerogels.

Table 2.2 Chronological development of aerogel as functional materials

Year	Types of Aerogels	Precursor Material	Preparation Method	References
1931	Silica aerogel	Sodium silicate	Supercritical drying	(Kistler, 1931)
1932	Organic & Metal oxides Aerogels	-Metal oxides –Organic compounds	Supercritical drying	(Kistler, 2002)
1950	Hydrophobic silica aerogels	Single and combinations of metal oxides with silica	Silylation with trichloro-methyl silane to produce water repellents	(Bheekhun et al., 2013)
1968	Sol-gel route silica aerogel	Single and combinations of metal oxides with silica	Sol-gel route replaced water glass with TMOS & removed at supercritical condition	(Bheekhun et al., 2013)
1974	Sol-gel route silica aerogel	Single and combinations of metal oxides with silica	Sol-gel route silica aerogel	(Poelz and Riethmüller, 1982)
1989	Organic and carbon aerogels	Organic polymer	Sol-gel route silica aerogel	(Pekala, 1989)
1992	Low density & high porosity silica aerogel	Single and combinations of metal oxides with silica	Acid-base process & substitution of the alcohol with an aprotic solvent	(Tillotson and Hrubesh, 1992)
1996	Silica aerogel	-Metal oxide -Organic polymers	Developing rapid supercritical extraction (RSCE)	(Roth et al., 2008)
1997	Ultralight aerogels or X-aerogels	-Metals -Organic polymers	Crosslinking di-isocyanates into the silica structures inside the aerogels.	(Leventis et al., 2002)

2006	Cellulose-based aerogels	Cellulose derivatives	Nontoxic iso-cyanate, via the sole gel route, with a tin-based catalyst.	(Fischer et al., 2006)
2008	Cellulose nanofibres (CNF) aerogel	Cellulose nanofibres (CNF)	Facile vacuum drying of aqueous CNF gel.	(Pääkkö et al., 2008)
2009	Metal aerogel	Metals, Organic & polymers	Smelting interpenetrating of resorcinol-formaldehyde and iron oxide xerogels	(Leventis et al., 2009)
2012	Cellulose nanowhisker foams	Fully bleached commercial softwood Kraft pulp	Prepared via a freeze casting method	(Dash et al., 2012)
2014	Aerogel Based Plasters	Silica + natural plaster	Granular silica aerogel mixed with natural plaster in different percentages	(Buratti et al., 2014)
2015	Nanocellulose aerogel with water absorbency & shape recovery	Cellulose nanofibrils	Crosslinking of CNF by the reaction between the C–C double bond of maleic acid-functionalised CNF & hypophosphite.	(Kim et al., 2015)
2016	Superhydrophobic and ultralight cellulose-based aerogel	Cellulose-based aerogel	Novel physical-chemical foaming method, plasma treatment, and silane modification	(Zhang et al., 2016)
2018	Low-cost method of silica aerogel	Fly ash and trona ore	Ambient pressure drying technique	(Wu et al., 2018)
Current	Biopolymer-based aerogels with unique properties	Several bioresources depends on the type of biopolymers	Materials with superior properties for wide range of applications	Current

2.2.2 Preparation of biopolymers-based aerogels

In recent years, there have been notable developments in developing various forms of aerogels, such as biomass-derived, inorganic carbon-based, polymer-based, and silica-based aerogels, among others (Mariana et al., 2022). Aerogels can be made from a wide range of materials, and the properties of the aerogel depend on the material used (Khalil et al., 2022). However, the absence of unique characteristics in a single material restricts the versatility of many pure aerogels. As a result, composite aerogels offer a solution for numerous potential applications by allowing for the enhancement, introduction, and development of new materials for a variety of new uses. The past few years witnessed the development of several techniques for the fabrication of biopolymer-based nanostructured bioaerogel. But all of these techniques follow the same basic principle of gelation of polymeric suspension, ageing, and finally drying (Abdul Khalil et al., 2020). Figure 2.2 presents the basic principle of bioaerogel fabrication.

