Processes and Methods for Creating New Types of Personal Protective Gears

A Major Qualifying Project Report
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Advisor, Professor Balaji Panchapakesan (WPI)
Graduate Student and Assistant Lab Manager, Aref Aasi (WPI)
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Executive Summary

In light of the global pandemic caused by Covid-19, personal protection from airborne threats such as viruses and bacteria has become desired more than ever before. Our Major Qualifying Project (MQP) group has recognized this demand with the guidance of our advisor, Prof. Balaji Panchapakesan. Identifying this problem, the focus of the project became focused on creating a piece of personal equipment that could effectively protect individuals from these threats. Based on our research, we also believed this to be an excellent opportunity to explore a material called carbon nanotubes, specifically single walled for their favorable properties. Upon further discussion, it was determined that the scope of our project was to design and develop a piece of personal protective equipment that incorporates single walled carbon nanotubes (SWCNT) as the effective filter.

Viruses are particles that contain genetic material (RNA or DNA) with a protein coating. To replicate, they require living cells and destroy them once finished. If cells are infected, it can lead to disease and pose a great threat to humans and other living beings. Viruses can be spread through the air or through contact of surfaces. The coronaviruses are about 0.1µm in size while other viruses can vary from 0.042 to 0.65 µm. These small particles can enter the human body through the eyes, nose, and mouth. To stop this, personal protective equipment such as masks and respirators are the most effective at keeping these dangerous particles from entering the most susceptible areas of our body. Research has found that carbon nanotube filters are greater than 95% effective at stopping particles of that size since their pore size is approximately 600 nm in diameter. Carbon nanotubes are also great conductors of heat and electricity and maintain their structure under UV light making sanitization a possibility.

In order to design this personal protective equipment, SWCNTs needed to be synthesized. To achieve this, our team performed a simple vacuum filtration technique to deposit SWCNT suspended in isopropyl alcohol onto a PTFE membrane. This simple process was adjusted and modified several times throughout the duration of the project in efforts to successfully synthesize the films. Unfortunately, we were unsuccessful in synthesizing the films. This is a procedure that has not been perfected yet and in hopes that someone will continue our work, we have added some suggestions for future work in this paper.

Several concepts of design were finalized and designed upon including nose pieces and integrated face masks. Since masks require a level of flexibility and CNT filters need to maintain rigidity, we decided on a nose piece the direction of design. Taking into account how the design would impact the user's experience, we concern ourselves with decisions such as material selection, number of uses to withstand, the number of parts in its final assembly and how they are to be secured to the user. Thermoplastic polyurethane was decided as the ideal material for its elastic nature to ensure comfort of the user while being durable and easy to manufacture.

Integrating the CNT filter was a design challenge that we believed to be crucial in the success of this project. Once in use, the CNT filter would be exposed to constant oscillating force produced from the user's breath. We explored heat bonding and adhesives as viable options and suggested further testing on both method's tensile strength.

Finally, although we were unsuccessful in synthesizing the CNT filters, we wanted to address potential areas of improvement for future work not only in the CNT synthesis process but in other aspects of the project as well. Modifications to our synthesis process were suggested in addition to proposing other methods such as a CN-Parylene membrane fabrication process. Had we successfully created the filters, we would have tested them and classified them. Some of the tests included UV light/heat/electricity exposure, gold particle filtration, and live virus filtration. We also believe that if this product is to be adopted by the public, they will need to be manufactured on a large scale. We suggest investigating the feasibility of injection molding.

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1.0 Introduction

In late December 2019, a novel strand of coronavirus called Covid-19 was discovered in Wuhan, China. It quickly spread to nearby countries and eventually spread around the world creating a global pandemic. In the height of this global pandemic, it was realized that personal protective equipment (PPE), such as face masks, is crucial to the slowing of spread of the virus. The effectiveness of different PPE varied greatly from cloth coverings to tested N95 masks. Current PPE can cause ear irritation from the elastics or cause glasses to fog during exhaling. Now, over a year later, we are still struggling to control and prevent the spread of this deadly virus and need effective PPE.

Our goal is to design a new type of PPE that is highly effective at filtering and combating the spread of Covid-19 while at the same time solving some of the issues associated with current masks. In our research, we found that a material called carbon nanotubes (CNT) is highly effective at filtering particles. CNTs have been applied in a variety of applications because of their favorable thermal, electrical, and mechanical properties.

Given the issue at hand, our team wanted to synthesize our own carbon nanotube films and then incorporate them into our designed PPE. We explored different types of PPE such as nose pieces and integrated face masks that are discussed later in this project. Special consideration for the consumer’s comfort, safety, convenience, etc. were focused on during the design of the PPE housing for the CNT film. The general concept remains that the PPE would force all inhaled and exhaled air through a CNT film that would filter any viruses or bacteria from the breath.

We found it important to acknowledge the unique circumstances we faced as a project team due to the limitations caused by COVID-19. At the beginning of both Fall 2020 and Spring 2021 semester, the WPI campus did not allow visitors in the labs. Due to this constraint and other external factors, our project's timeline was delayed, and only limited results were obtained. We understand that this project may be revisited and therefore have included an extensive section discussing our group's vision for future work.

2.0 Background

The COVID-19 pandemic has had a vast impact on our daily lives, and while the situation is unique to most of us, these sorts of outbreaks are by no means new. There have been many viral epidemics in the past, and while most have not reached the magnitude that the current situation has, they often follow many similar patterns. Understanding the driving forces behind these outbreaks will give us a much better idea of how to prevent them.

2.1 Viruses

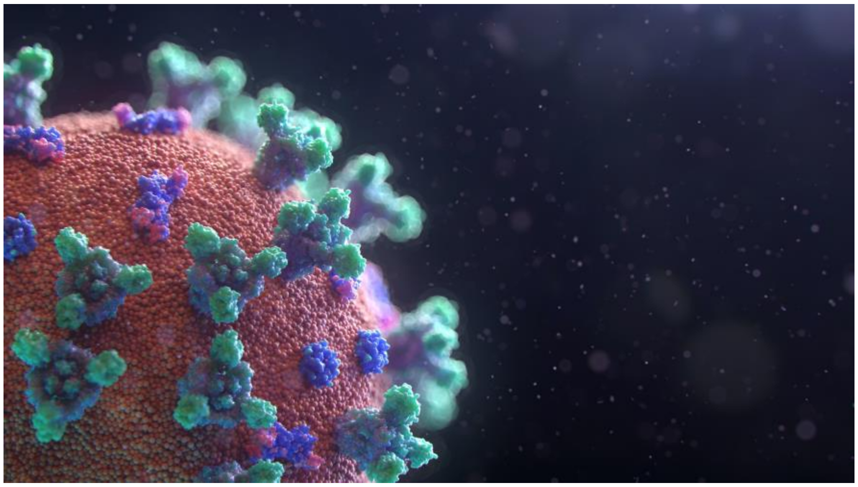


Figure 1: Animation of a Virus Particle [1]

Viruses, also called virions, are particles that contain genetic material (RNA or DNA). According to an article by Sally Robertson in 2020, the nucleic acid core which holds this genetic material is contained in a protein coat [2]. Virions require living cells to replicate. Once virions enter the body, viral receptors on the exterior of the virion enable them to enter the cells of the body through a process called endocytosis [2]. The virion then releases the genetic material contained in its protein envelope, called a capsid [3]. Once inside the cell's cytoplasm, the genetic material replicates within the cell, causing it to produce more virions [3]. These newly formed virus particles - identical to that which entered the cell - are released from the cell and free to infect more cells [3]. The host cell may or may not die in the process once the new virions are released. If it does not, the host cell continues to produce the virions [3]. These particles, once inside the body, can cause numerous immune responses, ranging from a cough, sore throat, fever, and body ache [4].

These miniscule particles can have detrimental effects on the human population. Viruses, and the illnesses associated with them, have impacted the world throughout history. In Marseille, France in 1720, the bubonic plague ravaged the French population, resulting in 40,000 to 60,000 deaths [5]. Additionally, throughout the world, there were outbreaks of cholera in 1817 [6] and influenza in 1918 [7]. This trend of a devastating epidemic or pandemic every one hundred years has continued into the twenty-first century with the COVID-19 pandemic.

2.1.1 Why is it an issue?

The human body contains trillions of microbes, or microorganisms such as bacteria [8]. These microbes are beneficial in many ways and have a profound benefit in the gastrointestinal tract. According to an article by the National Center for Biotechnology Information, "...microbes synthesize vitamins, break down food into absorbable nutrients, and stimulate our immune systems”. [9] Though these microbes can be beneficial in most situations, some can cause illness and can even be fatal.

