“Our greatest glory consists not in never falling but in rising every time we fall”

- O. Goldsmith

Development of an Inventory Tracking and Monitoring System for Chemicals Using Conductive Paper -based Passive Radio Frequency Identification Technology

by

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ABSTRACT

Laboratory safety has always been a concern for many institutions and companies. New safety protocols are always being implemented in order to ensure the safety of employees working in potentially hazardous chemical environments. A central chemical database through Radio Frequency Identification (RFID) readers of which the antennas are positioned at the entrance and exit of the chemical storage room was built to achieve automatic inventory management, real-time monitoring and enhanced safety functions. The results show that the chemical inventory system can update automatically without any manual input, the system can alert potential risks including expired chemicals and incompatible chemicals

RFID is a wireless method that utilizes radio-frequency electromagnetic fields to transfer information and identify objects. A passive RFID tag consists of substrate, a chip and antenna. Whereas most RFID tags exploit a classical metallic conductor as the antenna, this project aims to develop and characterize a carbon-based one, which is more environmentally friendly. A RFID antenna was prepared using cellulose nanofibrils (CNF), polyvinyl alcohol (PVA) and reduced graphene oxide (rGO) as raw materials. An antenna with high conductivity and mechanical properties was obtained.

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List of Symbols, Nomenclature or Abbreviations

ASIS- Application Specific Integrated Circuit

CAS- Chemical Abstracts Service

CNF- Cellulose nanofibrils

EPC- Electronic Product Code

GO- Graphene Oxide

rGO- Reduced graphene oxide

IC- Integrated Circuit

LF- Low Frequency

NPR- Negative Poisson's Ratio

PCB- Printed Circuit Boards

PVA- Polyvinyl Alcohol

PHP- Hypertext Preprocessor

RFID- Radio Frequency Identification

UHF- Ultra High Frequency

ICT- Information and Communication Technology

Chapter 1

Introduction

1.1 Background

1.1.1 Inventory Tracking and Monitoring System

Safety issues have received more and more attention recently, especially in chemical laboratories (Fivizzani, 2016). Not only because lab safety can potentially cause equipment damage, wasted time and environmental pollution, severe incidents in an academic laboratory can result in injuries, and even fatalities. Many measures have been implemented to minimize or even eliminate laboratory accidents, including personal protective equipment, first aid kits, inventory management, safety training, etc. Among these measures, inventory management has received much attention because of its preventive feature and possibility of applying new technology (Perkel, 2015).

Inventory management plays a key role in a chemical environment, especially for universities. Unlike in industries, high student turnover, lack of training and various kinds of reagents in small amounts are expected in a university laboratory. It challenges lab managers on management of chemical expiry date, authority control, chemical tracking, incompatible chemicals, etc. (Williams & Bosnak, 2008). An accurate inventory management contributes to maintain healthy cash flow and can reduce or eliminate expired chemicals that are risky. Together with authority control and chemical tracking, lab safety is expected to be improved substantially.

Barcodes were widely used for basic inventory management purposes in universities, and not long ago, considered as the only means of identifying and tracking products as the items travelled across the world to different retail destinations (Mosseler, 2016). A barcode is an optical tag that can be read by a special machine and describes certain information about the object that carries the barcode. It becomes commercially successful in automatic identification and data capture. However, radio frequency identification (RFID) has shown to be a much more comprehensive alternative when it comes to greater perceptibility in supply chain networks, higher product velocity, more resourceful inventory management, lower labor cost and human error, (Thanapal, Prabhu, & Jakhar, 2017). It also has several advantages like memory storage, multi-object identification, and ability to communicate from a greater distance, with no line of sight and authority control.

RFID has been proven to be a promising technology and is widely used for tracking, e-payment, supply chain management and inventory management due to its contactless communication, long read range and low-cost features. According to a study by IDTechEX, RFID is a fast-growing technology. From a total market value of 900 million USD in 2000 and 7.88 billion USD in 2013, it is expected to reach a total market value of 30.24 billion USD by 2024. RFID has been implemented in diverse industries such as logistics, supply chain management and quick response system. More importantly, RFID can also be used to make the inventory control system more efficient (Zhu, Mukhopadhyay, & Kurata, 2012). Unlike a barcode, RFID utilizes electromagnetic fields to identify and track tags attached to objects automatically which do not need to be positioned in a line of sight with a scanner, and multiple objects can be scanned at the same time. There are two parts in RFID technology: a tag and a RFID reader that links to a computer system. The tag contains an integrated circuit (IC) for storing object information, which is transmitted via an antenna to the reader. The reader converts the radio waves to a more usable form of data. Information collected from the tags is then transferred through a communication interface to a host computer system where the data can be stored in a database and analyzed later.

Table 1. Comparison of RFID with other technologies

	Information carrier	Amount of Information	Write & Read	Read mode	Safety	Anti - jamming ability	lifetime	cost
Barcode	paper, Plastic film, etc.	-	read only	CCD / laser scan	-	--	-	--
Magnetic card	magnetic material	+	write / Read	Electro-magnetic transform	+	-	--	-
IC	EEPROM	++	write / Read	electronic write & read	++	+	+	+
RFID	EEPROM	++	write / Read	wireless	++	++	++	+

There are two types of RFID tag technology: active and passive. Active RFID tags have their own transmitter and power source which are commonly used on rail cars and large reusable containers. Active tags can also provide a longer read range that is up to 100m. Instead of having an internal power, passive RFID tags are powered by the electromagnetic energy that is transmitted from an RFID reader, it only consists of internal antenna and an IC which stores the object's information. Compared to active tags, passive tags have a much simpler structure and lower price that makes them commonly used for access control, tracking, and supply chain especially in scenarios that do not require long read range.

Table 2. Advantages of passive and active RFID tags

Passive RFID Tags	Active RFID Tags
Smaller tags	Longer read range
lower price	Increased abilities with partnered technologies: GPS, sensors, etc.
Thinner/more flexible	Rugged tag options
Higher range of tag options	
No battery	

Passive RFID tags operate at different frequencies because of environmental influences like electrical noise, temperature, liquids, and physical stress. There are three different frequencies that are generally used for passive RFID tags in various industries (B. Huang, 2007):

- Low frequency (LF):125-134 KHz, it has the longest wavelength and shortest read range which is about 1-10 centimeters. LF type is usually used for livestock tracking because it is less likely be affected much by water, body tissue and metal.

- High frequency (HF) and Near-Field Communication (NFC): 13.56 MHz, HF passive RFID tags are commonly used in access control, e-payment systems and passport security. It has a medium wavelength with a read range from 1 centimeter to 1 meter. This read range is better suited for security applications because of the longer reading range.

- Ultra-high frequency (UHF): 300MHz-3GHz. Thanks to its large frequency range, UHF are the most widely used tags and can be designed to function at wide read range from a few centimeters to ten meters in the passive form. It should be noted that UHF is specified in different regions within the frequency. For example, 866-869 MHz is in Europe, in America it is 902-928 MHz and meanwhile 950-956 MHz in most of Asian countries

There are three standard formats of RFID tags:

1. Read-only (R/O): the tags are preprogrammed and cannot be modified. R/O format is usually used for ensuring uniqueness such as security purpose. It is the cheapest solution due to simple structure i.e., less amount of memory

2. Read write (R/W): R/W tags can be updated as many times as needed. They are useful because of their ability to accommodate a dynamic environment. R/W can be locked to avoid mistaken changes.

3. Write once read many times (WORM): similar to R/O tags, can only be written once, but WORM tags are not preprogrammed so they allow operational flexibility. They are usually programmed according to users' purposes. A well-known WORM technology is CD-Rs which can only be written once but read many times.

RFID earned comprehensive attention because of its wide application capability such as pharmaceutical (Catarinucci, Colella, De Blasi, Patrono, & Tarricone, 2012), warehousing (Lehpamer, 2012), agriculture (Potyrailo et al., 2012), and sensors (Potyrailo, Surman, Nagraj, & Burns, 2011) industries. With the emerging new retail concept: unmanned supermarkets, where RFID technology is used for identification and e-payment purposes, the future of RFID technology is even more promising. More attention, both industry and academic is expected to come.

Similar to the new retail concept, using RFID as the measure of inventory management in labs, chemical tracking, authority control, chemical incompatibility, enhanced safety function and automatic inventory update can be achieved. Thus, the application of RFID in labs is considered to have huge potential compared with old barcode technology.

1.1.2 Conductive paper technology

Conductive paper is a well-developed technology. There are many ways to produce conductive paper.

Filler addition

Filler usually is added to the fiber suspension in the stock preparation stage. By using specific fillers, the conventional paper can be imparted with conductive, magnetic, catalytic and flame retardant properties (Jabbour, Chaussy, Eyraud, & Beneventi, 2012). Fillers used in conductive paper include graphite and carbon black. The paper conductivity depends on the amount of filler addition, dispersion of fillers, and conductivity of selected fillers themselves.

Coating

Coating is a common practice used to improve printability, optical property and smoothness of the paper. Similar to filler addition, by surface coating of conductive coating colors, paper can be produced to targeted conductivity

Printing

Conductive paper can be made by printing conductive ink onto paper surface.

Laminating

A conductive layer can be laminated onto paper substrate, making the paper products electro-conductive.

1.2 Problem Statement and Significance of the study

This project aims to develop conductive paper-based RFID technology to improve chemical inventory management and consequently reduce accidents caused by chemical incompatibility, expiration of chemicals, unauthorized operation, etc. There have been several incidents happen over the past years at the University of New Brunswick which were caused by the reasons listed above. A safe working environment is important for everyone, especially in a chemical environment. By improving chemical inventory management together with authority control, chemical expiration control, and tracking, laboratory safety is also expected to improve.

To improve the current RFID technology, the second research topic is to replace the metal antenna of the RFID tag with carbon-based materials. Advanced carbon materials exhibit more favorable properties than most metals such as mechanical reliability, weight savings, and excellent environmental toughness (Tang, Santare, & Advani, 2003). Currently, no studies show that materials produced by conventional methods could reach a high conductivity of over 1500 S/m, which has considerable influence on the efficiency of RFID antenna function, such as the read distance.

This study seeks to advance such knowledge by exploiting the capabilities of natural conductive compounds of graphene and poly vinyl alcohol (PVA) to produce a novel material for use with existing technologies including but not limited to RFID tags.

1.3 Contributions

The main contributions of this work can be summarized below:

1. Inventory management system: the project aims on building up a chemical tracking system based on RFID technology for chemical tracking, location, authority control and enhanced safety function.

2. Preparation of the antenna materials: the ratio of graphene and PVA in a film will be optimized and its influences on conductivity and strength of the antenna will be studied. With this knowledge, we will fabricate a film with characteristics necessary to function as an antenna for RFID tags which is capable of receiving and transmitting an electromagnetic signal generated within North America UHF RFID standard (902-928 MHz).

3. Investigation of end-use properties: it is to investigate the relationships of film formulas and overall conductivity and mechanical strength.

1.4 Outline of the Thesis

Chapter 2: Literature review. This chapter provides some background documentation relating to the RFID technology, implementation of RFID technology in different industries such as supply chain, logistic, inventory management, tracking; conductive polymer and its development, implantation and future.

Chapter 3: Experimental Techniques. This chapter gives a detailed description of experiment set-up, such as materials, methods used for fabricating the conductive film, as well as instruments used for the above purposes.

Chapter 4: Results and Discussion. This chapter discusses the formula of the conductive film. Results of this testing are included, along with details of conductive and mechanical strength at each PVA content level.

Chapter 5: Inventory Tracking and Monitoring System. This chapter gives a detailed description of the RFID tag, and four functions of the inventory system.

Chapter 6: Conclusions. This chapter summarizes the work done in this study and recommendation for future work.

Chapter 2

Literature Review

2.1 Conductive film fabricated by carbon-based materials and polymers

Conductive films usually consist of conductive fillers including metals, or carbon-based materials such as carbon fibers, graphene, or carbon black. Polymers such as PVA and PVC, are the backbone of the film, but are commonly non- conductive. By blending polymers and conductive fillers, conductive polymer composite can be made, which can find many applications like electronic equipment, floor heating elements and electromagnetic interference shielding (Xiao, Tong, Savoca, & Oosten, 2001). Recently, the application for sensing parts has also drawn attention. Unlike metallic material, conductive polymer has the advantages of easy shaping, low transport costs due to its low density and the ability to tailor make conductivity, and its nature of corrosion resistance.

2.1.1 Carbon-based conductive materials

The chosen conductive materials play a key role in the composite conductivity and its own critical percolation concentration. For example, graphene, carbon black and carbon fiber behave differently when used as the conductive material.

2.1.1.1 Graphene

Graphene is a two-dimensional carbon material which owns outstanding mechanical properties and electrical conductivity. Thanks to its atom thickness and honeycomb shape carbon structure which give excellent conductivity and mechanical properties, many applications such as sensors, functional conductive materials, or motors were developed.

2.1.1.2 Mechanical properties

Large deformation can be found along the stress direction when graphene is loaded with tensile stress. Young's modulus is widely used to characterize this mechanical property, which is the ratio of tensile stress and strain. Researchers found Young's modulus of graphene rises dramatically due to the suppression of rippling, an indication of excellent mechanical properties (Los, Fasolino, & Katsnelson, 2016). In order to uncover the mysteries behind this phenomenon, researchers proposed two modes of deformation- Pathway –I (PW-I) and PW-II. There are two important parameters in these two modes: bond angles and bond length. In PW-I mode, when loaded with tensile stress, only the bond angles change while the lengths remain. On the contrary, the bond lengths change while angles remain in PW-II mode (Jiang & Park, 2016). The tensile strain exceeds about 6% when graphene is stretched along one in-plane orientation, which is known as Negative Poisson's Ratio (NPR). The interesting phenomenon can be explained by PW-II mode because of the relatively lower energy of graphene (Jiang & Park, 2016). It is found that NPR of graphene only happens when the temperature is below 2400K and in uniaxial tension along the armchair direction, but also can occur in bilayer and multilayer "graphene" (Deng et al., 2017).

Graphene can fracture when loaded with tension or tearing. Researchers studied the mechanics of torn graphene and found that the initial crack length determines the path and the edge of the crack and the toughness of graphene is 11.24 J/m^2. Using molecular simulations and fracture mechanics analysis, observations showed that the fracture forces from the spherical indenter can only be directly mapped onto cylindrical indenters, but not the uniaxial strength.