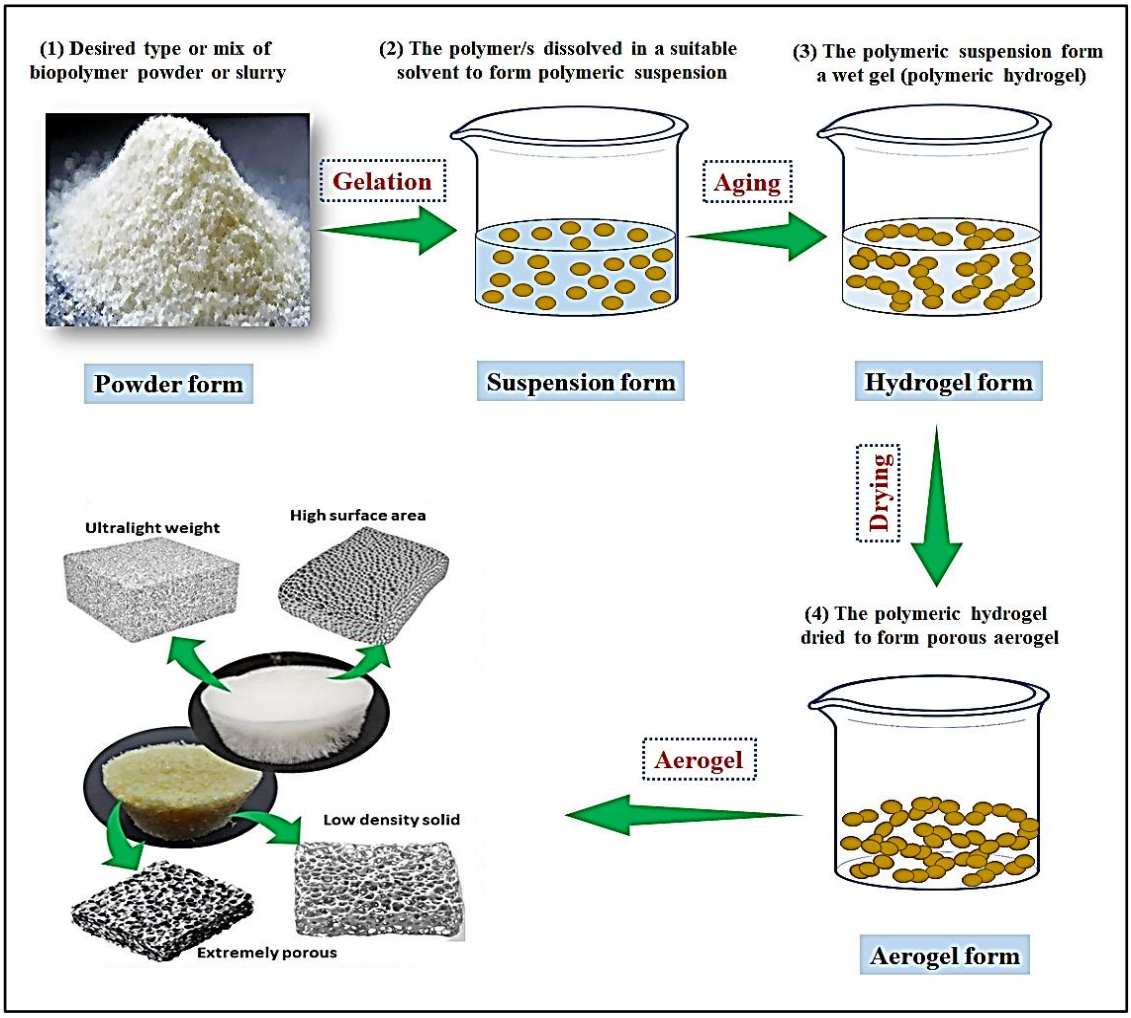

Figure 2.2 Illustration of the basic principle of nanostructured bioaerogel fabrication

Aerogel with different properties can be obtained by varying the precursor material/s and/or the parameters of these three steps (Barrios et al., 2019; Khalil et al., 2022). The unique properties of nanostructured bioaerogel arise from the extraordinary flexibility as well as resilience of the sol–gel process to form the polymeric wet-gel, followed by drying stage. Drying of the wet-gel (hydrogel) is critical process that affect the properties of the material, different drying method has been reported to give different form of materials; supercritical and freeze-drying mostly result in the formation of hydrogel (Darpentigny et al., 2020; Rizal et al., 2021a), while ambient drying produce xerogel (Niu et al., 2019).