The five main categories of microbes include viruses, bacteria, fungi, protozoa, and helminths [9]. Viruses can infiltrate the body and cause catastrophic effects. However, infection does not always lead to disease. Only a small portion of the total infected population will develop a disease in response to being infected [9]. Viruses replicate within the cells of the human body. This begins to damage the cells of the body and causes the immune system to respond. This response is ultimately what causes the symptoms of a given disease. Once the virus, a foreign particle, is inside the body, the immune system is activated and tasked with removing those particles [9]. Immune responses are what cause the common symptoms of illness such as fever and headache [9].

The symptoms of each virus can vary, leading to different diseases. For instance, COVID-19, caused by the SARS-CoV-2 virus, has been documented to cause shortness of breath and difficulty breathing in those infected [10]. This attack on the lungs can lead to pneumonia and even death, as seen by the 2.43 million deaths caused by COVID-19 in less than a year (as of February 18th, 2021), according to the Johns Hopkins University of Medicine Coronavirus Resource Center [11].

Viruses can have significant negative impacts on not only those infected, but as well as the entire population, as seen in recent times by mandatory lockdowns to stop the spread of COVID-19. The world has experienced the depredation that viruses can cause to the human population in the year 2020. The SARS-CoV-2 virus has caused a “new normal” for the human population, including face masks, social distancing, and virtual learning for academic institutions. While viruses cannot be eliminated from the world, efforts can be taken to protect human beings from the devastating effects that viruses can cause.

2.2 Spread of Virus Through the Air

Microbes can spread at exceptional rates due to the availability of international travel. This poses a risk of an accelerated spread as those traveling may not know they are infected if they are not actively showing symptoms. According to the National Center for Biotechnology Information, approximately 2 million people travel internationally each day [9].

Viruses can spread through a variety of methods such as physical contact with the virus, interaction with animals and transmission through the air.

2.2.1 Contact

Viruses and other microbes can be spread via direct and indirect contact with an infected person. Direct contact is defined as physical contact with the virus. For example, this can include the spread of sexually transmitted diseases, as well as contact with cold sores of a person infected with herpes. Indirect contact includes contact with a surface that has recently been used by an infected person [9].

2.2.2 Interaction with Animals

Animals are also capable of spreading potentially fatal diseases to humans. For instance, mosquitoes can transmit malaria and other diseases to humans [9]. Zoological transmission of viruses has been observed recently with the SARS-CoV-2 pandemic. A report by Kevin Kunzmann (2021) states that the virus that causes COVID-19 can be traced back to bats and pangolins, prior to exposure to humans [12].

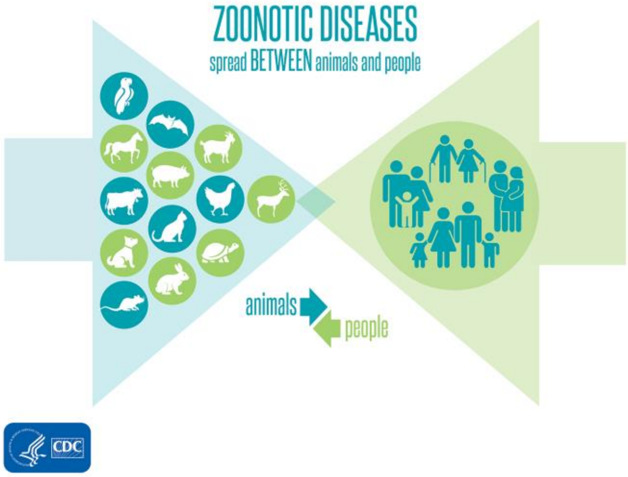


Figure 2: Animal to Human Transmission

2.2.3 Airborne Transmission

Common symptoms of viral infections include sneezing and coughing. This enables the virus to be expelled from the infected body and potentially infect a new host. Even while talking, droplets can be introduced into the air that contain viral particles. Airborne transmission occurs when a microbe such as a virus can suspend in the air on droplets or particles. If a person were to come into contact with those particles, they could enter the healthy host through their eyes, nose, and mouth. Once inside, the virus is capable of replicating and causing disease [9].

The most recent airborne virus that has impacted millions is SARS-CoV-2 [13]. Evidently, limiting the spread of viruses by airborne transmission is essential to preventing another pandemic.

2.2.4 Size of Common Viruses

The following chart contains the diameter of common viruses:

Virus	Size (µm)
Coronaviruses (including SARS-CoV-2) [14]	0.1
Ebola [15]	0.08
Influenza [16]	~0.1
Hepatitis [17]	0.042
HIV [18]	0.145
Meningococcal [19]	0.650

Figure 3: Table of common virus sizes

2.2 Personal Protective Equipment

PPE in the medical field is regarded as one of the most effective methods to prevent the spread of airborne viruses. PPE refers to any equipment or clothing that will protect the wearer from harmful elements in their work environment. In medicine, these elements are mainly chemical or biological hazards, such as the transmission of pathogens. Health workers are required to wear PPE as a precautionary measure, for their own safety and for the safety of their patients. Medical PPE items include nitrile gloves, fluid-resistant gowns, shoe coverings, hair caps, face masks/respirators. Face masks and respirators are crucial to defending the eyes, nose, and mouth, which are the most vital areas to protect against infectious agents.

2.2.1 Existing Face Masks

The most effective and widely used form of PPE that is used to combat airborne viruses is the medical face mask. Masks are frequently used by medical personnel when in a more sterile environment but are commonly employed in many countries to prevent viral spread. These efforts have shown to be effective. In 2002, during the first wave of the severe acute respiratory syndrome (SARS) pandemic, Toronto's healthcare environments were the outbreak locations for 59.5% of all the cases [20]. Healthcare workers were required to wear N95 respirators, but these were only used during contact with patients. Workers who had less experience wearing these masks showed increased signs of stress. Additionally, individuals quarantining at home were required to wear a smaller surgical mask when near others. Those who conducted this study suggest that less restrictive mask use could control the spread of SARS by means of respiratory droplets [20]. Another study in 2004 found that there was a 70% reduction in risk of contracting SARS that could be associated with the use of face masks as viral protection [21]. The masks act as a physical barrier between to stop larger droplets containing the virus from passing through. However, the effectiveness of this barrier is largely determined by the material from which the mask is made. The most commonly used variation of surgical masks is the 3-ply surgical mask. This design consists of two outer layers designed to catch moisture in the air, with a central layer acting to catch airborne pathogens of a certain size that try to pass through [22]. Masks such as these have experienced widespread use during the COVID-19, typically being made of disposable materials such as paper. The 3 fabric layers are nonwoven materials, which means they've been either spunbond or melt blown. These two processes involve melting polymers to be formed into a fabric material. An example of a fabric made from this is felt.

The 3-ply mask is not the only form of facial PPE used to defend from viruses. More advanced masks have been developed to combat airborne viruses with greater efficiency. One such example is the N95 surgical mask, generally used to protect medical workers from particularly contagious diseases. N95 masks have a particulate filtration efficiency of 99.9%, rendering them amongst the most effective masks available [22]. Their material is a similar synthetic mesh made through melt blowing. Heavy duty masks like this have been shown to cause increased stress based on the capabilities of the wearer. For example, in a study done in 2004, it was reported that workers spraying pesticides and wearing N95 masks experienced increased heat stress due to humidity and higher temperatures within the mask [23]. Additionally, masks of this caliber are not available for mass distribution, and the COVID-19 pandemic has led to a shortage of these masks.

This has led to an increased production of masks made from simpler materials, as well as the creation of masks from household goods. While not providing the same level of protection as their surgical counterparts, most simpler masks still provide a degree of protection to the wearer and are far better than wearing nothing [24]. These masks generally contain a nonwoven polymer layer, but the outer layers are simply cloth, and are often made without water resistant materials. Cloth or homemade masks also provide the benefit of reusability. In a time where facial PPE is used daily by most of the population, it is necessary to be able to decontaminate and reuse masks when possible. Masks can generally be decontaminated at home using heat or pressure [22]. The ease of the cleaning process has made these masks commonplace during the COVID-19 pandemic. All forms of medical face masks serve to protect the wearer from airborne pathogens to some degree, and while they are the most common way to protect one’s mouth and nose, they are by no means the only method.