Shear deformation was also studied by many researchers. The modulus has been calculated with many methods using simulation that covers from 0.228 TPa to 0.47 TPa (Tsai & Tu, 2010). Under different temperature conduction from 0 to 2000K, it can be observed that the shear modulus of both armchair and zigzag direction increases with the temperature below 800K and starts to turn around when the temperature is beyond 800K (Min & Aluru, 2011). The mechanism of this phenomenon is still unknown and needs further research. Some other researchers also found many interesting phenomena, when the temperature goes up from 0K-2000K, the shear strength reduces from ≈60 GPa to ≈30 GPa (Min & Aluru, 2011). In general, the shear modulus values are scattered based on many literature reviews.

2.1.1.3 Graphene oxide

Graphene oxide is a typical graphene material including chemical reduced graphene oxide, thermally reduced graphene oxide (rGO), etc. Compared with physically fabricated graphene, rGO is produced by chemical methods and there are topological defects that can be observed from Raman spectra, which is due to the oxidation procedure that introduces the defects to the planes. We can see an extra peak below the G band at about 1600 cm^{-1} (Adak, Chhetri, Murmu, Samanta, & Kuila, 2018). The stiffness of GO was found to be up to 40 GPa, but the strength was only about 120 MPa (Xiang et al., 2013). The Young's modulus, formation, characteristics and other properties of GO have been extensively studied.

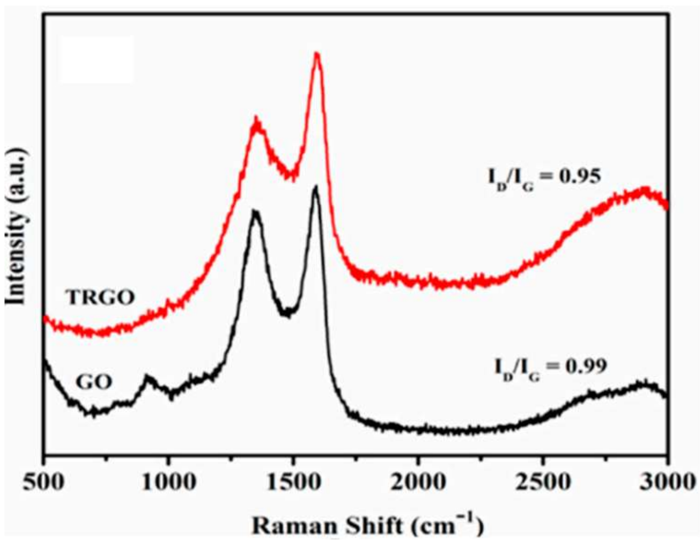

Figure 1. A typical Raman spectrum of GO (Cao et al., 2018)

Compared with graphene, it should be noted there are three key characteristics of graphene oxide that draw attention of researchers

1. Cost effectiveness

   Produced by chemical methods from graphite, graphene oxide is one of the most cost-effective ways to produce graphene-like materials due to low cost of graphite and high yield of using chemical method

2. High hydrophilicity

   Graphene oxide exhibits high hydrophilic property and can form a stable aqueous colloid system

3. High conductivity of rGO

   The reduced GO (rGO) exhibits high conductivity

2.2 Use of polymers in conductive film

One of the critical aspects in the production of conductive film is the use of polymers, so that sufficient mechanical strength of the film can be obtained. In order to minimize the content of conductive material, a percolation threshold of conductive material in the polymer is necessary.

2.2.1 Polymer polarity

Some researchers investigated the influences of different polymer matrices on the percolation threshold. It is suggested that the polarity of polymers has an impact on the content of conductive materials at a given conductivity; the higher polarity of the polymer, the greater the threshold (Gubbels et al., 1994). It was further demonstrated that the surface tension of a given polymer has a similar effect on the threshold of filler content. A strong correlation also has been found between the increasing polarity of polymer and enhanced conductivity.

2.2.2 Viscosity of polymer solution

The viscosity of a given polymer solution also has effects on the properties of the conductive-filler containing films. The higher the given polymer solution viscosity, the higher the threshold of percolation (Sau, Chaki, & Khastgir, 1998). Due to a high shearing force that would be required for dispersing high viscosity polymer solutions, the structure of the conductive material may change. Consequently, a higher conductive filler content may be needed to form a conductive network.

Take carbon fibers as an example, higher viscosity of a given polymer solution will result in shorter fibers during mixing at a very high shearing condition, thus a higher carbon fiber content is required to achieve the targeted conductivity.

2.3 Mechanism of conduction

Different mechanisms may apply to different conductive materials due to their inherent differences, for instance, types of material, its concentration, and types of the polymer. In general, there are three classes of mechanisms that apply to most of the cases based on distributions of the conductive particles in the composite.

- Threshold of percolation

It was reported that the conductive filler content (evenly dispersed conductive spherical shape) of up to 10% (volume percent) in an insulating medium would be required to reach conductive threshold (Zhang et al., 2007).

- Adjoining

High field strength can be expected when the narrow gaps, for example, formed between conductive fillers, are close enough (within a few nanometers). As a result, the internal field emission could account partially for the conductivity of the composite. Based on the radiation theory of the electric field, the emission current is excited by the high electric field gap (Saarinen, Vartiainen & Peiponen, 2006). Several special cases of internal field emissions were found, the tunneling effect is of the most interest. Based on the theory of quantum tunneling effect, the electrical conduction can jump across a gap or tunnel through energy barriers between conducting elements in the polymer matrix, not only take place by interparticle. The tunneling effect is expected to happen when the gap between/among conductive areas is within a few nanometers and they can be considered the same as interparticle contact (Polley & Boonstra, 1957). By contrast, lower concentration (threshold of percolation limit) of conductive filler can be expected in this theory compared with conduction path one. Many researchers also believe that some conductive behaviors of a filler-polymer composite are due to tunneling effect, which is supported by experimental results.

- Touching

The movement of electrons through the polymer matrices that formed by a few continuous chains from one end to the other causes the phenomenon of electrical conduction. The theory is well-known as conduction path theory. From this theory it is believed that the formation of a conductive network that by physical contacts of conductive fillers plays a key role (Baltá Calleja, Ezquerra, Rueda, & Alonso-López, 1984). It is not hard to see there is a higher chance to form a continuous conductive network as the conductive filler concentration increases (Grekila & Tien, 1965). When studying a high-density polyethylene and carbon fiber composites mixed with different concentrations of carbon black, it can be observed carbon black particles improved carbon fiber contacts by acting as the filler that filled the gaps between/among carbon fibers, thus improving the "touching". There is a critical filler concentration below which the fillers are just dispersed in the polymer matrix and cannot contribute to the conductivity improvement as no obvious conductive area/networks are formed. At this concentration, the system conductivity depends on the polymer matrix that is commonly not conductive. Increasing the filler does not affect the general conductivity. Once reaching the critical content, the filler starts to occupy most of the gaps and the sparse conductive networks in the matrix start to connect with each other and result in a large increase in conductivity-quantitative to qualitative change. Beyond the critical concentration, the filler will benefit the formation of conductive networks, thus helping the conductivity of the system. As a result, increasing filler content increases conductivity. The formation of individual aggregates relies on geometrical and morphological aspects which are size, structure and porosity. Researchers found smaller particles benefit the formation of conducting paths. Furthermore, surface chemistry influences the aggregate structure and shape (Sircar & Lamond, 1978).

Manufacture and application of conductive composite has drawn much attention and made great progress. In order to achieve high conductivity and meanwhile cost effectiveness, the parameters discussed above should be controlled including degradation of fillers, size, shape, aspect, etc.

2.4 RFID in Supply Chain Management

It is believed RFID technology holds a bright future in supply chain management by providing real time, multi-objects, wireless, no line-of-site needed, unique and reusable tags features. With the development of globalization and increasing competition, many organizations expand their internal operations into various supply networks across continents in order to achieve competitive advantages. Unlike a point to point supply, it involves a series of processes and enabling systems, for instance cost evaluation, inventory control, production optimization which support business strategies and influence operational, strategic and tactical decisions (Stadtler, 2005). With the growth of information and communication technology (ICT), the integration of ICT and supply chain has drawn the public's attention, because of its capability to allow quick response, enhanced coordination of materials, resulting in better cash flows and improved competitiveness (Kumar, Singh, & Shankar, 2013). RFID is one of the most promising technologies among all these ICTs. Since 2005, major retailers including Wal-Mart and Metro Group have mandated their top suppliers tag cases and pallets with RFID. Wal-Mart reported that RFID technology helps reduce 21% out-of-stocks and manual orders and achieved up to three times faster goods replenishment. It was also reported that RFID helps Metro Group reduce time and labor cost significantly (Leung, Cheung, & Chu, 2014).

Supply chain strategy can be categorized to lean and agile (Ambe, 2010). A lean supply chain strategy aims on reducing waste and being as efficient as possible. It is supposed to be adopted for functional products in a predictable market. Verifying whether an organization implements supply chain practices match its supply chain strategy is a common way to evaluate the effectiveness. For example, reduced inventory can be a common best supply chain practice for a lean strategy evaluation. The purpose of an agile supply chain strategy is used for innovative products in a volatile market that gives the organization the ability to react fast to the changing market. Customer satisfaction is a good example of supply chain practice for an agile supply chain strategy.

Adapting RFID technology to supply chain management including but not limited to manufacturing, retailing, shipping, port operations, oil exploration, agriculture and packaging, has been growing during the last decades by its features of non-contact, wireless, multi-objects and real-time communication (Angeles, 2005).

There are seven aspects that are usually included in supply chain management: inventory management, supply and demand management, logistic and physical distribution management, process optimization and improvement, closed-loop product lifecycle management, and RFID system security and user privacy.

2.4.1 Inventory management

The key processes in fulfilling requirements of customers and effectiveness of supply chain are replenishment and order fulfillment policies which are widely used to determine the frequency and size of orders to achieve maximum cash flow and customer satisfaction (Dai & Tseng, 2012). Replenishment is governed by inventory levels and vice versa.

The bullwhip effect is a distribution channel phenomenon that forecasts yield supply chain inefficiencies. In most of the business activities, demand is always unstable and difficult to forecast, thus, companies always need to optimize the allocation of inventory and other resources by predicting customer needs. Forecasts are based on statistics and are generally not perfectly accurate, so additional inventory as safety stocks in their operations is needed. In the supply chain, from downstream to upstream, from the end customer to the original supplier, the safety stock required by each component will be more and more, which becomes more chaotic and unpredictable when information ramps up (Geary, Disney, & Towill, 2006). Thus, by controlling the bullwhip effect in the supply chain, reduction of safety stock and optimized material resources can be achieved (Wamba & Boeck, 2008). RFID can help to achieve sufficient and more accurate information flow that is necessary for controlling the bullwhip effect. As a result of globalization, the supply chain of many organizations covers multiple countries or even continents, which is driven by production cost, labor, and tax. The complexity of supply chain also exposes products to smuggling and counterfeiting which is another key subject under inventory management-inventory security. Again, RFID can be beneficial to the above challenges.

Based on bullwhip effect, inventory inaccuracy can significantly affect information flow that can thus create chaos along the supply chain. It is the discrepancy between physical and recorded inventory levels (Kang & Gershwin, 2005). It is reported that 65% of the retail stores inventory records were inaccurate and such inaccuracies could reduce retailers' profit by up to 10% due to higher cost of inventory and the cash flow (DeHoratius & Raman, 2008). RFID can help with transaction errors, backdoor shrinkage, misplaced inventory and real time updates that cause inventory inaccuracy.

2.4.2 Supply and Demand Management

The purpose of supply and demand management is to proactively synchronize the supply and demand in order to minimize disruptions that can help with reducing the safety stock. It involves the process of assessing and balancing the capabilities of supply chains against consumers' requirements. By synchronizing and balancing supply and demand, which increases forecasting efficiency, flexibility and reducing variability can be achieved (Ross, 2015).

2.4.3 Factory Operations

Management of manufacturing processes involves a series of technologies and methods that could define their processes and features. It is worth noting that manufacturing management is not the same as enterprise resource planning (ERP) that is widely used nowadays. ERP is only for scheduling manufacturing according to raw materials or other resources, compiling cost data (Love, 2007) and is one of the means included in the manufacturing process management. Efficiency of factory operation can be improved by reducing delivery time, shortening production times, and more importantly, the response to new markets or market changes. These can be achieved by utilizing manufacturing process control management, which is a hub that allows the integration of various tools and activities to realize production line setups and the possibility of alternative products.

In order to achieve the above improved efficiency, the technologies and methods that included in the manufacturing management are commonly agreed as: production planning, automatic manufacturing, cost estimation, process control, quality control, reliable measurements, etc. Meanwhile, communication with other systems is also necessary and usually is carried by ERP (Meyer, Fuchs, & Thiel, 2009)

2.4.4 Physical Distribution Management

Physical distribution management includes planning, control and operational activities that relate to logistics from raw materials to manufacturing location and products from manufacturing location to the market. It is an important part of logistics management, which is not only the flow of goods, but also the information and payments in a supply chain which can be considered as transportation, warehousing, inventory management and order processing (Stadtler & Kilger, 2008).

2.4.5 Process Optimization

Process optimization is the discipline of adjusting a process to optimize some specified series of parameters without violating some constraint. The most common goals are minimizing cost and maximizing throughput and/or efficiency. When optimizing a process, the goal is to maximize one or more of the process specifications, while keeping all others within their constraints. Process optimization in supply chain management usually is adjusting, equipment optimization, operating procedures, and control (Castillo, 2007). RFID plays a key role to achieve suitable information flow which is required by optimizing performance.

2.4.6 Product Lifecycle Management

Product Lifecycle Management (PLM) began in 1985 and is widely implemented in industries. It includes the management through engineering design and manufacture, to distribution, utilization, reuse and recycling if any. The PLM system helps industries cope with modern fast paced challenges of new product development that is critical for global competitive markets (Annacchino, 2007). The goals of PLM are to shorten the time required to introduce new products to market, improve quality, reduce costs, increase revenue and reduce environmental impacts of the lifecycle.