In the gelation phase, dissolution of the biopolymer/s in the solvent occurs, which then led to network formation (cross-linking) in the second phase in the aging process., which is critical to form homogenous nanostructured aerogel (Owens et al., 2016). Some biopolymers are able to directly form networks in the gelation phase such as chitosan and gelatin, while other biopolymers like cellulose require the addition of curing factors or cross-linker/s to form the network (López-Iglesias et al., 2020; Onwukamike et al., 2019). Finally, removing of the solvent is known as drying phase, which is referred to as gel–aerogel transition (Iswar et al., 2017).

Freeze-drying, also referred to as lyophilization, is a process where solvents within a gel are frozen using various cooling agents such as a refrigerator, dry ice, or liquid nitrogen, at temperatures of −20 °C, −78 °C, or −196 °C, respectively (Wu et al., 2019). Once the gel is frozen, the solidified solvent undergoes sublimation, which removes it from the gel matrix. The key factors that influence the final pore structure and surface area of the resulting aerogel are the temperature, rate, and direction of freezing. These parameters control the crystallization rate and growth direction of ice within the gel (Simón-Herrero et al., 2016). A slower freezing rate typically leads to the formation of larger ice crystals, resulting in a macro-porous structure, whereas a faster freezing rate promotes a more uniform pore size distribution within the mesoporous range. Additionally, the freezing direction has a significant impact on the length, orientation, and interconnectivity of the pores. The process can be carried out using either directional or non-directional freeze-drying methods, as illustrated in Figure 2.3(a–d). Directional freeze-drying is generally preferred because it allows for control over the ice growth direction, which produces a unidirectional, anisotropic pore structure (Figure 2.3(e–f)). This unidirectional structure is beneficial for applications requiring enhanced water flux. On the other hand, non-directional freeze-drying results

in aerogels with randomly oriented pores, as shown in Figure 2.3(b–c), which are less favorable for high water flux applications. However, one of the limitations of the freeze-drying process is that during the growth of ice crystals, cracks may form, and the cryogel structure may experience shrinkage, which can compromise the structural integrity of the aerogel (Gurav et al., 2010; Paul and Ahankari, 2023).