2.2.2 Existing Nose Filters

Albeit less common than medical face masks, nose filters have been used frequently as a means of filtering airborne particles. Although the nose itself acts as a filter, the mucus and nose hairs only stop 80% of particles larger than 12.5 μm [25]. This means that viruses and most airborne allergens can pass freely into the body. Nose filters have seen use for this issue, primarily for seasonal allergies, such as pollen. Some current nose filters have the ability to catch particles larger than 8 μm, which can successfully filter smaller types of pollen. The material used for the shell of these filters is a soft medical grade silicone, and the filter itself is polypropylene with an adhesive. These filters were reported to significantly reduce nasal symptoms in patients when used in an outdoor environment [26]. However, there was no reduction in the oral symptoms experienced by these patients. Filters used for these purposes are also considered to be comfortable. In a 2016 study, it was found that most patients who used the nose filter outdoors for a prolonged time expressed interest in using them again [27]. The filters have yet to see widespread use amongst patients, but the results of the study indicate their potential as a marketable product. Currently, nose filters alone have never been used or adequately tested as a method of airborne viral filtration. While the comfort of the filters should not be an issue, it remains to be seen if nose filters alone will be able to adequately filter airborne viruses.

2.3 Carbon Nano Materials

Carbon is a unique element that has 4 valence electrons that allows it to polymerize at the atomic level and form very long chains connected by single, double, or triple covalent bonds [28]. These properties allow the carbon to take on various allotropic modifications including Graphene, diamond and the newest discovered, CNTs. Materials in general are categorized as "nano" if their particles are between 1 and 100 nm in size [28]. These materials are made of carbon nanoparticles and must be man-made and possess numerous favorable characteristics such as material strength, electrical conductivity, thermal insulation, and other electrochemical properties. For this project specifically, CNTs possess excellent filtration characteristics which are discussed in the section below.

2.3.1 Carbon Nanotubes

Discovered in 1991 by the Japanese researcher S. Iijima, CNTs are a specific carbon nanomaterial that are cylindrical shaped in structure [28]. They are formed by rolling a flat sheet of graphene into a cylindrical shape that is one carbon atom thick held together by sp2 bonds [29] in a ‘honeycomb’ lattice structure. There are two main categories that carbon nanomaterials can take on: single wall CNT or multi wall CNT [29]. From [28], “SWCNTs are composed of a 1–2 nm diameter closed graphite tube rolled (seamless) from an individual graphite sheet, whereas MWCNTs are the product of the “Matryoshka”-like nesting of multiple individual graphite cylinders with diameters typically ranging from 2 to up to 25 nm and a gap between tubes similar to the interlayer spacing in graphite of approximately 0.34 nm”. For the purpose of this project, SWCNTs will be used and created using the vacuum filtration technique described by Lu and Panchapakesan [30]. Once these SWCNTs are created, they will have tensile strength between 50 and 200 GPa which is approximately one order of magnitude greater than that of carbon fibers making it one of the strongest known materials [31]. It is also measured to have fracture strains between 5% and 20% and an elastic modulus value on the order of 1 tetrapascal or 1000 GPa. CNTs were chosen for this project because of how their closely packed particles make them effective filters, electrical conductivity allows the flow of current which can kill bacteria. In addition, these materials are very light and strong which allows them to easily be applied to personal protective equipment.

2.3.2 Feasibility of CNTs as Antiviral Surfaces

With the assistance of Prof. Panchapakesan, it was realized that CNT films have the potential to be used as an antiviral surface that can filter small particles such as bacteria and viruses. Given the dangers posed by viruses, the ease of transmission, and the relevance to the global pandemic that has existed for over a year at the time this was written, it was determined CNT antiviral surfaces could be a viable option to protecting people from SARS-CoV 19 and other potential viral threats. This section discusses research that supports our theory and demonstrates the feasibility of using CNTs as antiviral surfaces.

In general, the materials and filtration performance of CNTs have been researched and there is substantial data available. Using the vacuum filtration, the nanotubes are deposited onto a filter producing either Single-wall or multi-wall CNTs. The most common filters are fibrous usually made from cellulose, glass, or polymer fibers [32]. Multi-wall carbon nanotubes (MWCNT) have proven to filter airborne particles at a 99% efficiency [32]. The vacuum filtration process also orients the tubes perpendicular to the direction of filtration and therefore airflow when implemented in some sort of housing which maximizes the tube's surface area to the airflow. Ultimately, the filter's performance will be determined by the porosity and distribution of pore size [32]. Compared to the independent Cellulose filter's 73.89% efficiency, the MWCNT filters have a porosity of 93.58% and pore sizes of ~600 nm and a narrow mesopore distribution [32]. This evidence suggests CNTs will be effective at filtering particles and should be explored further.

Due to the unique material properties of Carbon Nanotubes, there are other potential advantages to using them as particle filters. Research indicates that the protective protein membrane of SARS-CoV can be denatured and become inactive by heating at 56°C for at least 20 min or applying UVC (200–280 nm) for up to 6 minutes at a distance of 3cm as seen in Figure 4 [33]. If the SWCNT is effective at trapping and filtering viruses through airflow which appears to be true as previously discussed, sterilization of the filter can be achieved with UVC light or heat given the strong conductance and heat transfer properties of SCWNTs. This is particularly appealing to consumers and environmental groups who want to limit the incurred costs and the amount of waste created.

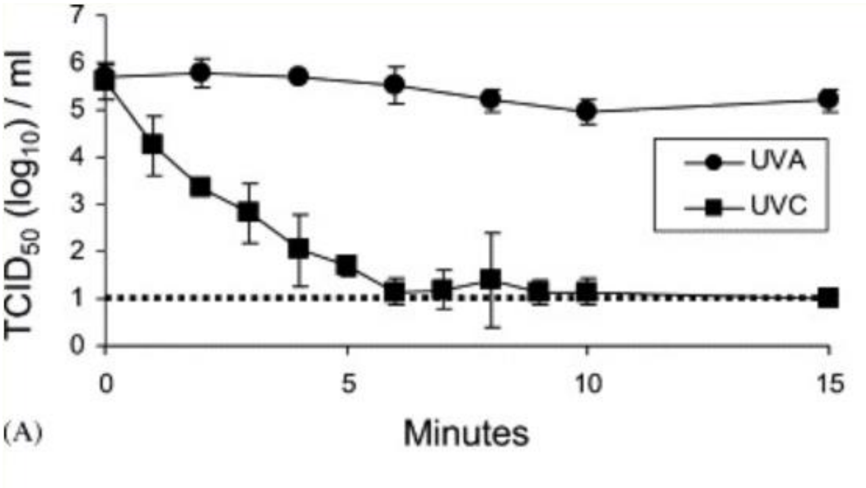
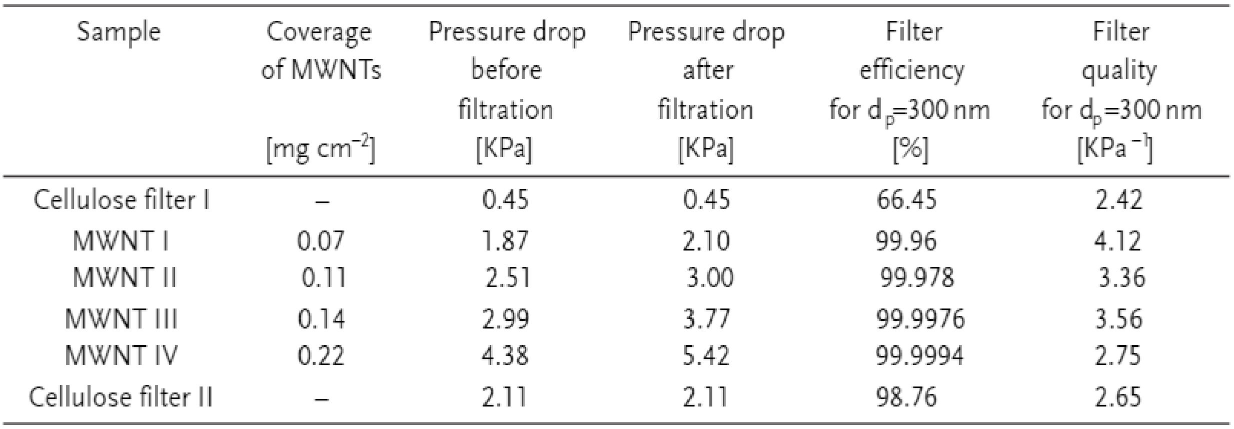


Figure 4: UVC light's ability to deactivate viruses over time [33].