2.4.7 RFID System Security and User Privacy

Convenience and security are sometimes contradicting. With the wide spread of RFID technology, the sensitivity and accessibility of RFID systems have drawn the public's attention to security and user privacy. Coincidentally, the major research of RFID focuses on developing a robust technique to ensure the security and privacy of RFID systems don't hurt its convenience (Ray, Abawajy, & Chowdhury, 2014). Other focuses are using RFID as a tracking system by EPC technology (Shi, Li, He, & Sim, 2012) and improving the efficiency of RFID (Hess, Seuschek, Braun, Oliveri, & Baldini, 2012). There are several ways to explore for RFID security and privacy. For instance, message authentication and random number generation (Alomair, Lazos, & Poovendran, 2011), apply RFID technology to protect patient privacy (Revere, Black, & Zalila, 2010), and test/study the existing approaches that can secure the user's privacy (Chen, Zhu, Li, Wen, & Gong, 2015).

According to recent publications, when applying RFID technology in the supply chain management, improved information capture and passing throughout the whole supply chain can be expected, thus positively benefiting all the above aspects. The literature demonstrates that RFID can potentially improve efficiency, productivity and information responsiveness, which leads to reduced cost, fast product development, accurate inventory, optimal replenishment of stock, and superior competitiveness. It also gives the possibility of managing the lifecycle of products in a closed loop, from design, engineering, manufacturing and end use to disposal or recycling.

It has been reported since 2009 that the application of RFID in industries has been steadily increasing (Date, Ramaswamy, & Gangwar, 2015). The reasons are believed to be initial hype, successes in adopting RFID to industries and later shifted interests to security, user privacy and integration with other emerging technologies which keep the RFID under the spotlight for a longer time than expected. One of the most popular research interests is cost-versus-benefit analysis, especially as mentioned above the application of RFID in inventory management, process optimization and logistics are the areas that give the highest returns to the investment of supply chain. Other interests are system security, product lifecycle management, factory operations and supply and demand management, which are too important and there is no less benefits from RFID application in the areas (G. Huang, Li, Yuan, Gao, & Rao, 2012). It is believed that with the flourish of RFID utilized in industries, new risks in security and privacy will evolve continuously and will challenge researchers to cope with them (Wang, Liu, & Chen, 2015). It's worth noting that security and privacy challenges are considered as an interdisciplinary subject which is related to IT and possibly can be improved by the development progress in IT. In the area of product lifecycle information management, RFID plays a key role together with other technologies and infrastructure to support fast decisions (Ranasinghe, Harrison, Främling, & McFarlane, 2011).

Nowadays, RFID has been widely used to support supply chain management in various specialties, it is essential to clearly understand its benefits and drawbacks for further evaluation. There are three methods conducted to analyze RFID investment like benefits, costs, and challenges. Most empirical studies use various methodologies and focus on the value that comes from industries. However, depending on how researchers read the data, conclusions may differ from person to person. Other than that, the stage of adoption can also impact the result, it is noted that in-depth understanding is necessary (Bhattacharya, 2015) especially comparing the results of three different methods at same or similar pre-conditions can give a big picture to assist assessing the benefits of RFID application.

Research shows that most of the inquiries about RFID application in supply chain management are on merchandizing (business to customers), but lack of business to business (B2B), for instance; commodity, equipment, oil and gas, pulp and paper, steel, cold supply chains, etc. and have not been widely implemented yet, which is a result of incorrect implementation (Leung et al., 2014).

Chapter 3

Experimental

3.1 Materials

The following materials were used as received: Sulfuric acid (98.08%, Fisher), potassium persulfate (≥99.0%, Sigma-Aldrich), phosphorus pentoxide (99%, Sigma-Aldrich), potassium permanganate (≥99.0%, Sigma-Aldrich), hydrogen peroxide (30%, Sigma-Aldrich), graphite (<20 μm, synthetic, Sigma-Aldrich), cellulose nanofibril (1 wt%, Cellulose Lab).

L-Ascorbic acid (≥99.0%, crystalline) was made to solution at 15 wt% concentration. PVA (Mw 85000-124000, 99+% hydrolyzed) was made to solution at 10 wt% concentration. Hydrochloric acid (36.5-38 wt%, Fisher) was diluted to 5 wt% concentration. Deionized H_2O was exclusively used for all experiments.

3.2 Methods

3.2.1 Preparation of Materials

3.2.1.1 Preparation of Graphene Oxide

The graphene oxide was prepared based on Hummer's method as follows:

1. Pre-oxidation

5g Phosphorus pentoxide and 5g potassium persulfate were slowly added into 25ml concentrated sulfuric acid at 90℃, then stirred for 20 mins until completely dissolved. The solution was reduced to 80℃ then added 6g graphite and stirred for 4.5 hours in the water bath to keep the temperature stable at 80℃ and then added 1L deionized water stirred overnight. The above product was filtered and washed by using large amount of deionized water to neutral pH, then dried to semi-dried state.

In this step, sulphuric acid, and potassium persulfate reacts with graphite and form graphite intercalation compounds (GIC) at high temperature.

2. Oxidation

Added 230ml concentrated sulfuric acid to a flask and put it under iced bath to cool it down to 0℃. Slowly added 30g potassium permanganate and the obtained pre-oxidized graphite to the flask while kept stirring at the temperature not greater than 10℃ until completely dissolved. Increased the iced water bath temperature to 35℃ and kept reacting for 2 hours at this temperature.

During the oxidation procedure, potassium permanganate the insertion of the oxidizing agent into the preoccupied graphite galleries.

3. Reaction termination

Slowly added 460ml deionized water to the above solution and kept the temperature no greater than 50℃. With the water adding to the system, activity of the reactants reduced gradually until adding deionized water would not result in obvious temperature change. Added another 1.4L deionized water and kept stirring for 2 hrs.

4. Product purification

The purpose of this step is to remove residual potassium permanganate and neutralize the system and form GO solution.

Removal of potassium permanganate

Added 25ml hydrogen peroxide to the above solution, during this process the color changed from dark brown to brown then to khaki and eventually orange. Kept stirring for 30 min then let it stand overnight. Removed supernatant and washed the precipitant by large amount of 5% hydrochloric acid. Then washed the precipitant by large amount of deionized water until neutral. The solution then centrifuged for thickening.

Ultrasonic mixing and dialysis treatment

Diluted the obtained graphene oxide and used ultrasonic treatment for 10 min and dialysis for 1-2 weeks to obtain a uniformly dispersed monolayer graphene solution.

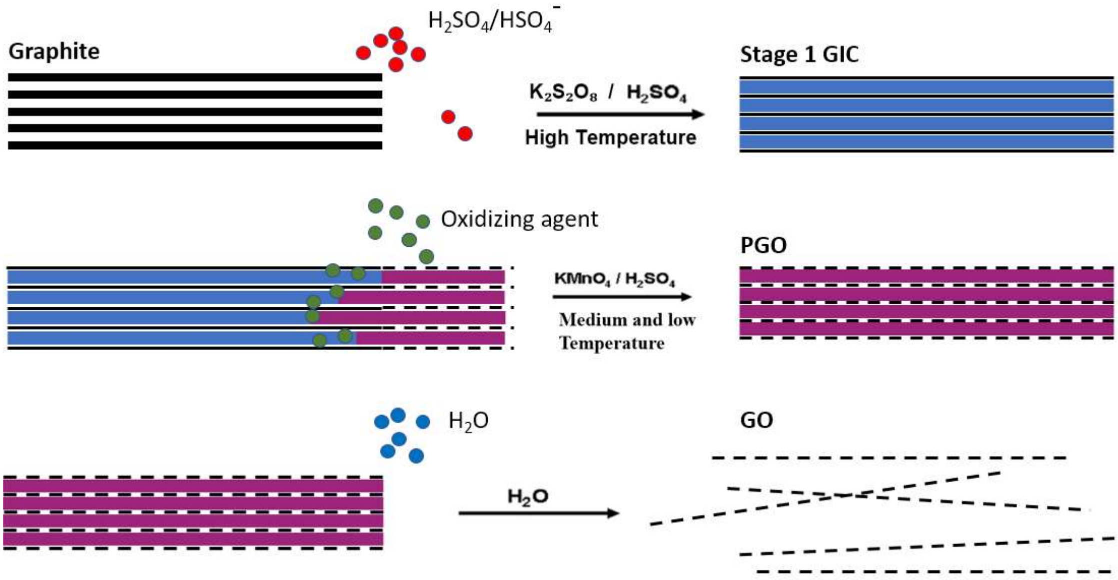

Figure 2. Schematics of conversion of bulk graphite into graphene oxide

3.2.1.2 Preparation of the conductive film

Conductive film with PVA as strengthening agent

1. Prepared 5% PVA solution

2. Measured the obtained graphene oxide solution concentration and mixed with PVA at a designed ratio to control total solid content of the solution to 50 mg. Graphene oxide was used for film stock because of its good dispersibility in water.

3. Ultrasonicated the above mixture for 10 min to form a uniform solution of PVA and graphene oxide

4. Use pressure filtration to filtrate overnight. The filter was connected to a high-pressure nitrogen gas cylinder to keep the pressure at stable 30 kPa.

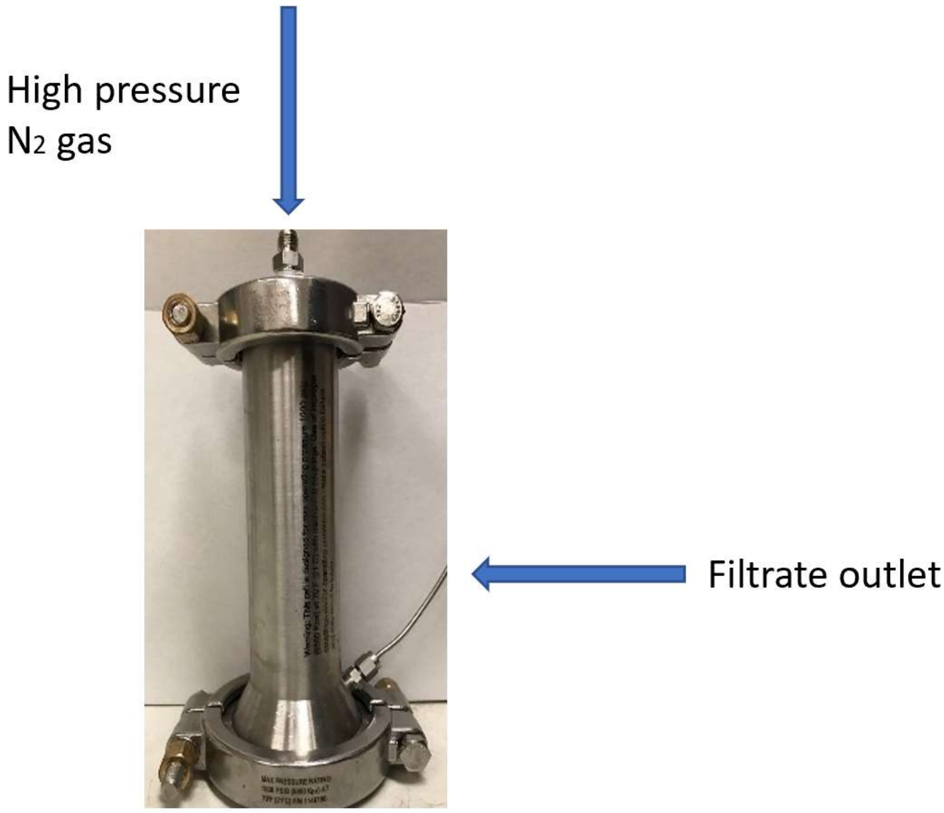

Figure 3. Schematic diagram of pressure filtration

5. A Nylon membrane with 0.22 μm pore size was used as the filter medium. The film and the membrane then soaked in ethanol for separation. A graphene oxide and PVA film then formed and separated from the nylon membrane.

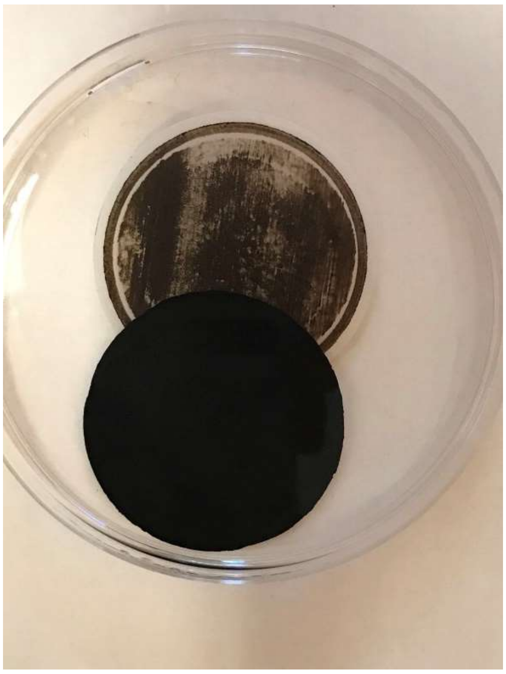

Figure 4. Obtained film after pressure filtration

6. Dried the obtained GO/PVA film in an oven and then reduced in 15% L-ascorbic acid solution. The purpose of reducing the film is to turn the GO to rGO which exhibits very high conductivity.

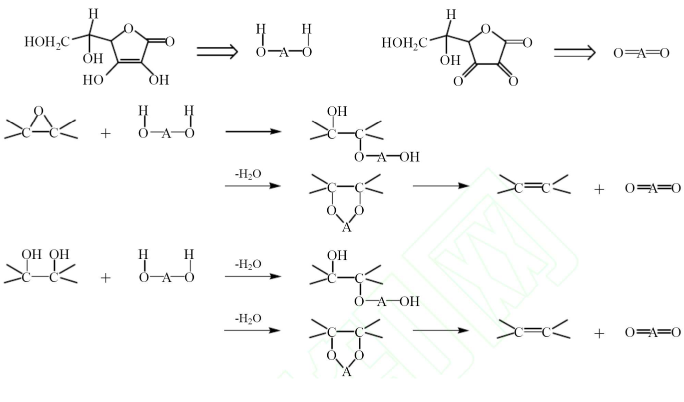

Figure 5. Estimated mechanism of using L-ascorbic acid reduce graphene oxide

7. Dried the reduced GO/PVA film. A rGO/PVA conductive film was obtained for further property tests.

Figure 6. Conductive film obtained after reducing

Conductive film with cellulose nanofibril (CNF) as strengthening agent

1. CNF was used as received, (1%, Cellulose Lab)

2. Measured the obtained graphene oxide solution concentration and mixed with CNF at a designed ratio to control total solid content of the solution to 50 mg. Graphene oxide was used for film stock because of its good dispersibility in water.