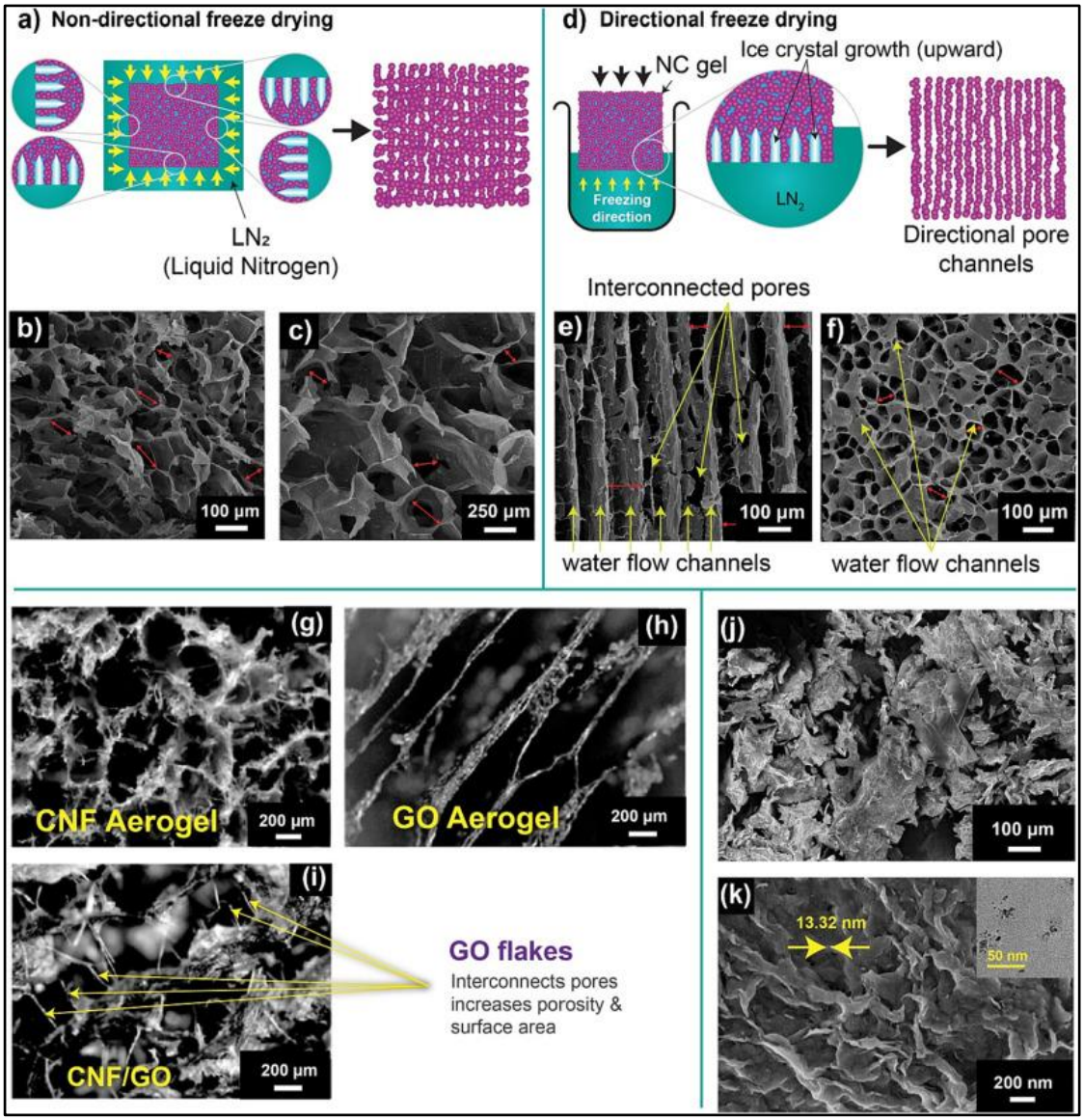

Figure 2.3 Directional freezing and ice crystal growth in aerogel. (a) Unidirectional freezing of NC gel. (b–c) Cross-sectional and vertical sectional SEM image of directional freeze-dried CCMA aerogel, respectively. (d) Refrigeration (non-directional) freezing o gel. (e–f) Cross-sectional and vertical sectional SEM image of non-directional freeze-dried CCMA aerogel, respectively (Rong et al., 2021). SEM images of (g–i) CNF, GO, CNF/GO aerogels, respectively (Nguyen et al., 2021). (j–k)

FESEM image showing broken 3D channels of DNC-CMC and presence of Bentonite nanoparticles, respectively (Sharma et al., 2020).

The fabrication techniques of nanostructured aerogels can be divided into two categories; conventional techniques which includes freeze-drying (Chen et al., 2019), gas foaming (Mi et al., 2019), phase separation (Liu et al., 2019), and electrospinning (Pirzada et al., 2020). These techniques are extensively discussed by Abdul Khalil et al (Khalil et al., 2020). The recent years witnessed developing of faster and computer-aided techniques able to professionally design the properties of the nanostructured aerogels. These techniques are known as rapid prototyping techniques, which includes 3D printing (Kam et al., 2019), fused deposition modelling (Saoud et al., 2018), selective laser sintering (Zhang et al., 2021b), and Stereolithography (Tang et al., 2019). These techniques offer facile fabrication without the need for any complex tools or equipment where the biopolymer/s are used as ink (bio- injected ink).

The properties of aerogels such as porosity, shape, pore size and volume as well as mechanical properties can be all adjusted by varying the ratio of the precursor materials and changing the preparation conditions (Muhammad et al., 2023). Such type of fabrication techniques is referred to as rapid prototyping techniques, due to its easiness compared with traditional techniques. Moreover, using the computer in mixing the precursor material also helped in determining the optimum combination of each hybrid, in addition to the control of physical, morphological and mechanical properties of the aerogels (Chia and Wu, 2015). Table 2.2 highlighted the main differences between traditional and advanced bioaerogel fabrication techniques.