One concern of ours is the potential restriction of airflow through the filter. The pressure drop across the filter is used to quantify the airflow restriction. The laminar flow within the filter yields direct proportionality between the face velocity and pressure drop [32]. It can be expected as the thickness of the filter and the density of CNTs increases, the airflow is more restricted resulting in a larger pressure drop across the filter. As seen in Figure 5, research indicates that pressure drops of at least 1.42 kPa (0.21 PSI) can be expected through MWCNT filters. SWCNT will likely produce smaller pressure drops and therefore of particular interest for the direction of this paper.



Sample	Coverage of MWNTs [mg cm^{-2}]	Pressure drop before filtration [KPa]	Pressure drop after filtration [KPa]	Filter efficiency for d_p=300 nm [%]	Filter quality for d_p=300 nm [KPa^{-1}]
Cellulose filter I	–	0.45	0.45	66.45	2.42
MWNT I	0.07	1.87	2.10	99.96	4.12
MWNT II	0.11	2.51	3.00	99.978	3.36
MWNT III	0.14	2.99	3.77	99.9976	3.56
MWNT IV	0.22	4.38	5.42	99.9994	2.75
Cellulose filter II	–	2.11	2.11	98.76	2.65

Figure 5: Characteristics of cellulose filters and MWCNT coated filters [32]

Another research team has started to investigate the integration of a CNT membrane into garments. They suggest the benefits of this integration include an effective barrier against biological threats in addition to breathability [34]. Their work suggests that even though the CNT pores are a few mm wide and have a porosity of less than 5.5%, the water-vapor transport rates of these CNT membranes is greater than commercial breathable fabrics [34]. As proof, they exposed the membranes to 3 nm charged dyes, 5 nm uncharged gold (Au) nanoparticles, and 40-60 nm Dengue virus and all three resulted in complete rejection suggesting complete rejection of any particles greater than or equal to 5 nm in size.

In addition to the Dengue virus proving to be stopped but CNT membranes, other viruses and bacteria have been tested. One team leveraged the unique electrochemical properties of CNT to apply the concomitant electrolysis effects in hopes of killing the virus bacteriophage MS2 [35]. After applying 2 and 3 V of electric potentials, they found that no culturable viruses were detected in the effluent [35]. As promising as that sounds, there is a possibility that viruses absorbed by the MWCT filters could be released if used over an extended period of time. To demonstrate the effects of electrolysis, Figure 6 shows E. coli bacteria breaking down at 1V, 2V, and 3V of applied electrolysis and how they compare to bacteria without any electrolysis applied.

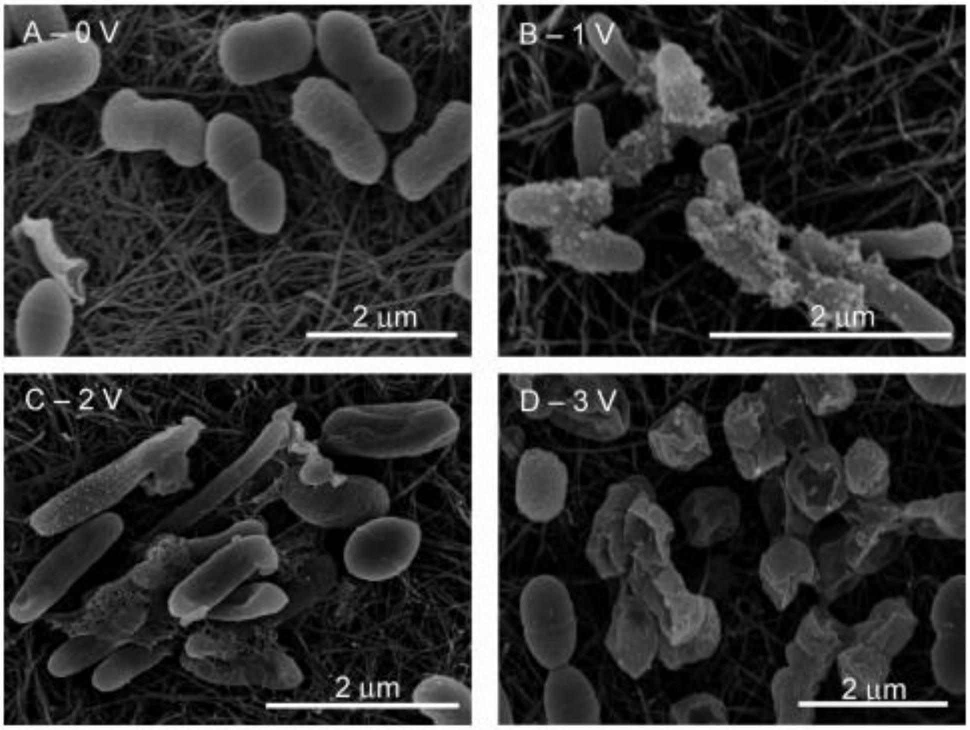


Figure 6: Breakdown of E. coli at various voltages [35]

Virus interaction with non-CNT materials has also been researched. Warnes et. al. have performed a study exposing human coronavirus 229E to polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), ceramic tiles, glass, silicone rubber and stainless steel. They found that the virus remains infectious for at least 5 days when exposed to these surfaces [36]. various copper alloys also explored. They found that the copper broke down the viral genomes and disintegrated the envelope [36]. As seen in Figure 7, copper can deactivate the virus in under 60 min [36]. Other alloys like copper nickels, proved to eventually deactivate the virus but required a copper concentration of at least 90% to produce an equivalent degree of inactivation that was measured with brasses containing 70% copper [36]. Figure 7 shows that when exposed to an adequate level of copper, the viral genome is fragmented to the point where the RNA is unable to replicate and therefore renders the inactivation irreversible [36].

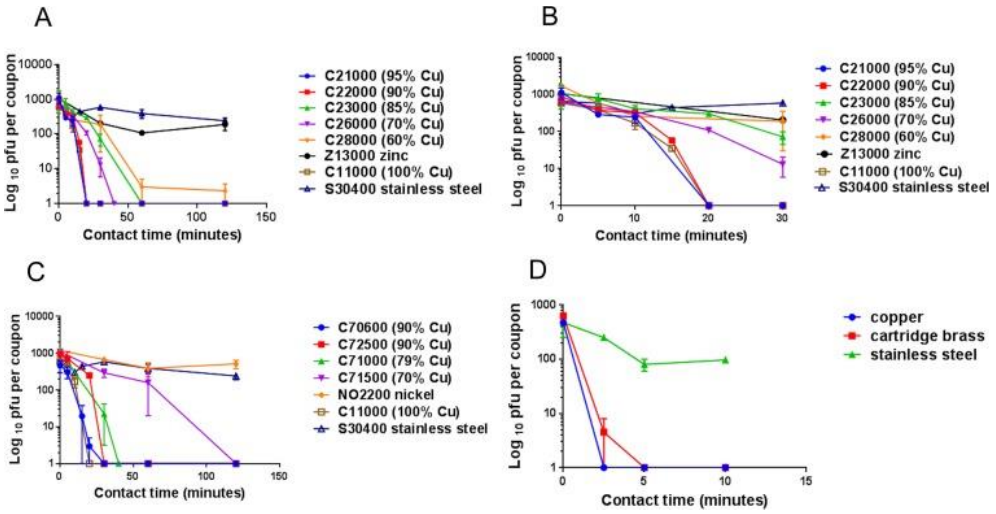


Figure 7: Different metal compound's ability to deactivate virus' genome over given time [36].

All this research has led our team, with the assistance of our advisor Balaji Panchapakesan, to investigate SWCNTs and their applicability to personal protective equipment (PPE). Research has shown that SWCNTs can cause viruses to deactivate and ultimately prevent the virus from spreading.

2.3.3 CNT Synthesis Using Vacuum Filtration

Vacuum filtration, shown in Figure 8, is one method that is used to synthesize SWCNTs. The process is simple in nature and involves few steps. A solution is poured into a cup with an open bottom. At the base of the cup, a membrane or filter collects the solid matter suspended in the solution above in the cup. Below the membrane/filter, a vacuum is hooked up perpendicularly to create a negative pressure below the membrane and force filtration to occur. Finally, a flask catches all liquid that passes through the membrane below. The apparatus set up can be seen below. Specifically, for our carbon nanotubes, research suggests that once the vacuum filtration process is completed, the surfactant residuals are washed and then removed, followed by exposure to heat to promote van der Waals forces [37]. Finally, the membrane should be placed on the glass substrate and purified to dissolve the membrane.