3. Ultrasonicated the above mixture for 10 min to form a uniform solution of CNF and graphene oxide

4. Use pressure filtration to filtrate overnight. The filter was connected to a high-pressure nitrogen gas cylinder to keep the pressure at stable 20 kPa.

5. A Nylon membrane with 0.22 μm pore size was used as the filter medium. The film and the membrane then soaked in ethanol for separation. A graphene oxide and CNF film then formed and separated from the nylon membrane.

6. Dried the obtained GO/CNF film in an oven and then reduced in 15% L-ascorbic acid solution. The purpose of reducing the film is to turn the GO to rGO, which exhibits a high conductivity.

7. Dried the reduced GO/CNF film. A rGO/TEMPO-ed CNF conductive film was obtained for further property tests.

3.3 Testing

Electrical Resistivity and Conductivity Testing

A Keithley Model 2750 multimeter and custom-made four-probe test apparatus were used to measure the resistivity of the PVA/rGO film using the four-point probes method.

The method uses one pair of probes for current carrying and one pair for voltage-sensing to achieve more accurate measurements. Compared with traditional two-point probes one, the individual pairs for current and voltage eliminates the lead and contact resistance from the probes, especially for the objects that have very low resistance values.

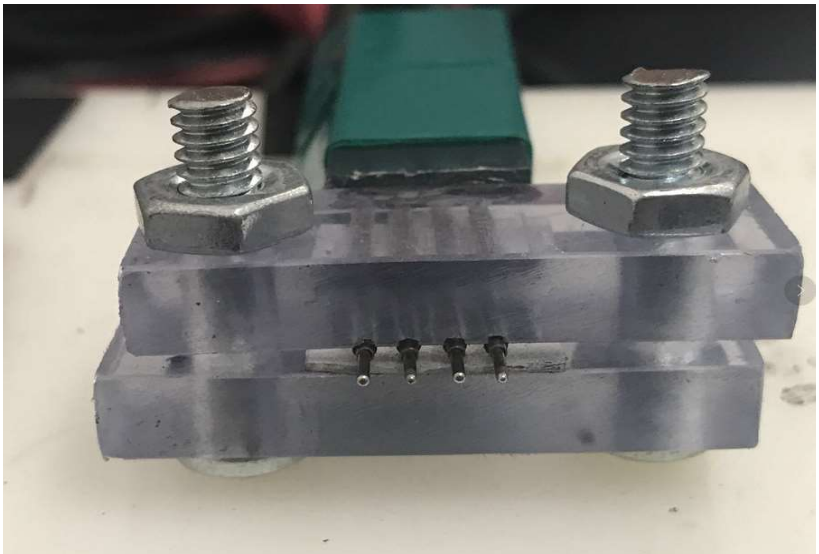

Figure 7. Custom-made four-probe test apparatus

When using 4-point probes method, a pair of force connections supplies current which generates a voltage drop through the impedance to be measured according to Ohm's law, V=IR. Meanwhile, another pair of sense connections which are adjacent to the target impedance, as a result the voltage drop in the force contacts or leads are not included. The voltage drop in the sense leads is negligible, because almost no current flows to the measuring instrument. When the 4 probes are arranged in a straight line, press on the surface of the prepared films

For resistivity of a semi-infinite sample:

$$\rho = \frac{V}{I}C$$

ρ - Resistivity

V - Voltage between probe 2 and 3

C - Probe coefficient

Where C is the probe coefficient related to distances between probes:

$$C = \frac{2\pi}{\frac{1}{s_1} + \frac{1}{s_2} - \frac{1}{s_1 + s_2} + \frac{1}{s_2 + s_3}}$$

S - Distance between two neighbor probes

The custom-made four-probe test apparatus has:

$S = S_1 = S_2 = S_3$

$$\rho = 2\pi S \cdot \frac{V}{I}$$

A semi-infinite set is bounded in one direction, and unbounded in another (Jayaswal et al., 2018). The prepared films are not a semi-infinite sheet, a calibration parameter F is needed:

$$\rho = 2\pi SF \cdot \frac{V}{I}$$

F - Correction of thickness, lateral length and distance of probes and edge, when t <<s, we get current rings instead of spheres. Therefore, the expression for the area A=2πxt.

$$R = \int_{x2}^{x1} \rho \frac{dx}{2\pi xt} = \int_{s}^{2s} \frac{\rho}{2\pi t}\frac{dx}{x} = \frac{S\rho}{2\pi t}\ln x = \frac{\rho}{\pi t}\ln 2$$

X - Distance to the probe in thickness direction

for R=V/I, the sheet resistivity for a thin sheet is:

$$\rho = \frac{\pi t}{\ln 2} \cdot \frac{V}{I} = 4.532t \cdot \frac{V}{I}$$

t - Sample thickness

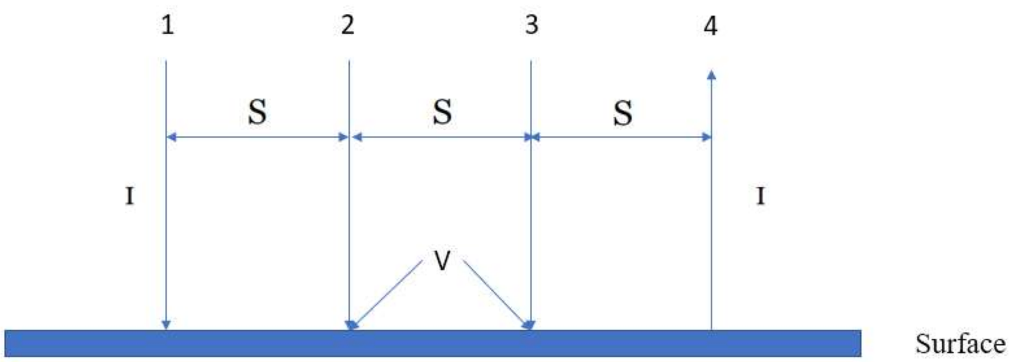

Figure 8. Schematic of 4-point probe configuration

The prepared films were conditioned in a constant temperature and moisture lab for 24 hours at 22±1℃ and 50±2%. The conductivity of each film was determined by the average of 5 measurements.

Thickness measurement

Thickness of prepared films was measured using an electronic thickness tester (THWING-ALBERT INSTRUMENT COMPANY). All prepared films were conditioned in a constant temperature and moisture lab for 24 hours at 22±1℃ and 50±2% before taking to test. The thickness of each film was determined by the average of 5 measurements.

Figure 9. Film thickness tester

Strength Property Testing

A Tinius Olsen 2000 stress and strain tester was employed to evaluate the stress and strain of samples according to TAPPI standards. The prepared films were cut to strips with 15mm width by a standard die cutter. All the samples were conditioned in a standard environment at 22±1℃ and 50±2% for 24 hours before testing.

Figure 10. Stress and strain tester

3.3 Inventory Tracking and Monitoring System

3.3.1 System Structure

Apache was used as the web server in the system and its key function is to parse any request from client software (browser, mobile phone) including chemical inventory search, user login in and out, etc. Once Apache gets the request from the client software, it will display the correct results according to the code within the inventory database.

PHP is a server-side scripting language stands for Hypertext Preprocessor and was used to achieve a dynamic database in the system. A dynamic database or website allows users to have a real-time database such as stock in date, expiry date and quantity that can change with time or an event.

MySQL is the "inventory" of this system or widely known as the database. It allows PHP and Apache to work together to input and output date in a readable format to a browser.

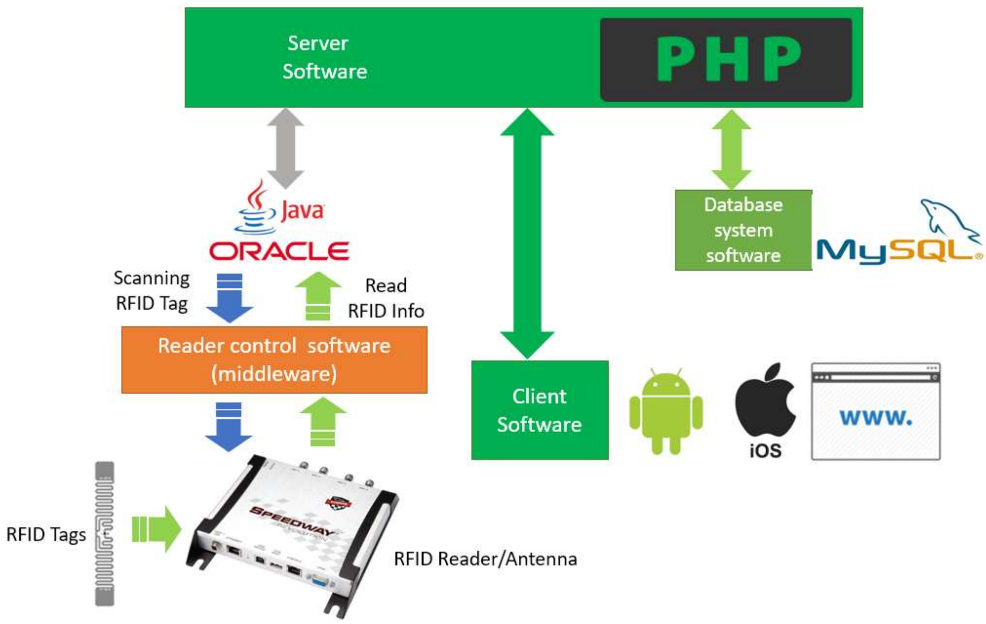

Figure 11. Schematic Structure of Inventory Tracking and Monitoring System

A simple way to understand the structure of this inventory tracking and monitoring system is to imagine the system is a restaurant. Customers come to the restaurant and each of them expects different dishes, unlike a buffet where everything is prepared beforehand and customers could only choose what is available, waiters in the restaurant are encouraged to interact and complete any special needs.

Apache is the chef of this restaurant and whatever people ask for, the chef prepares it in a quick, flexible way. He is also able to handle a multitude of different types of foods. In the system, Apache is in charge of parsing the request that from PHP for instance login, register, inventory search, etc.

PHP is the waiter that bridges the customers and kitchen. He is able to carry the requests back to the kitchen with specific instructions how each customer would like the food to be cooked.

The Inventory Tracking and Monitoring System is similar to this restaurant, it allows users (customers) to register, sign-in/out, search or update inventory, check expiry data of chemicals, etc. (order something different and specific). There are two methods of input, from a client software or RFID antennas.

- From a client software:

A typical client software is a browser for instance Microsoft Internet Explorer. A user can sign into the system by inputting the address in a browser and his/her username and password. Both the parsed username and password go to the Apache server and PHP takes the order and searches within MySQL database. If the username is registered and matches the password, PHP takes the result back to Apache and related information will go back to the client software.

- From RFID antennas:

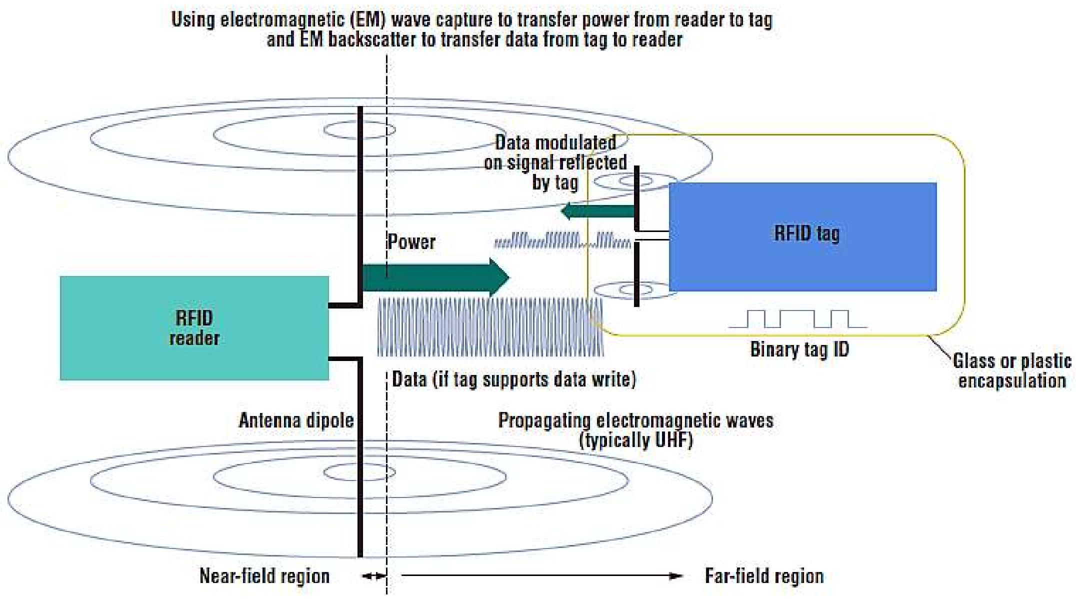

Figure 12. Communication between RFID tag and reader/antenna

Real time inventory is achieved by way of RFID input. Unlike input from users, input from RFID is automatic as long as the tag is in the communication range of the reader/antenna. A RFID tag that has the information of expiry date, CAS number, supplier, and phase gets powered up by the electromagnetic field that is from a reader/antenna and gives back all the stored data, after that it is similar to the input from a client software.

3.3.2 Data Classes

There are three classes of information included in the system: static, dynamic and user information

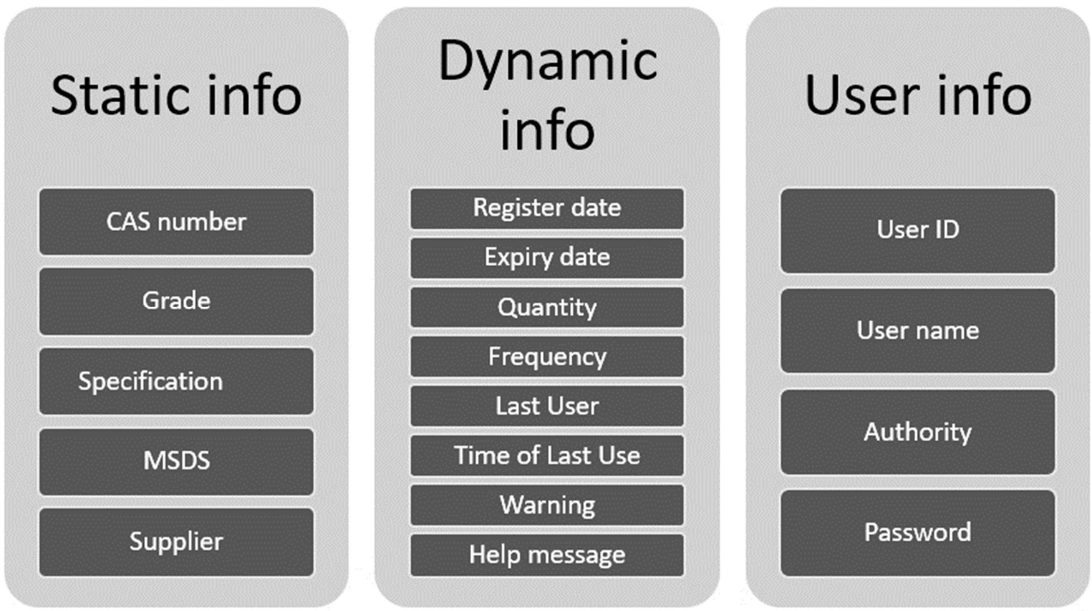

Figure 13. Information Classes

The static information mainly consists of CAS number, MSDS, supplier, etc. that cannot be changed after being registered in the database. All the static information is stored in the RFID tag and database (except MSDS stored in the server) and can be displayed in client software.