Table 2.3 Comparison between conventional and advanced bioaerogel fabrication techniques

Functionality	Conventional techniques	Rapid prototyping techniques
Time consuming and computer-aid	Consume longer time, without computer aid	Rapid fabrication with computer-aid
Easiness and Manpower requirements	Require more manpower	Minimize manpower required
Aerogel homogeneity	Difficult to obtain homogeneous structures	Easier to obtain homogeneous structures
Accurate controllable properties and aerogel shape	Relatively unspecific	Highly specific
Aerogel porosity and pore shape	Random and irregular pores shape	Highly regular and interconnected pores
Aerogel toxicity	Depending on the technique (more toxic)	Less toxic in some techniques
Production costs	More expensive, consume more materials	Consume minimum materials, generally low cost of production

2.2.3 Properties of biopolymers-based aerogels

Nanostructured bioaerogels are special type of porous materials that possess unique properties depending on the precursor material/s. These aerogels are typically made from polysaccharides like cellulose, starch, chitosan, alginate, and pectin, which are abundant and renewable sources of materials that can replace petroleum-based products (Bernardes et al., 2021). Due to their abundance, biodegradability, regeneration, and sustainability, bio-aerogels are gaining popularity and are being

developed as a replacement for traditional aerogels (Guastaferro et al., 2021b). These aerogels also have been reported to possess remarkable air-purifying properties (Idumah, 2021). However, the mechanical properties of bio-aerogels require improvement, and there is potential for further exploration of their ability to adsorb PM2.5 (Abdullah et al., 2022).

Although natural-based materials are low cost, abundant, eco-friendly, and support proper utilization of waste, their high water and moisture absorption is inferior compared to the efficiency of synthetic materials (Abdullah et al., 2022; Maleki and Huesing, 2021). Their main disadvantages stem from their poor oleophilic/hydrophobic properties. In order to improve these characteristics, combined technology including sol gel technique and also plasma treatment for achieving hydrophobic biopolymeric aerogels is hypothesized to be stable in water and to have higher capacity for PM removal especially in humid condition (Zhao et al., 2020c). The specific properties of the aerogels will depend on the type of biopolymer used and the preparation method employed.

2.2.3(a) Nanocellulose-based aerogels

nanocellulose aerogel has several unique properties, it has an extremely low density, which makes it one of the lightest solid materials available (Chen et al., 2021). Its density typically ranges from 0.01 to 0.5 g/cm^3, which is much lower than most other materials (Zhu et al., 2018). Owing to its nanopores, nanocellulose aerogel has an extremely high surface area per unit volume. Nanocellulose aerogel has excellent thermal insulation properties, making it useful as a building insulation material or as a protective coating for industrial equipment (Nguyen et al., 2021). Despite its low density, nanocellulose aerogel has been reported to have high mechanical strength and can withstand significant compression without breaking, in addition to highly water

absorption due to its porous structure (Liu et al., 2022a). This property makes it useful in various applications such as water treatment, where it can absorb contaminants from water.

Cellulose based aerogel, a highly porous nanostructured material, display the typical features of aerogels with many advantages. In previous study, (Zhang et al., 2018) compared the morphological structure of each of cellulose nano fiber and cellulose nanocrystals aerogels individually and in different mix ratios as presented in figure 2.4. They reported that mixed (CNC and CNF) aerogel showed better performance than the pure aerogel for each of them. However, all the aerogels that they prepared had 3D network structure and rich pores are formed by the disorder of the ice crystals growing. It can be observed in the obtained SEM figures that there are some differences in the morphology; CNC based aerogel is spherical in shape while the CNF based aerogel showed rice-shape, which resulted from the longer filament of CNF compared to CNC.