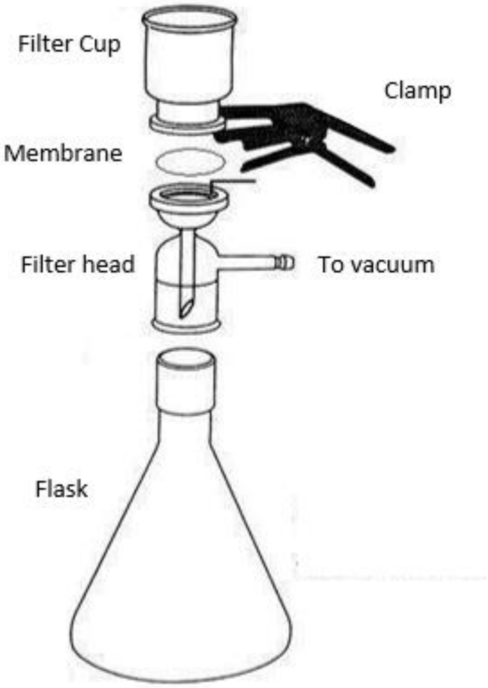


Figure 8: Diagram of the vacuum filtration method

3.0 CNT Filter Synthesis Process

The Carbon nanotubes that would be implemented into the designed nose piece were synthesized using a vacuum filtration method. Under the guidance of Prof. Panchapakesan and his two graduate students, the following procedure was conducted.

First, the SWCNT compound made of 16mg of small diameter, super purified, SWNTs (HiPco) [38] produced by Nano Integris was combined with 100 mL of Isopropyl Alcohol (IPA). This solution was then sonicated for 20 hours minimum to decompose the SWNTs and suspend them in the IPA. Upon completion, the vacuum filtration apparatus was set up and a membrane was placed below the funnel above the porous plate. Throughout the duration of the project, various membranes were used and are outlined below. The membrane was pre-wet with ~10mL of IPA.

The IPA used to prewet the membrane was left to filter for about 5 minutes or just until the IPA had been fully filtered. Just before finishing filtering the IPA, the CNT solution was poured into the funnel and left to filter. As the solution filtered, the suspended CNT material was deposited onto the membrane. The membrane with the deposited CNT was either removed from the apparatus and washed in IPA followed by DI water or it was subjected to 100mL of IPA followed by 100 mL of DI water in the vacuum filtration process. The final step is to let the membrane/CNT dry and then separate the two species. This process was varied from trial to trial and expanded upon below in addition to the other modifications made throughout the trials:

- Membrane
    - Option 1: Fluoropore hydrophobic 220 nm membrane
    - Option 2: Omnipore hydrophilic PTFE 220 nm membrane [39]
- Prewet
    - Option 1: 100 mL of IPA
    - Option 2: 10 mL of IPA
- Washing
    - Option 1: 100mL of IPA then 100 mL of DI water through Vacuum filtration
    - Option 2: Wash the membrane with the deposited filter in IPA bath followed by DI water bath.
- Dry and separation
    - Option 1: Dry at 80 ℃ in a curing oven for 2 hours and then separate from the membrane using tweezers.
    - Option 2: Air dry at ambient temperature with microscope slides placed on the edges to prevent curling. Use tweezers to separate the slides.
    - Option 3: Immediately after washing, Separate the CNT film and membrane.

*Pictures of the experiment can be seen in Appendix A.

4.0 Experiment and Design

The primary objective of our project was to create a new form of PPE utilizing CNT filters. However, the specific type of PPE we wanted to design was largely ambiguous during the project's initial phases. Given the properties of CNT as a material, it was determined that integrating the filters into a face mask would prove a challenge. Masks need to have some level of flexibility, whereas the CNT filters needed to maintain rigidity to be effective. Our group deemed that the best way to implement these filters in PPE would be through nasal filters. Integrating the filter into a nose plug would allow the filters to maintain their shape while still offering advanced protection to the wearer.

4.1 Nose plug design

The design of our nose piece had begun as an individual assignment between our group. Collectively we decided to draft our first ideas individually to give us a larger variety of prototypes to work on. We believed this was the best process because we each planned on researching slightly different aspects of the final product. Throughout the design process of our product we had many questions arise; What materials should the nose plug consist of? Will the final product contain multiple parts or one solid structure? How many uses can one nose plug withstand? Each of these questions were answered differently within each design giving us different pros and cons as to why each specific design should work the best. The four designs each have their own advantages as to why it would be a feasible solution, as well as their disadvantages towards failure.

The first question to answer was which material would work best for our needs. We needed a polymer that had the properties like that of a human tissue, and that can rapidly recover from deformation with little to no hysteresis [40]. Specifically, we needed a class of polymers classified as elastomers; such that could be either 3D printed, or injection molded (the two methods of manufacturing chosen for this product) [41]. These decisions were based on developing a product that could be worn without any discomforts, the filter needs to feel as if it is not even there. After further research, we found that the material that best fit our requirements was one classified as a thermoplastic polyurethane (TPU). TPUs are ideal due to its thermoplastic and elastic natures that are necessary for both the manufacturing aspect as well as the product's durability. Diving deeper into the world of TPUs, we learned of a specific class of TPUs would better suit our needs, Polycarbonate-based polyurethane silicone (PCU-Sil), which is developed by co-polymerizing silicone with polycarbonate-urethane [40]. Our decision to move forward with PCU-Sil was supported by the properties that make this material ideal; Pure silicones lack the mechanical integrity needed for specific devices, however, copolymerization with polycarbonate-urethane preserves thermoplastic properties while providing improved mechanical properties including softness and stretchability, synergistic improvements in biocompatibility, and reduced susceptibility to metal ion oxidation. All these properties are needed to fulfill our needs for manufacturing, as well as the outcome of our product and its active lifetime.

The next step in our design process was to consider the overall difficulty in manufacturing. Will these products be developed best as a single solid structure, or will they perform best with several moving parts? We have decided to move forward with production using 3D printing methods due to the current state the world is in from coronavirus and how much it has impacted the industrial sector across the globe [42]. Additionally, this was our preferred method of manufacturing given our time frame, and we made the best of it due to its extreme accuracy and use of remote production. Within our three designs, the dimensions and shapes are very precise and obscure. 3D printers handle these situations with ease allowing us to focus more on the design, rather than manufacturing. Individually we came up with four designs to test and evaluate to decide upon moving forward with and creating a physical prototype.

4.1.1 Nose Block Filter

One of our initial designs, as seen in Figure 9, was modelled after a micro CPAP device (Continuous Positive Airway Pressure) [43]. This device, used for sleep apnea, consists of a base with two silicone nose pieces [43]. The CNT filter would be inserted into the base, filtering viral and other airborne particles. The silicone inserts would provide comfort for the user, while providing a secure fit. However, this design was not pursued, as it was too large and would be an inconvenience for the user.

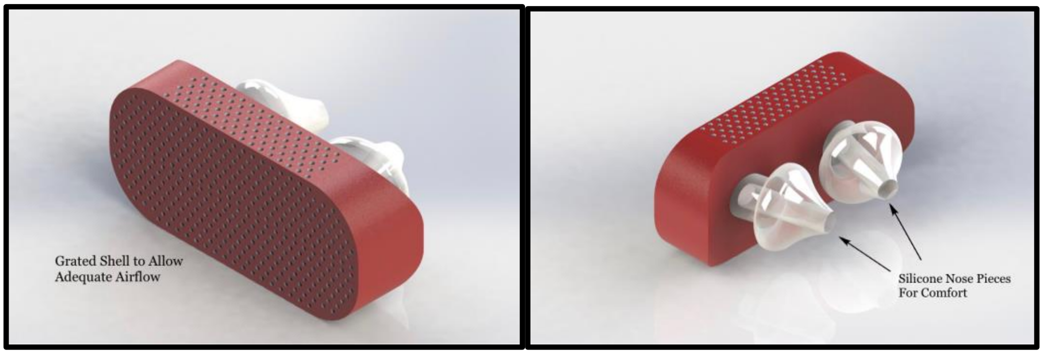


Figure 9: Nose block design.

4.1.2 Single Nostril Clips

Another design that we proposed was inspired by the clip of a clicking ballpoint pen. In this design, shown in Figure 10, the SWCNT film would be glued or heat pressed to the base (side with the smaller diameter) of the piece and sandwiched between two supportive ventilation grates. The ventilation grates hole sizes were designed to provide the necessary support to the SWCNT film during breathing while permitting sufficient airflow. The user would wear separate pieces in each nostril. The piece would be secured to the nose with friction created from the thickness of the nostril applying stress and causing strain to the arm.