Table 3. Static information storage and display

Items	RFID tag storage	Database storage	Client Software display
CAS number	√	√	√
MSDS	√		√
Grade	√	√	√
specification	√	√	√
State	√	√	√
Supplier	√	√	√

Chemical Abstract Services Registry Number also known as CAS number is an authoritative collection of disclosed chemical substance information. It is a unique numerical identifier assigned by Chemical Abstracts Services and can be used in the inventory tracking and monitory system and linked with MSDS in the database.

Material Safety Data Sheet- MSDS is an important component of product stewardship that has related safety and health information. There are 9 items that are mandatory on an MSDS in Canada:

1. Product Information: product identifier (name), manufacturer and suppliers' names, addresses, and emergency phone numbers

2. Hazardous Ingredients

3. Physical Data

4. Fire or Explosion Hazard Data

5. Reactivity Data: information on the chemical instability of a product and the substances it may react with

6. Toxicological Properties: health effects

7. Preventive Measures

8. First Aid Measures

9. Preparation Information: who is responsible for preparation and date of preparation of MSDS

There are 7 grades commonly used in a lab and 1 digit is used in a RFID tag to identify the chemical grade.

Table 4. Chemical grade category

Grade	Description
A.C.S.	A chemical grade of highest purity and meets or exceeds purity standards set by American Chemical Society (ACS)
Reagent	High purity generally equal to A.C.S. grade and suitable for use in many laboratory and analytical applications.
U.S.P.	A chemical grade of sufficient purity to meet or exceed requirements of the United States Pharmacopeia (USP); acceptable for food, drug, or medicinal use; may be used for most laboratory purposes.
N.F.	A grade of sufficient purity to meet or exceed requirements of the United Stated National Formulary.
Lab	A chemical grade of relatively high quality with exact levels of impurities unknown; usually pure enough for educational applications. Not pure enough to be offered for food, drug, or medicinal use of any kind.
Purified	Also called pure or practical grade and indicates good quality chemicals meeting no official standard; can be used in most cases for educational applications. Not pure enough to be offered for food, drug, or medicinal use of any kind.
Technical	Good quality chemical grade used for commercial and industrial purposes. Not pure enough to be offered for food, drug, or medicinal use of any kind.

Chemical phase describes the state of the chemical, numbers 1,2,3,4 are assigned to gas, liquid, solid and solution respectively.

The dynamic information consists of registery date, expiry date, quantity, usage frequency, last user, and so on. The user information consists of user IDs, authority password, etc. The purpose of classifying the information is due to different coding requirements.

Table 5. Dynamic information storage and display

Items	RFID tag storage	Database storage	APP display
Stock in Date	√		√
Expiration Date	√		√
Quantity		√	√
Usage frequency		√	
Last User Name		√	√
Last Usage Time		√	√
Help message		√	√
Expiration Alarm	√		√
Chemical location	√		√
Unauthorized User	√		√

There are 6 types of data related to user information: user ID, username, authority, password, location and duration of chemical usage by user. The storage and display are shown below:

Table 6. User information storage and display

Items	RFID tag storage	Database storage	APP display
User ID	√	√	√
User name		√	√
User authority		√	√
User password		√	√
User Location		√	√
User usage time		√	√

Only the user ID is stored in the RFID tag (user tag), other related information is stored in the server after users register in the system and are one to one corresponded with username. The managing authority can only be assigned by the lab manager that has the authority to access user location, usage time, etc.

Chapter 4

Results

4.1 Carbon based material vs metal antenna

When it comes to RFID tags, most of the companies will not be recycling them because of the labor cost (Luttropp & Johansson, 2010). Thus, replacing the metal antenna by carbon based conductive materials is not only an environmentally friendly process, but also advanced carbon materials possess some features that metals do not have.

As discussed in Chapter 2, advanced carbon materials exhibit some favorable properties compared with most metals such as: mechanical reliability, weight savings and excellent environmental toughness. Considering RFID tags application environment, mechanical reliability and excellent environmental toughness are very important. For instance, when applying the tags onto special-shaped surfaces like chemical bottles, lumpy corrugated paper, buckets, etc., good mechanical properties, especially high strain, are required. In the case of logistics, extreme conditions like temperature and humidity happen from time to time, that requires the tags hold high environmental toughness.

The drawbacks of carbon materials are: limited in their performance owing to high sheet resistance (B. Huang, 2007), and leads to more loss of the device itself and lower radiation efficiency and gain (Mobashsher, Islam, & Misran, 2010), particularly in passive electronics like RFID antenna. To overcome the above difficulties, a carbon-based material that features both good conductivity and mechanical properties was selected, fabricated and tested.

4.2 Characterization

4.2.1 Prepared Graphene

Graphene is a single layer of carbon hexagonal lattice that are held together. The excellent characteristics like super high conductivity and high mechanical properties are from the 2p orbitals, which form the p state bands that delocalize over the sheet of carbons that constitute graphene. It is impermeable to gases and exhibits a high mobility of charge carriers. To achieve a high conductivity, graphene is an ideal carbon-based material that exhibits extremely high conductivity.

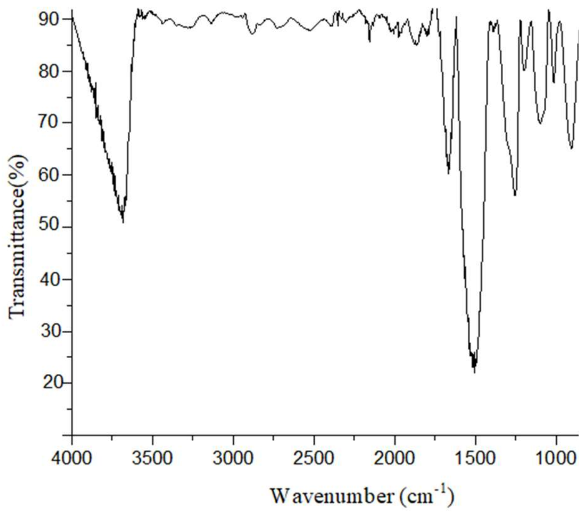

Figure 14. FTIR-ATR spectrum of prepared rGO

Unlike the graphene prepared by mechanical methods, Hummers method uses chemicals to break the graphite layers. It shows in **Fig. 14** that a broad absorption band occurred at 3650 cm^{-1} in spectrum which is associated with the stretching vibration of hydroxyl groups that come from the H_2O molecules. The strong peaks at 1550 cm^{-1} and 1720 cm^{-1} can be attributed to the stretching vibration of carbonyl and carboxyl groups. Other groups like -COOH, C-OH, C-O can also be found based on the observation of FTIR.

There are three steps involved during the formation of GO (Dimiev & Tour, 2014):

1. Sulphuric acid, potassium persulfate reacts with graphite to form graphite intercalation compounds (GIC) at high temperatures.

2. The stage-1 GIC is converted into an oxidized and c-axis ordered form of graphite, which we define as PGO; it involves insertion of the oxidizing agent into the preoccupied graphite galleries at medium temperatures.

3. PGO is converted into GO after exposure to water where there is no remaining c-axis order.

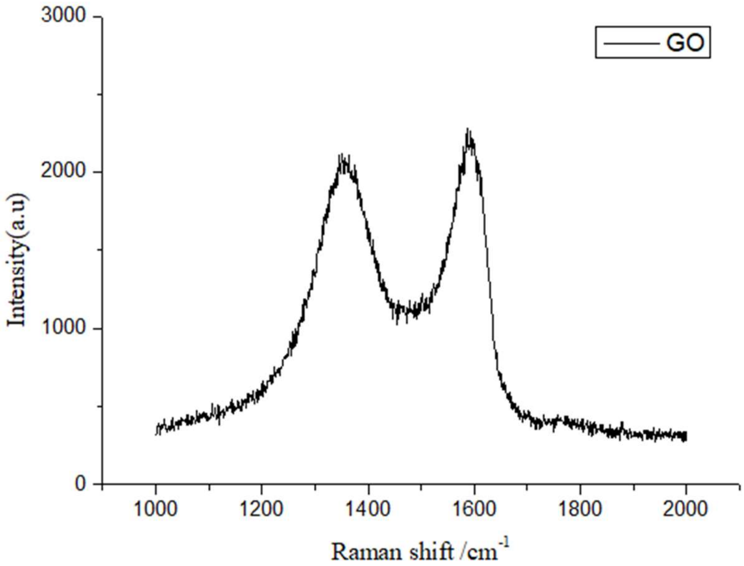

Figure 15. Raman spectra of graphene oxide

Fig. 15 shows that there is a strong G band at 1592 cm^{-1} and a weak D band at 1350cm^{-1}. Both G band and D band are attributed to the first order scattering from E_{2g} phonon of sp^2 carbon bonding and structural defects.

4.2.2 Cellulose nanofibril

Cellulose nanofibril (CNF) is a sort of cellulosic material that is the main content of plants and it is the most abundant natural polymer on the earth, more importantly it is harmless to human body.

CNF is flexible, possesses large aspect ratio, large specific surface area and extensive hydrogen-bonding ability. Because of the above properties, CNF has been utilized as a strength agent, oxygen resistant agent, and stabilizer.

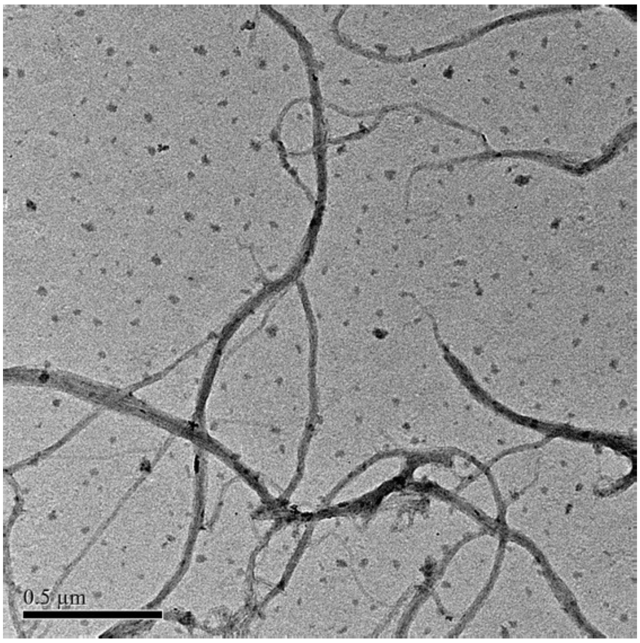

Figure 16. TEM of CNF

4.3 Conductivity

There are many electrically conductive non-metal materials available, for instance polypyrrol, graphite, carbon black, and graphene. As discussed in literature review, graphite, polypyrrol and other carbon-based particles have much lower electrical conductivity compared with metals, considering RFID application, conductivity is a key property that is highly related to communication distance, graphene is the most ideal non-metal conductive filler that can be used for conductive film in this case.

4.3.1 Graphene/CNF film

Graphene itself has no film forming ability, thus other additives are selected to mix with graphene for mechanical and film forming purposes. The films were kept at 50 mg total solid content before filtration and the CNF contents were chosen to be 30%, 50% and 70% in order to achieve a balance of conductivity and mechanical properties.

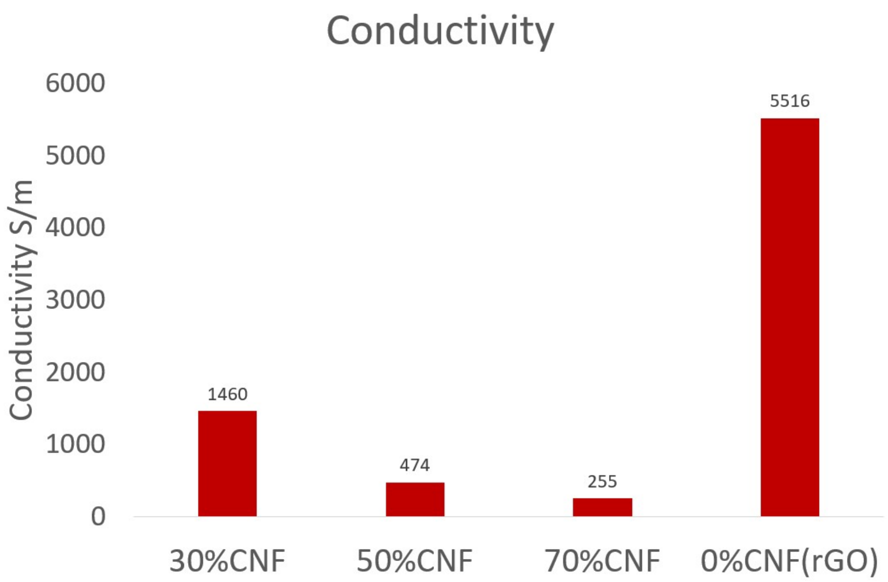

Figure 17. Effect of CNF content on the conductivity of the PVA film

As discussed, because CNF holds extensive hydrogen bonding and large specific surface area, it can act as the skeleton of the film and hydro bond with graphene, even with up to 30% content CNF in the film, over 1400 S/m conductivity can still be achieved. But when further increasing to 50% and 70%, the conductivity dropped dramatically from 1459 S/m to 474 then 255 S/m. It is found that CNF plays a key role in enhancing the interaction of graphene (Peng et al., 2018) and this could be the reason that high conductivity could be achieved by relatively low CNF content. As discussed in 2.3, the fiber-shaped CNF and its extensive hydrogen bond improved the distribution and orientation of graphene in the film, and the touching mechanism is mainly responsible for the conductive networks although the adjoining mechanism may also come into play.