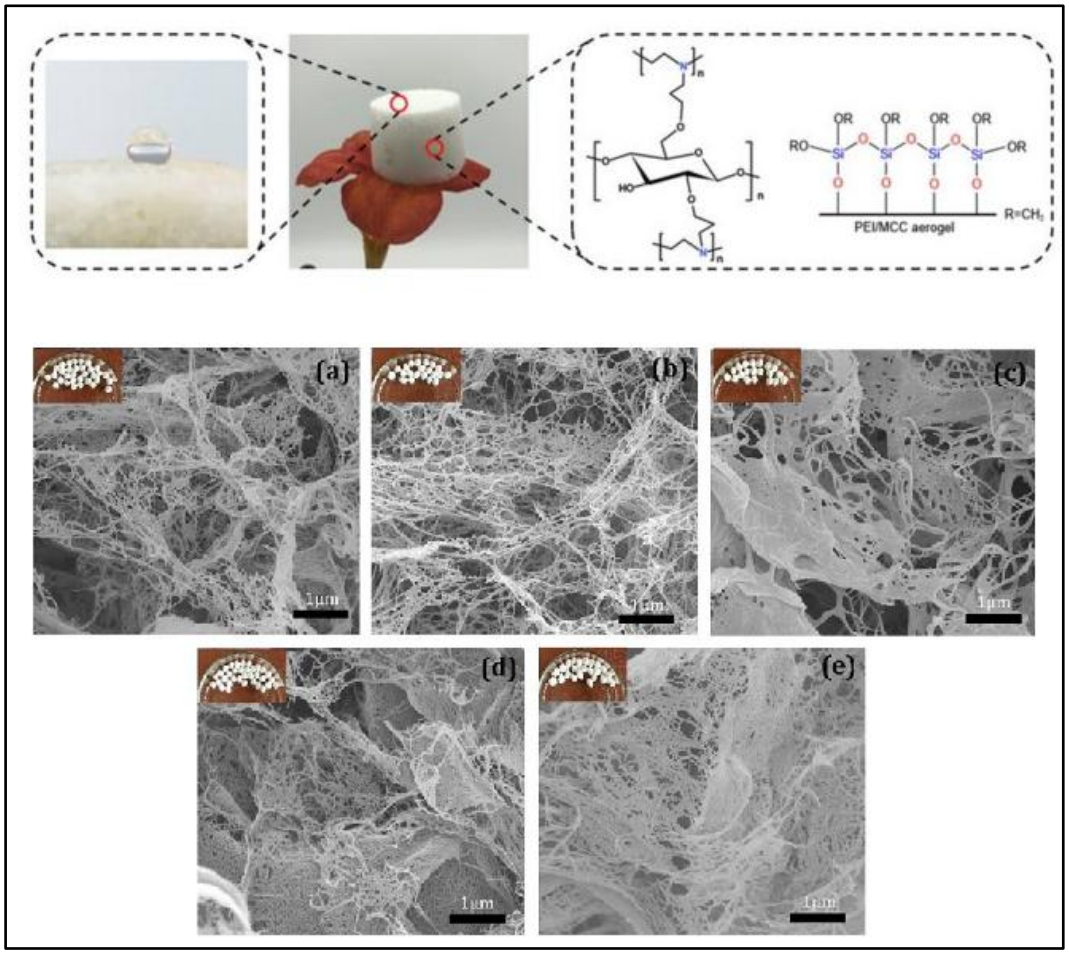

Figure 2.4 SEM images of aerogels prepared using different ratios of cellulose nanocrystals (CNC) and cellulose nano fibers (CNF): (a) CNC/CNF (3:1), (b) CNC/CNF (1:3), (c) CNC/CNF (1:1), (d) CNC, (e) CNF. Adapted from Zhang, et al. (2018) with permission from Elsevier (Zhang et al., 2018)

2.2.3(b) Chitosan-based aerogels

Chitosan aerogel has been reported to have high porosity, typically in the range of 80-99% depending on the concentration and preparation approach. Takeshita et al. (Takeshita et al., 2021) reported that the porosity of aerogel determined by its preparation method and can be controlled by adjusting various factors such as the concentration of chitosan, the type and concentration of crosslinking agent, the solvent used, and the drying method. Despite its high porosity, chitosan aerogel has good mechanical strength and can withstand compression without breaking (de Luna et al., 2019). Chitosan aerogel also was reported to have good thermal insulation properties due to its low thermal conductivity in addition to moderate antimicrobial properties,