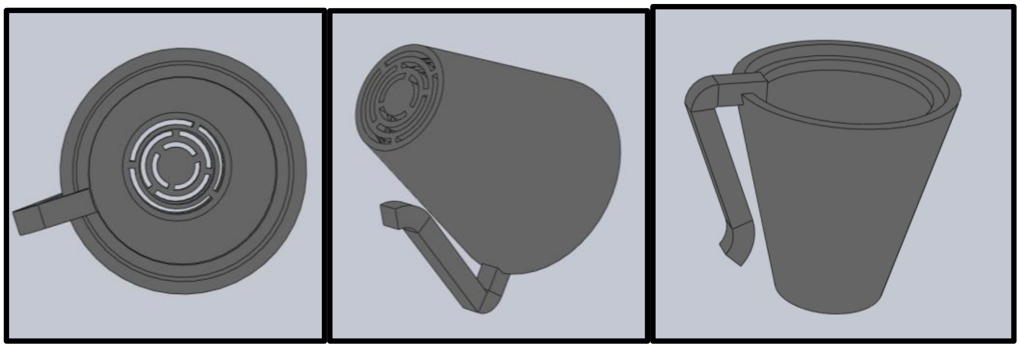


Figure 10: Single nostril plug design.

4.1.3 Face mask with Integrated Nose Filter

Since current nose filters in the market are ineffective against airborne viruses, we proposed a method that would utilize a nose piece and a mask together. The wearer’s mouth would remain exposed with only the nose filter but combined the effectiveness could exceed a standard mask. Such a design would be capable of utilizing any of our previous nose filters, or a simpler version designed to provide less invasive protection. The filter would be attached to a cloth mask with pronounced curvature around the nose, enabling a filter to be housed there, as seen in Figure 11. Considering the nature of the product, the upper material across the bridge of the nose would need to remain partially flexible to deform around an individual's facial structure, but other nearby material would need to be stiff to securely hold the nose piece. For cleaning purposes, the nose piece could be removed from the mask, and its filters could be easily replaced. Creating a mask that incorporates these components would yield several benefits, chief among them being the added protection to the nose. The ability of the filter to be firmly secured in the nose would in turn secure the entire mask in place, ensuring the wearer always keeps their entire face covered.

Figure 11: Mask with integrated nose filter design

4.1.4 Injection Molded Nose Plug Filter

The inspiration behind this specific design came with the need for an ease of manufacturing. Injection molding allows for use of a simple mold with the capabilities of mass production. This design, shown in Figure 12, is made for the wearers comfort, while still including necessary safety functions. The body of the nose plug, along with the insert, will be formed using our selected material of PCU-Sil, which has flexible characteristics. Inside of the main body, shown in Figure 12, there is a replaceable cartridge that contains the carbon nanotube filter. The filter will most likely need to be replaced after repeated use in non-ideal environments. Wearers will be able to use a single pair of plugs, which will come custom fit their own nostril size, and continue to replace the used filters for a longer life span of the product.

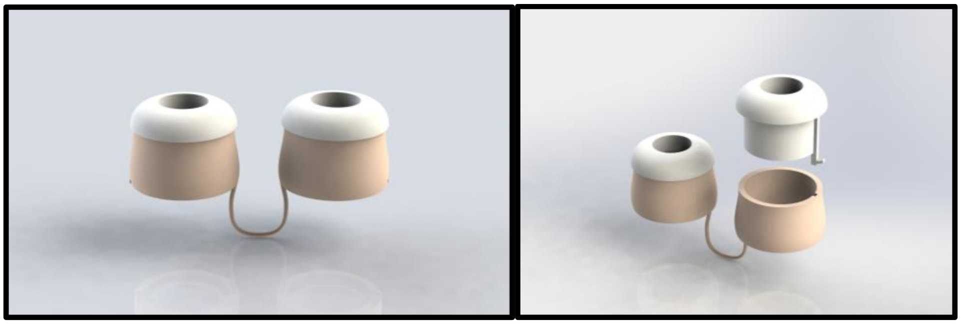


Figure 12: Injection mold nose plug design

4.2 SWCNT Filter Integration

Integrating the SWCNT filters into the nose plug was the final challenge to face in the design process. Multiple methods are optimal for the adhesion of our developed SWCNT filters however we needed to be diligent when deciding upon the leading bonding method. The bond between the filter and the nose plug must be able to withstand the average pressure of a human breath while preventing any leaks. The method of adhesion is critical because without a reliable solution the filter would essentially become useless. According to studies done at the University of Alberta, Edmonton, Canada, the calculated maximum velocity of the human nasal breath exhalation is to be around 0.6 m/s, as seen in Figure 13 [43]. Unfortunately, we did not have the time to conduct our own tests to evaluate different methods of adhesion to find a sufficient bond that can withstand air speeds up to 0.6 m/s. We recommend future tests to be carried out to find the adhesion method that works best.

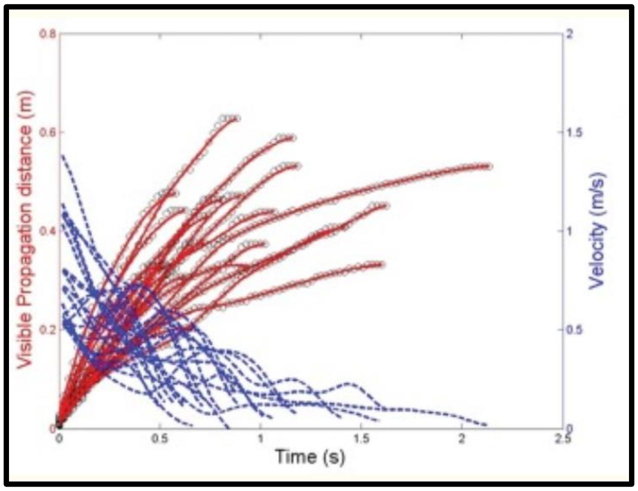


Figure 13: Time vs. Velocity Plot of Nasal Exhalation [43]

5.0 Results

While our group had a multitude of objectives that we were looking to achieve during this project, the circumstances prevented by this academic year made achieving these goals difficult. Our use of the lab was overall quite restricted, due to a combination of school policies and personal circumstances. Because of this, we had little in terms of tangible results to present, with most of our efforts geared towards designing our potential product. Our laboratory sessions primarily consisted of synthesizing our own SWCNT filters.

5.1 CNT Film Synthesis

In summary, we were unable to successfully synthesize the SWCNT films via the vacuum filtration method. The evidence of failure was common for all our trials. During the drying phase after then suspended particles were deposited on the membrane, the film cracked and curled around the edges after being exposed to 80℃ in the oven. Hypothesizing the rate of temperature change was too high which caused sudden contraction of the material. The next trials were left to dry at ambient temperature to allow drying over a longer period of time and under lower temperatures in effort to prevent sudden contraction. Upon completion of these trials, the same problem persisted due to cracking occurring through the filter. A second hypothesis was made that the additional filtration of 100 mL of IPA followed by 100 mL of DI water put too much stress on the CNTs. To reduce the stress on the CNT filter, after the CNTs were deposited onto the membrane, the membrane was removed and washed in IPA and DI water baths as described above in section 3.0. Failure due to cracking was still observed. A third hypothesis was made that the hydrophobic membrane had dimples that were too large which could have caused uneven distribution of CNT material when it gets deposited onto the membrane. This would likely cause failure points when stress was applied to the material in areas where the distribution of CNTs was low. In the following trials, a hydrophilic PTFE membrane was used with the same pore size but a smoother surface. The change from hydrophobic to hydrophilic membrane allows the IPA and DI water to filter through more efficiently which allows the CNT material to be uniformly deposited. Again, these trials were unsuccessful as cracking and curling of the edges were evident. A final theory was made that microscope slides could be placed around the edges of the filter & membrane to prevent curling during the drying phase. This technique was successful in preventing the curling of the edges but cracking in the middle prevented a satisfactory sized filter from being removed from the membrane. Instead, when attempted to be separated via tweezers, the membrane would flake apart into pieces roughly 1 mm^2 to 25 mm^2.

5.2 Nose Piece Prototype

When the time arose to print our first prototype, we knew our available printer would not be able to accurately withstand such small dimensions. To ensure we received sufficient data from testing, we decided to account for the lack in precision by scaling our first prototype. The resulting print was twice the size of the actual design. Increasing the overall size gave us extra room to examine the structural integrity as well as test methods for bonding the SWCNT filter to the plug itself.