4.3.2 Graphene/PVA

Based on the discussion of 4.1.1 and 4.1.2, graphene oxide was selected as the electrically conductive carbon-based material for its high conductivity after being reduced and relatively good mechanical property. PVA was chosen because of its excellent film-forming feature and strain property that could act as a glue in the film and gives high strain to the film. High molecular weight PVA (Mw 85000-124000), with over 99% hydrolysis degree, was selected due to high reduced temperature at 75°C and better strength.

Higher conductivity antenna gives greater distance that the tags can be read by the RFID reader. Greater distance could improve the readability especially in the complex environment of a warehouse including possible metallic shields, movement, or existed obstacles.

The prepared films were kept at 50 mg total solid content before filtration and the PVA content were chosen to be 20%, 30% and 40% in order to achieve a balance of conductivity and mechanical properties.

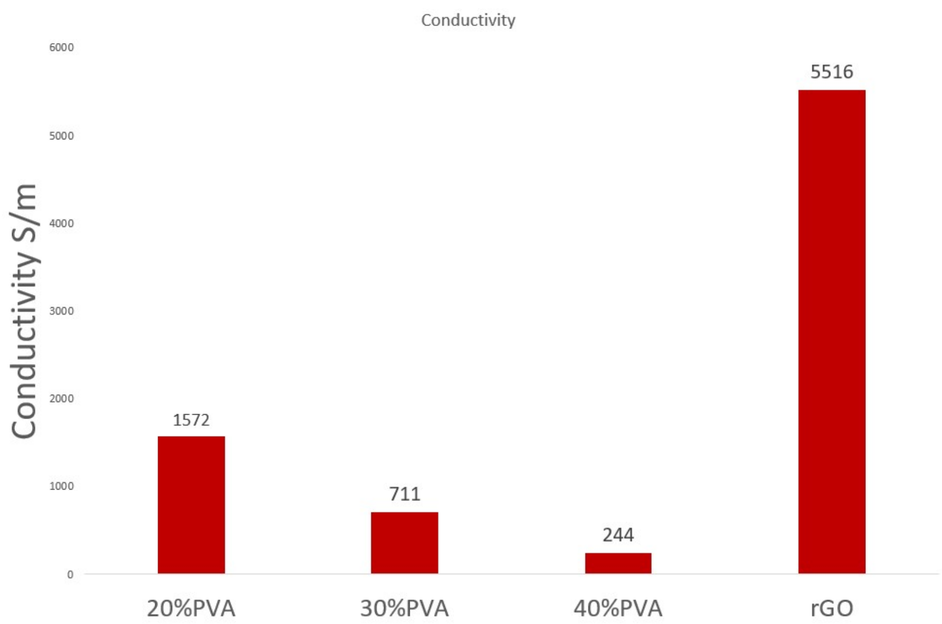

Figure 18**.** The effect on conductivity with respect to increase PVA content in the film

Conductivity plays a key role in communication distance if the film is used as the antenna of the RFID tags. Higher conductivity gives greater communication distance that results in better accessibility than in an unusual environment, it still can be received by RFID readers especially considering handhold RFID readers have lower communication distance and are widely used compared with other types of readers. Higher conductivity also gives the possibility to overcome the metal shield.

It should be noted that the conductivity of rGO without any PVA, was the highest at 5516 S/m and can be considered as the benchmark. With the increase of PVA content from 20%, 30% to 40%, it can be observed that the conductivity was reduced from 1572, 711, to 244 S/m due to the insulation property of PVA. It is in accordance with the discussion in 4.1 that graphene features excellent conductivity and increasing the graphene content in the film will significantly increase the conductivity of the film. It can be explained that there are more "paths" available for electrons that result in general higher conductivity, on the contrary, the insulation of PVA blocks the "paths" and increased PVA content negatively impacts the conductivity of the films. Compared with CNF/rGO film, 1459 S/m conductivity was achieved, it agrees with the conclusion in 4.2 that the connections are less blocked by the nanostructure among graphene particles, thus 30% CNF could reach almost the same conductivity as 20% PVA.

The relatively low conductivity of rGO can be attributed to the fact of Hummers method. As per discussion in Chapter 2, the presence of oxygen, hydrogen atoms in the carbon materials will decrease the electro-conductivity due to lack of conjugated structure.

The conductivity that is sufficient for antenna purposes was identified to be over 500 S/m according to other researchers (Rouse, Kurz, Petersen, & Colpitts, 2013). Some researchers coated graphite with the addition of latex and binder onto paper substrate and used as the antenna of RFID tags, the result shows the communication distance reaches 10m when conductivity was at the highest 874 S/m. Compared with the conductive film with PVA content at 20% and 30%, the conductivity reaches 1522 S/m and 711 S/m, both of the films can be considered as qualified in conductivity point of view.

Graphene is also widely used in conductive coatings, hydrogel and other conductive materials for various end uses. Sahiner and Demirci used graphene oxide embedded cryogels for sensor application, the conductivity was from 1.03×10^{-10} to 1.38×10^{-4} S/cm depending on the reduced chemicals (Sahiner & Demirci, 2017). Some researchers also used expanded graphite in an aqueous environment with the addition of cellulose Nanocrystals (CNF) as a dispersant to produce highly conductive cellulose composites, at optimal 4% CNF dosage, the conductivity reached about 2600 S/m which was reported as the highest by using graphite (Liu et al., 2018). The mechanical strength of the coating layer itself was not high and relied on the substrate for instance paper, but for RFID tag antenna purposes, it is challenging when applying the tag onto an irregular surface.

4.4 Mechanical Properties

Mechanical properties including tensile strength and Young's modulus could demonstrate the environmental toughness that tags can withstand. Tensile strength represents the force that will pull the film to the point where it breaks, and higher tensile strength gives higher chance that tags could work when being pulled in the application scenario. High Young's modulus shows the elongation before film break. Both of two mechanical properties can represent the toughness the tags can withstand during logistics, storage and transportation.

4.4.1 Mechanical Properties of Graphene/CNF Film

The nanostructure of CNF that could establish hydrogen bonds with graphene particles and act as normal cellulose fibers to be the skeleton of the film thus supposed to benefit the mechanical property of the conductive film. Upon attempt to measure the mechanical property, it was not measurable due to its too low stress. But if applied as a coating color on a paper, the required strength may be provided by the paper itself.

(Peng et al., 2018) used graphene (rGO) as the filler to achieve a mechanically strong and sensitive aerogel for sensor application, the results showed when CNF was at 80% the highest stress was up to 4-5 KPa which is similar to our conclusion. For the tag antenna application, over 5 MPa is recommended due to the environmental endurance requirements.

4.4.2 Mechanical Properties of Graphene/PVA Film

As discussed in 4.1.2, PVA features excellent film-forming and strain properties, it was selected to add into the film recipe to increase the stress and strain properties.

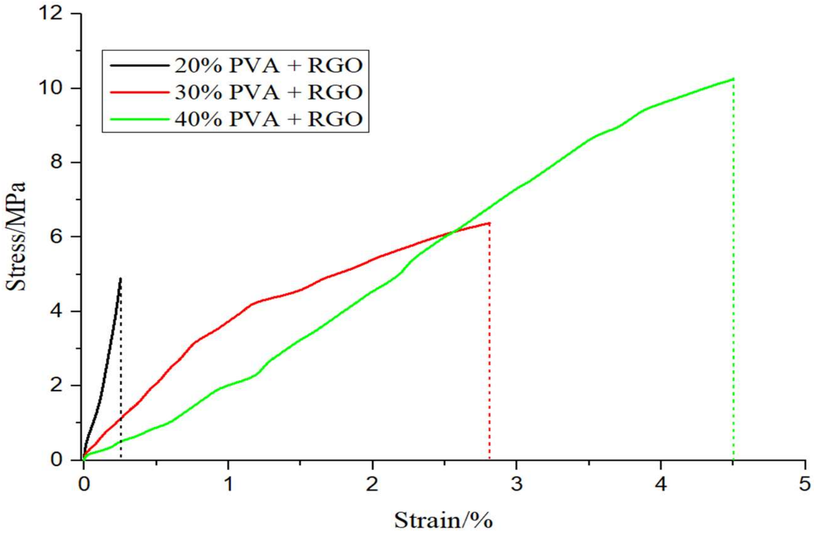

Figure 19. The effect on mechanical properties with respect to increasing the PVA content in the film

It shows in Fig.19 with the increased PVA content in films, the stress becomes greater. The stress of the film is about 5 MPa at 20% PVA content, and it goes up to as much as twice to over 10 MPa which the PVA content is at 40%. It indicates PVA has a great impact on the stress of the films.

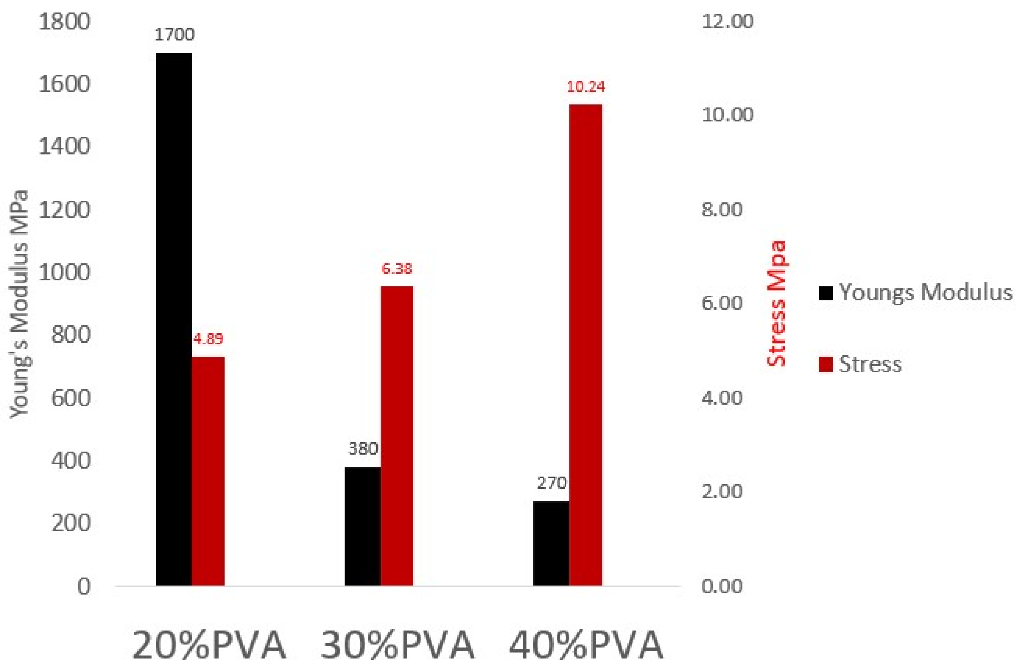

Figure 20. Young's Modulus and stress comparison

The results from Fig.19 and Fig.20 show that the stress of the film was a result of increased PVA content and higher PVA content gives higher Young's Modulus. Young's Modulus measures the stiffness of the conductive films and it defines the relationship between the stress and strain. It is used to predict how much the film extends under tension.

As discussed in Chapter 2, it is challenging to adopt RFID technology in supply chain management. One of the major concerns is that during storage, logistics including cargo, air or sea, the environment could be extreme, such as external force (tension, compression, stretching, etc.) which could damage the tags that result in inaccurate inventory, and damaged tags are not able to be recycled, which increases the cost. This can also be affected by extreme temperature and moisture. Both graphene and PVA display good chemical stability and are ideal as environmentally friendly carbon-based materials that could replace metal as the antenna of RFID tags.

4.5 Inventory Tracking and Monitoring System

Currently, only a few chemical labs have begun adopting RFID systems for inventory management and moreover most of them are in a simple form: focus only on inventory count and location, but not exact locations (shelves and rooms). A large portion of the system is in tracking large containers between the supplier and facilities, which is similar as RFID application in logistic management. There are several disadvantages that these systems have:

- Lab safety is never the highlight. Systems are geared for inventory control.

- Most often they use handheld readers for inventory checks. The current methods still require manual inventory, even though it's faster than barcodes.

- There are no mobile applications.

- The systems for RFID and chemical management tends to be complicated and reading intensive.

In consideration of the above situation, it is a promising area that a comprehensive RFID system could provide a simple and automatic system that merges safety and inventory management with RFID technology. Compared with current lab management system, our advantages are:

- Focus on enhancing lab safety by including additional safety features

- Seek to eliminate the tedious manual labor for taking inventory

- Our system combines everything in one truly interactive and easy to use system.

- Interactive, we mean an interactive interface that is not reading intensive

- We will be using paper-based RFID antennas, which will pave the road for green RFID technology

4.5.1 Passive RFID tag

There are 24 digits in a RFID tag and 20 of them can be customized according to Electronic Product Code (EPC) standard. The first 4 digits are E280, a universal header and cannot be customized. There are 7 digits used for Chemical Abstracts Service (CAS) number which are identical and used for chemical identification. The following 2 digits are used for state (solid, liquid or gas) and supplier identification. 4 digits are used for expiry date and another 4 digits for specification. The last digit is used for grade (analytical, industrial, etc.)

With customized 20 digits, a RFID tag can be utilized for the following purposes in our Inventory Tracking and Monitoring System as shown in Fig.21.

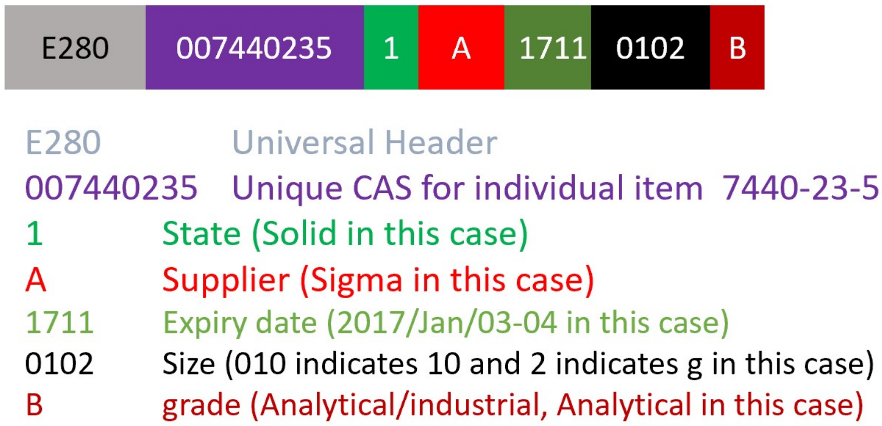

Figure 21. EPC standard used for chemical inventory management

4.5.2 Framework for the Key Functions

The framework for the functions consists of four main functions: authority, inventory, safety, and location.

4.5.3 Authority

The authority function allows us to monitor and control who has access to the chemicals. It is a key that managers are able to control the chemicals that only authorized users have access to the chemicals and continuously monitor them.

Unlike other laboratory management systems, instead of tagging only chemicals, there are two types of tags for users which have different authorities-manager tag and user tag. The manager and user tags are used for identification, location and safety purposes.

- User Tag, it is mandatory that
all the laboratory users have their own tags and carry the tag all the time when working in the lab.

- Manager Tag, it owns the highest authority that can update inventory, check the last location of laboratory users for safety reason, and receive alerts.

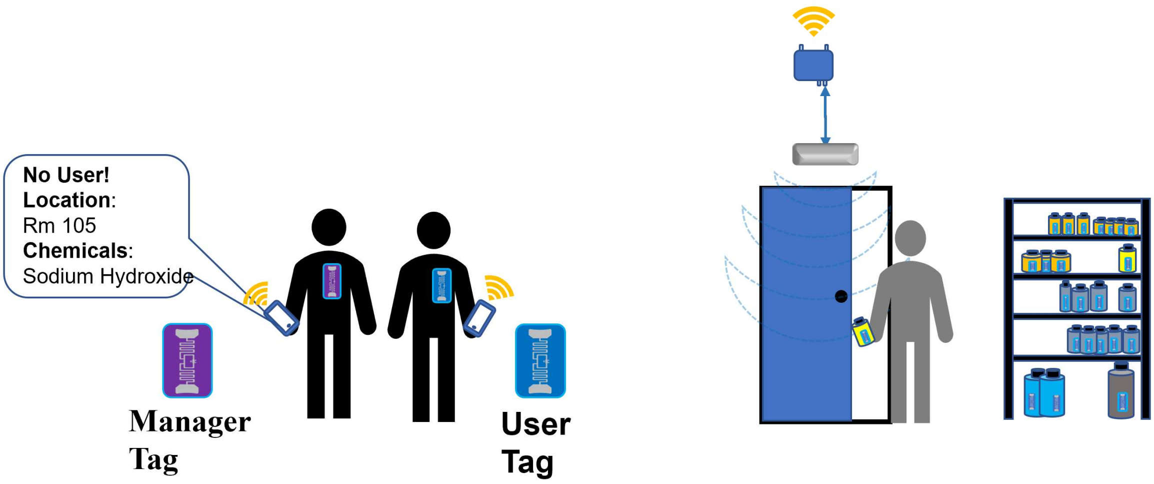

Figure 22. Schematic of RFID authority control

The RFID antenna is located at the entrance of the chemical storage room, for safety and location reasons, each chemical movement, for instance from the chemical storage to labs, must be in correspondence with a user/manager tag for system record purposes. Only the managers could see the users' location for privacy reason unless there is an accident that the user's location will be shared to all the related people. Any chemical movement without a user tag, it is considered as non-authority and will trigger the alert. The alert only goes to managers for further actions.

4.5.4 Inventory

The inventory function is designed to automatically update the inventory, eliminating manual labor for inventory. RFID is a wireless method of identification; multiple tags can be scanned simultaneously and wirelessly. By adopting these features to laboratory management system, we can build an automatic inventory database.

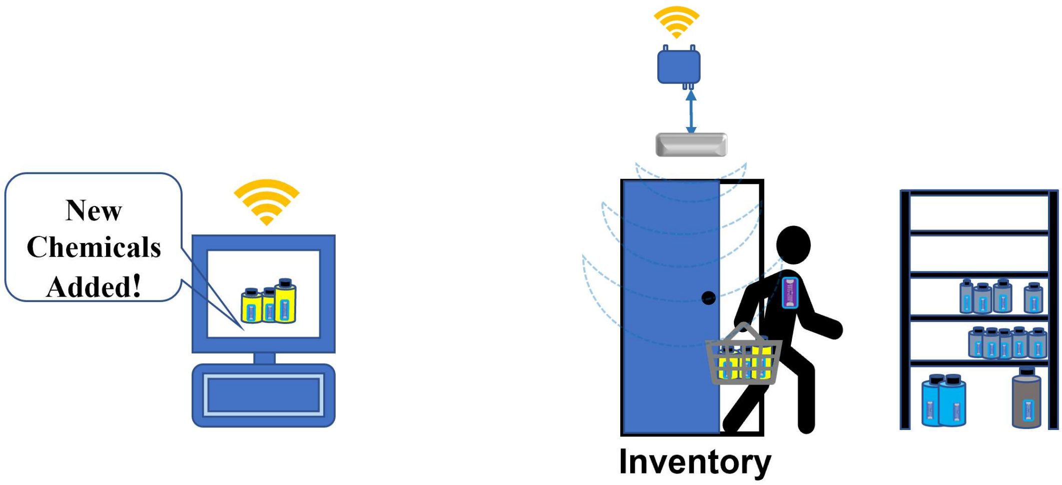

Figure 23. Schematic of automatic inventory update

Every chemical bottle has a unique tag and once new chemicals with tags (which are not in the inventory database), the RFID antenna will treat them as new chemicals and update the database automatically. The beauty of adopting RFID to inventory management here is that it does not need to be positioned in a line of sight with a scanner, which eliminates the “action” of updating inventory and more importantly with RFID technology, multiple objects can be scanned at the same time. Unlike a barcode system, RFID gives the capability to eliminate the tedious manual labor for taking inventory.

4.5.5 Safety

The safety function is designed to increase safety within the laboratory through a variety of features. Once again, we focus on safety within the lab environment

Safety is always the most important thing in a chemical environment. It is possible to improve the lab safety by utilizing the advantages of RFID tech for example, to avoid putting incompatible chemicals close to each other.

Putting conflict chemicals together is risky, for instance, acids and bases, more importantly, mixing some chemicals might be explosive. It is recommended not to store conflict chemicals on the same shelf. In order to monitor the chemical conflicts, there is a RFID antenna located on top of each chemical shelf. The antennas only monitor their own shelves.

If any user at any time puts a chemical that is conflict to the chemicals on the shelf, as the antennas are continuously monitoring the shelves, the system will recognize it and alert managers to take further actions.

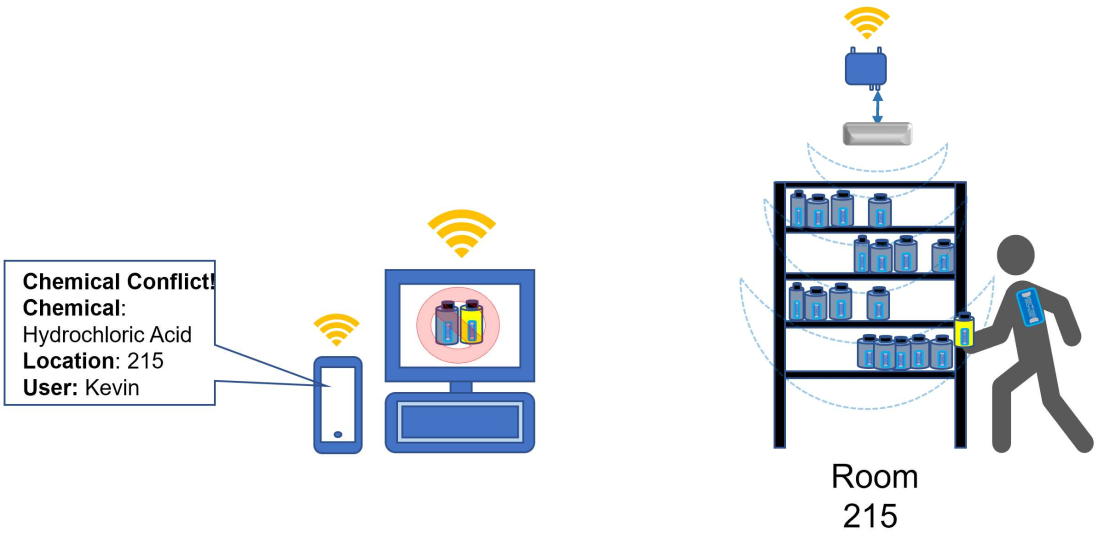

Figure 24. Schematic of chemical conflicts alert

It also happens that there are expired chemicals still staying in the laboratory for some reason. Expired chemicals not only negatively impact the experiment result and waste researchers' time, but if the lab is used for quality control purpose in a factory, the loss is inevitable. Expired chemicals can also be dangerous, for example, hydrogen peroxide can be explosive when expired.

There are two ways to prevent the loss from an expired chemical.

- Preventive

Like all maintenance in factories, preventive maintenance is always preferred. To prevent or reduce chemical expiration, as demonstrated in Fig.21, there are 4 digits used to record the expiry date in a tag and this is recorded in chemical inventory database. In the system, chemicals are marked in 3 different colors: red color indicates this chemical is already expired and should be disposed immediately. If a chemical is marked with yellow color, the expiry date is close and is an indication to all users to consume it first. White color chemicals do not need users' attention. Classifying chemicals by expiry date and marking them with different colors can give all the laboratory users indication how to consume the chemicals in a time order.

- Breakdown

Expired chemicals are not allowed in the lab. An alert will send to lab managers 24 hours before expiry date to further remind taking actions. If for some reason chemicals expire and no action has been taken before the date, chemicals are marked with red color and an alert with exact location will send to all lab users including managers to prevent use.

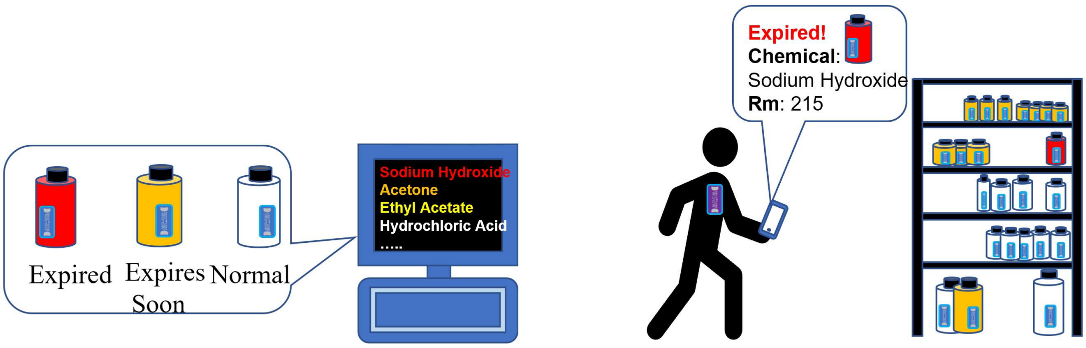

Figure 25. Chemicals marked with different colors

Functioned by both preventive and corrective methods, the inventory is supposed to be lower, making the lab safer.

4.5.6 Location

The last is the location function. The purpose of this function is to increase visibility of chemical locations down to the exact location to improve trackability.

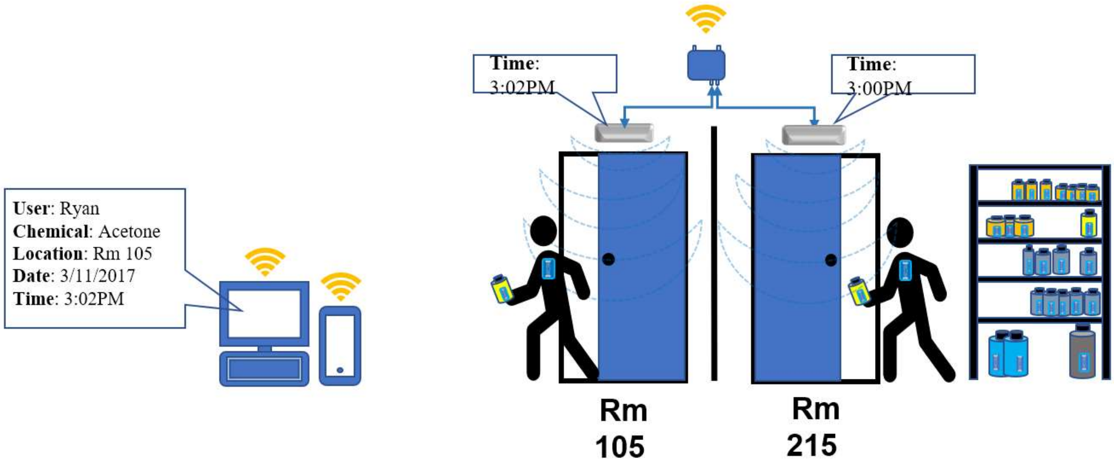

Figure 26. Location function

All the chemicals are required to return to storage room after use or at least before the end of the day for safety reasons. In most of the labs especially in schools, unlike in factories, there are more challenges for lab managers, like lack of orientation, unfriendly learning curve in a high turnover environment, over capacity, etc. Forgetting to return chemicals to the storage room happens often under this situation and it is risky to leave the chemicals in the lab without attention. It is challenging for managers if this happens too much, as the inventory is not accurate, which is costly. Some chemicals might require to be stored under certain special conditions like specific temperature or moisture, and it is possible that chemicals can be left in a lab for long time and turn expired eventually.

To reduce and prevent any unattended chemicals in the lab, it is necessary to track all the chemicals in real time.

To achieve real-time chemical tracking, there is a RFID antenna at the entrance of each lab and chemical storage room. The system records both user and chemical tags, the last location and time are recorded by the antenna at the entrance of each room. This information is very useful, especially when there are multiple labs sharing one chemical storage room, as in a university or high school. Borrowing chemicals among different departments is also common and the system could aid all the lab managers understand the inventory in a better way.

When users forget to return the chemicals to the storage room at the end of the day, an alert will send to the users and lab managers to remind in taking further actions.