6.0 Analysis & Future Work

Despite the lack of a true physical product, our group began this project with several larger goals in mind. We wanted to fully create and test a functional version of our PPE prototype, but were unable to do so due to the pandemic. The testing of our design would have been an iterative process, refining each aspect of our product to achieve our objective. Given our difficulties with synthesizing the filters, continuing to improve the procedure for said synthesis would be our first step.

6.1 SWCNT Synthesis

Ultimately, our group was unable to synthesize a functional carbon nanotube film. Our first film was created on October 14th, 2020. After the vacuum filtration process was completed the film was placed in the oven. Unfortunately, due to the curvature of the filter when placed into the oven, it folded over and was unusable, as seen in Figure 14.

Figure 14: Attempt from October 14th

For our second attempt, on November 3rd, 2020, we decided to place microscope slides on the filter to prevent it from folding over. Additionally, we let the filter sit at room temperature instead of placing it in the oven. The microscope slides would allow the filter to shrink while holding it in place. However, this film cracked in many places and was also unusable.

Our suggestions include placing tape or another adhesive on the filter to prevent movement of the filter while it dries. In addition, a different procedure should be created to prevent the film from creating bubbles in the filter. The clamp holding the Buchner flask and the cylindrical beaker together should also be properly sealed to prevent leakage on the filter, as seen in Figure 15.

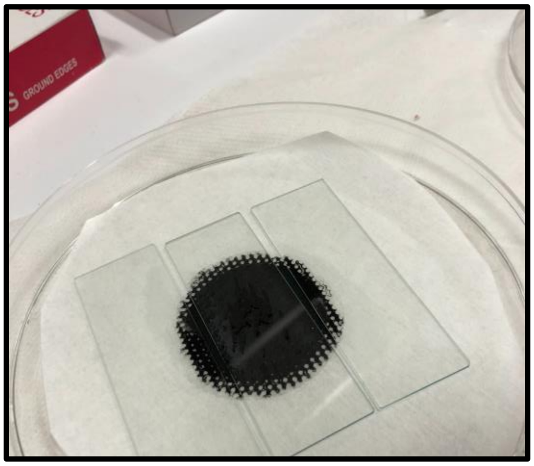


Figure 15: Attempt from November 3rd

Alternative method demonstrated in Appendix B:

6.2 Classification of SWCNT

Had the CNT films been successfully synthesized, it was anticipated that they would be tested and classified in numerous categories. Since synthesis was not successful, recommendations for future work have been made.

One potential area of interest is the quantification of air flow restriction from these filters. As discussed in section 2.3.2, some work has been done to measure the pressure drop across MWCNTs; however there has not been much research on the pressure drop across SWCNTs. We suggest SWCNTs made from a simple vacuum filtration technique be subjected to airflow at various known pressures and capture how much that pressure is reduced. This will indicate the feasibility of implementing SWCNTs in face masks.

Another idea is measuring the potential sanitation procedures by applying either UV lights, electricity, or heat. Research has shown carbon nanotube materials conduct heat and electricity very well. Since heat and electricity are methods of killing viruses and bacteria, we anticipate these being viable options for sanitations of CNT filters implemented in masks. UV light is also a good method of sanitation and testing the long-term impact it has on the material structure of SWCNTs can be valuable research.

The main classification we anticipated was quantifying the filtration effectiveness. To do this, we first anticipated exposing the filters to small particles a few nanometers in diameter. As discussed by Bui et al, they tested their CNT materials by exposing them with charged dyes 3nm in diameter and charged gold 5 nm in diameter [34]. Starting with non-activated particles is a safe way to demonstrate rejection of particles that size. Upon successful demonstration, subjecting the CNT filter to live viruses would be the next step. Successfully rejecting active viruses is crucial to the achievement of the design intent for integrating SWCNTs into personal protective equipment. Bui et al. accomplished this by exposing their samples to 40-60 nm Dengue virus from aqueous solutions and successfully rejecting them [34].

6.3 Testing the Filter

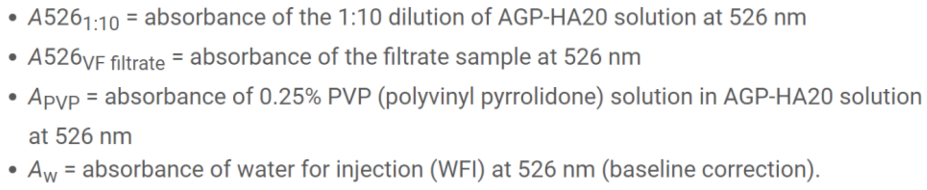
Testing the filters produced are essential to analyzing the efficiency of a carbon nanotube filter. To test this, live viral particles can be used. Aerosolized virus particles are deposited onto the filter sample [44]. These particles either pass through the filter or are stopped by the filter [44]. According to the article "Determination of Air Filter Anti-Viral Efficiency against an Airborne Infectious Virus" (2020), the equation used to calculate the concentration of particles that get stopped by the filter is as follows:

$$C_{air} = \frac{(Nup - Ndown) * Q * t}{Afilter} \text{ particles/cm}^2$$

Where C is the concentration of particles on the filter, Q is the flow rate of the aerosolized virus particles, t is the time of exposure, N_{up} is the concentration of viral particles before the filter, N_{down} is the concentration of viral particles after the filter, and A_{filter} is the area of the filter. After the filter is exposed to the virus particles the durability of the filters can be tested [45]. To properly test the durability, a gold particle integrity test can be performed [45]. This test involves exposing the filter to gold particles that are the same size as the pores of the filter prior to the aerosolized virus test [45]. The gold test is used mostly for Planova filters to assess the durability [45]. The gold particle removal rate can then be calculated using the following equation:

$$\varphi_i = \log_{10} \left[\frac{A526\ 1{:}10}{A526VFfiltrate - Apvp - Aw}\right]$$

Where:



- $A526_{1:10}$ = absorbance of the 1:10 dilution of AGP-HA20 solution at 526 nm
- $A526_{VF\ filtrate}$ = absorbance of the filtrate sample at 526 nm
- A_{PVP} = absorbance of 0.25% PVP (polyvinyl pyrrolidone) solution in AGP-HA20 solution at 526 nm
- A_W = absorbance of water for injection (WFI) at 526 nm (baseline correction).

φ_i = gold particle removal rate [45]

A particle removal rate of 1.69 is generally considered passing in terms of the Planova test [45]. This test would be conducted in a secondary location, such as a hospital.

In addition to testing the filtering qualities of the CNT filter, our nose piece must ultimately be breathable for the user. We aim to make the filter as discreet as possible, and one of those ways is to maximize the airflow of the filter. The human lungs exchange approximately 0.5

m^3 or 8 L of air per hour [46]. Our ideal filter would not hinder that capability in any way. Testing could be done to measure the airflow rate that passes through the filter, similar to the aerosolized virus test.

6.4 Material Selection

In the future, our design could be modified to incorporate different materials to provide comfort for the user. A material that could be used is silicone for the nose insert. This soft, flexible material would provide a secure fit in the nostrils of the user.

Additionally, the CNT filter can be layered with different materials to increase its filtering capabilities. Substitutional doping can be utilized to implant elements into the SWCNT by replacing one of the carbon atoms [47]. This can be achieved by a variety of methods, including thermal transfer and chemical vapor deposition, as was used in this project to produce the SWCNT filters [47].

Metal-infused SWCNTs attract H_2O_2, a solution that is known as an antiviral agent [48]. The H_2O_2 breaks down the lipid membrane of the virus, causing it to die [48]. A solution of 3% H_2O_2 in water has been proven to kill viruses on most surfaces [48]. According to the article "Pt-, Rh-, Ru-, and Cu-Single-Wall Carbon Nanotubes Are Exceptional Candidates for Design of Anti-Viral Surfaces: A Theoretical Study" (2020), "...a number of metals, including Pt, Pd, Ni, Cu, Rh, and Ru, promote the capture of H_2O_2 on SWCNT surfaces compared to just bare SWCNTs". Our CNT filter could be doped with these various metals and coated with an H_2O_2 solution to kill filter viruses.

6.5 Injection Molding

Ultimately, our CAD model for the injection mold was never produced, due to limitations on access to campus facilities. Ideally, we would have utilized the Washburn Laboratories, located on WPI's campus to produce these molds from 6061 aluminum alloy [49].

In addition to the injection molding, the viability of incorporating the filter into a mask could be further researched. The nose plug could be attached to a mask to provide additional protection for the user. The filter should work in both directions, as the essential function of a mask is to prevent the user from spreading a virus, rather than protecting the user from others.

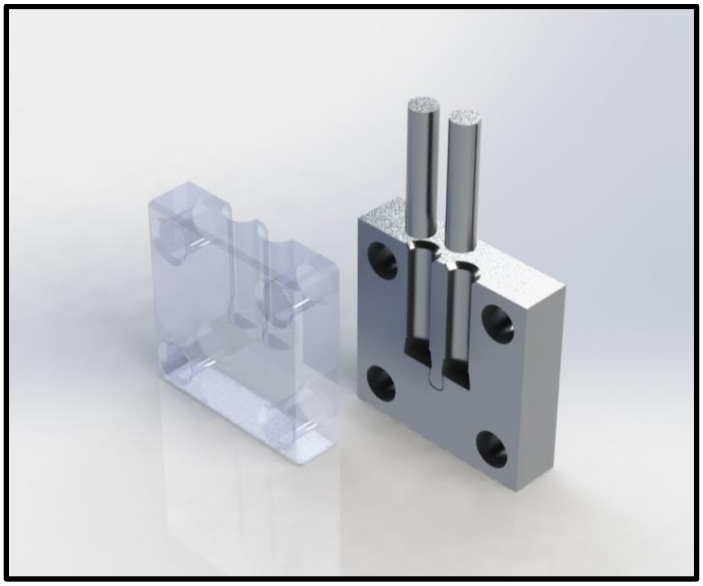


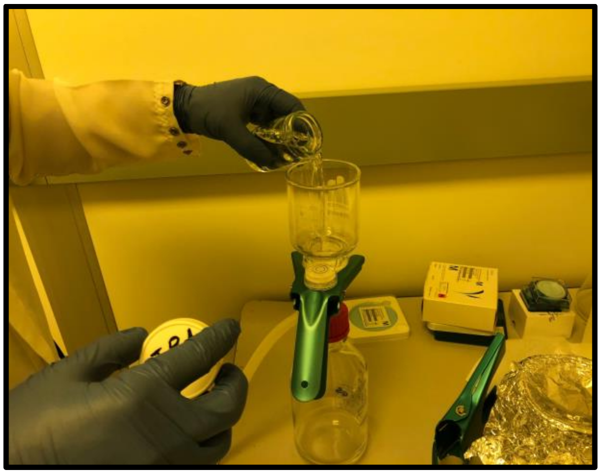
Figure 16: Injection Mold Tool Solidworks Design (Half-clear for image purpose)

6.6 Conclusion

Ultimately, we were unable to successfully create a functional carbon nanotube filter. Campus closures as well as quarantine restrictions created difficult challenges that our team had to overcome. However, the vast application of a carbon nanotube filter is worth further research. The proposed methods and ideas will hopefully come to fruition in a future project, as we feel it is an important topic. At the conclusion of this project, our team produced CAD models, as well as 3D printed models of the housing for the nose filter. Additionally, an injection mold for the nose filter was produced on SolidWorks. Due to campus restrictions, it was unable to be CNC machined. Our team hopes this project will be pursued further in the future.

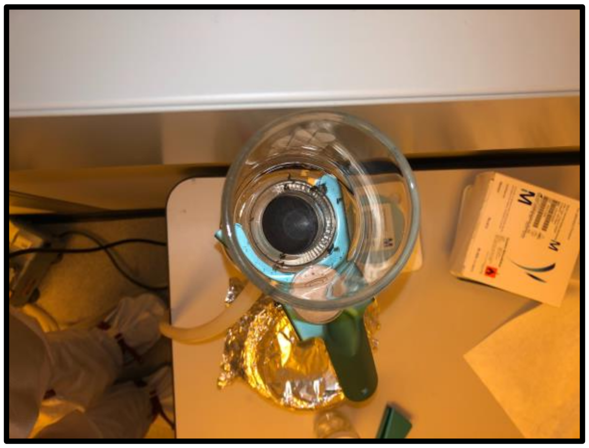
Appendices

Appendix A: Vacuum Filtration Process

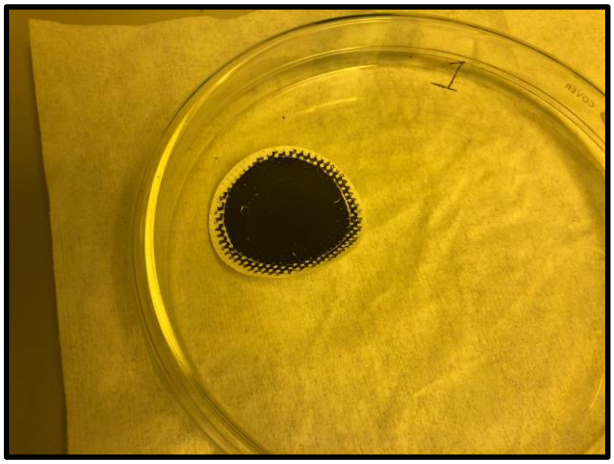


Prewetting filtering membrane with IPA solution.

SWCNT suspended in IPA filtering through membrane.



Birds eye view of completed vacuum filtration process.



SWCNT fully deposited onto the PTFE membrane and left to dry.

Appendix B: Alternative Method for CNT Process [34]

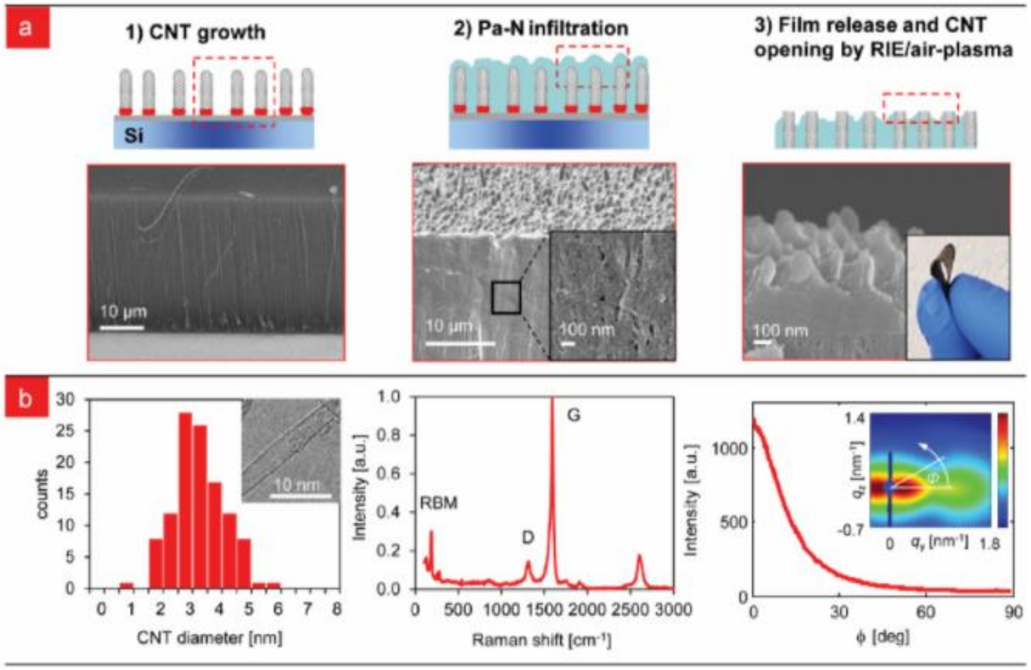


Figure 1. CNT-parylene membrane fabrication and structural characteristics. a) Top row: Schematic representation of the key fabrication steps. Bottom row: Cross-sectional SEM of (left) a CNT forest, (center) a CNT-parylene composite before etching, and (right) the membrane top surface after etching. Insets: The high-magnification SEM inset in the center shows the good conformal coating of the nanotubes after polymer deposition, whereas the inset on the right shows a photograph of a flexible, free-standing CNT-parylene composite. b) (left) CNT diameter distribution measured from high-resolution TEM images similar to the one displayed in the inset; (center) Raman spectroscopy of a typical SWNT forest; and (right) example of an azimuthal profile of X-ray scattering intensity used to quantify CNT tortuosity. The azimuthal angle ϕ is defined as shown in the 2D scattering intensity plot in the inset, which was obtained with the X-ray beam orthogonal to the vertically aligned CNTs.

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