Chapter 5

Conclusions

5.1 Summary of Work

In this inventory tracking and monitoring system for chemicals, a database has been built with Java, MySQL, and Apache languages. The system is capable of authority control, automatic inventory updates, safety that includes conflicting chemical alerts and expiry date alerts, and location functions. The system has been successfully demonstrated to NBIF. According to literature review, RFID is widely used in supply chain, but only a few labs are using it for inventory control purpose, and none of the cases adopt RFID to a comprehensive inventory system that focuses on automatic inventory and laboratory safety. It is promising that with the help of the inventory system in labs, a more efficient inventory and a saver laboratory can be expected.

In this study, a novel electro conductive film also has been fabricated using pressure filtration method that consists of graphene and PVA. The film can be later processed by various methods to be casted to an RFID tag antenna incorporated into an operational UHF RFID tag following North American standards. The conductivity and mechanical properties are studied. The following observations are noteworthy:

- Graphene was selected over other carbon-based conductive materials. The decision was based on its much higher conductivity, high environmental endurance and chemical stability.

- Based on the conductivity of 20% PVA and 30%PVA content, the films are capable of reaching 10m communication distance according to Mosseler's study.

- Stress and strain testing demonstrated that with the increased PVA content in the film, the stress went up to 10.24MPa with 4.89 Young's modulus.

5.2 Recommendations for future work

The project lays the framework for future work in terms of fabrication of a conductive composite, an inventory management system that coded by open source software. It may lead to the future investigation of:

- Location of chemicals can be upgraded to as accurate as table/shelve instead of rooms. And a "daily summary report" function that includes expired chemicals with expiry date, chemicals soon to expire, inventory statues, etc.
- Alternative methods to fabricate a graphene contained composite including coating, lamination, etc.

- Optimize the preparation of graphene oxide based on Hummer's method, for instance better reduction agent or procedure. Better mechanical properties or electrical conductivity can be expected.
- Due to the limited access of different types of graphene, using physically prepared graphene or graphene fibers as the conductive filler to further enhance the strength and conductivity would be of interest to investigate.

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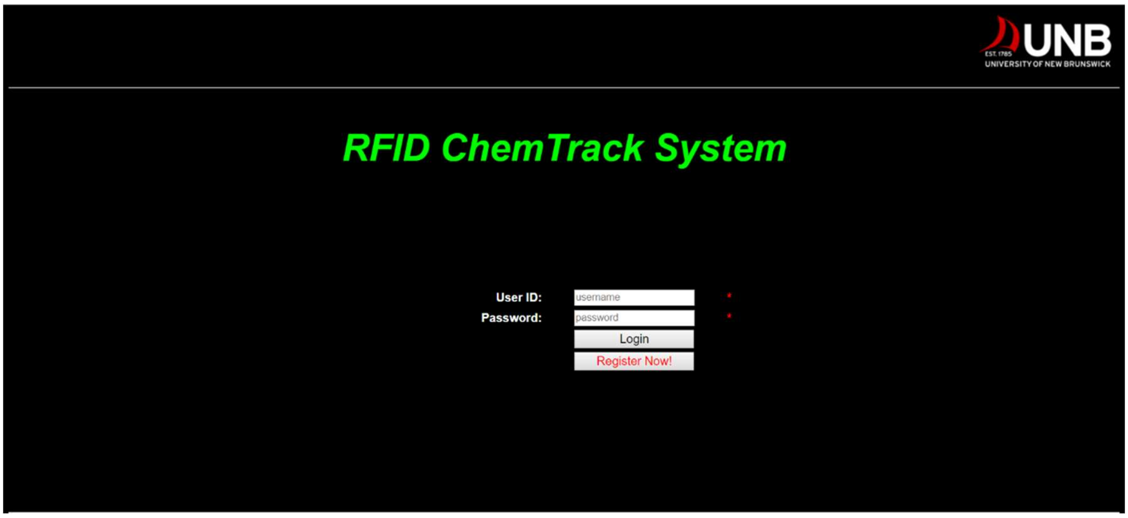
APPENDIX I

Interface of inventory management system



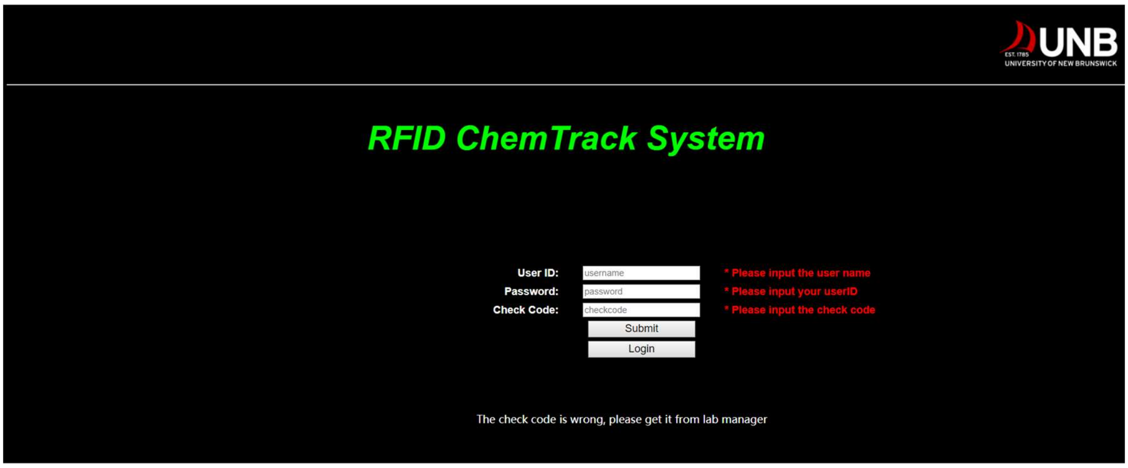


Figure 27. User registration

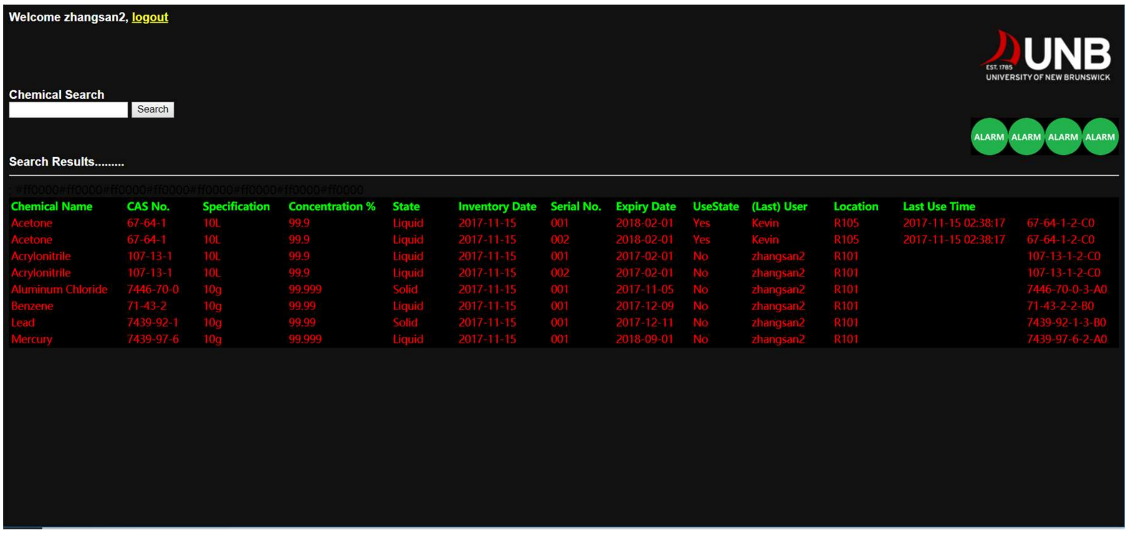


Figure 28. Chemical inventory with details after logging in

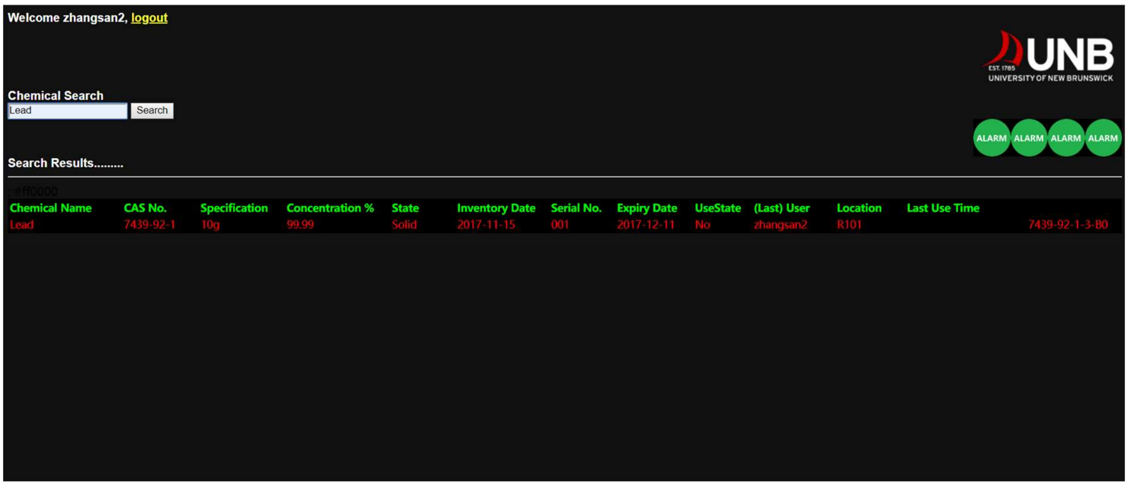
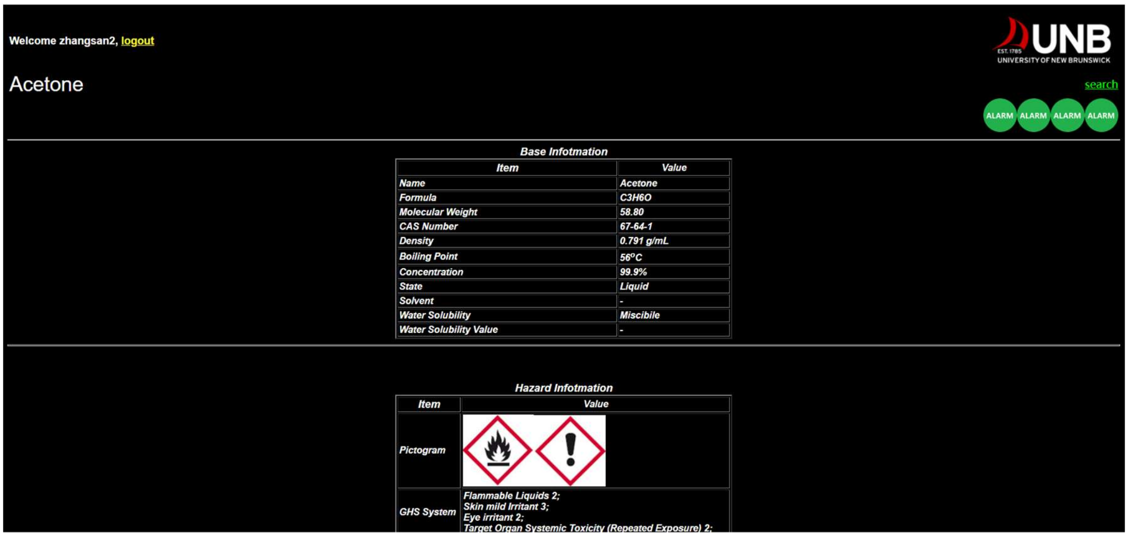


Figure 29. Searching



Welcome zhangsan2, logout

Acetone

search

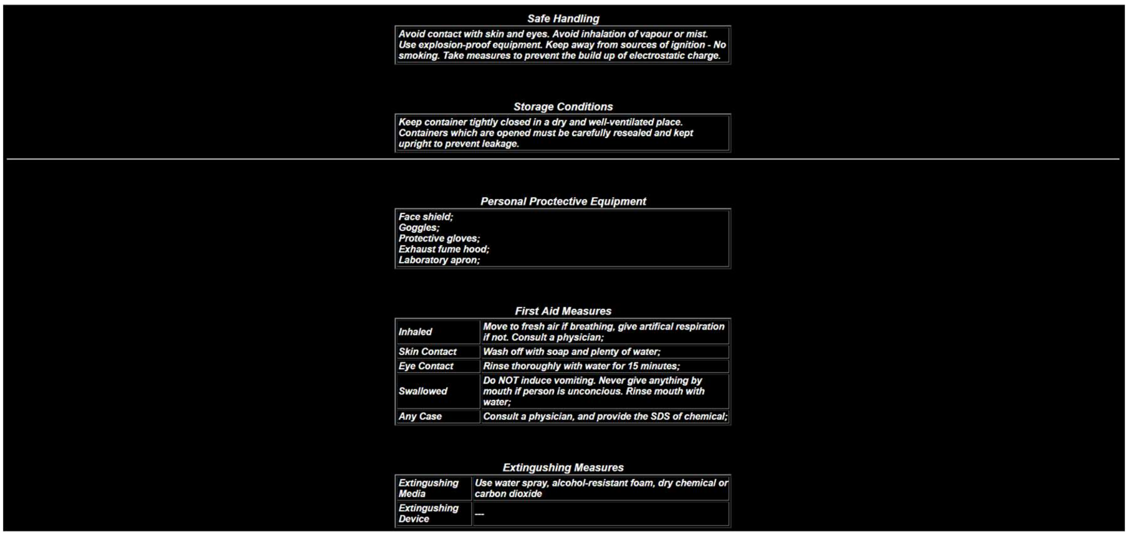
ALARM ALARM ALARM ALARM

Base Infotmation

Item	Value
Name	Acetone
Formula	C3H6O
Molecular Weight	58.80
CAS Number	67-64-1
Density	0.791 g/mL
Boiling Point	56ºC
Concentration	99.9%
State	Liquid
Solvent	-
Water Solubility	Miscibile
Water Solubility Value	-

Hazard Infotmation

Item	Value
Pictogram	
GHS System	Flammable Liquids 2; Skin mild Irritant 3; Eye irritant 2; Target Organ Systemic Toxicity (Repeated Exposure) 2;



Safe Handling

Avoid contact with skin and eyes. Avoid inhalation of vapour or mist. Use explosion-proof equipment. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.

Storage Conditions

Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Personal Proctective Equipment

Face shield;
Goggles;
Protective gloves;
Exhaust fume hood;
Laboratory apron;

First Aid Measures

Inhaled	Move to fresh air if breathing, give artifical respiration if not. Consult a physician;
Skin Contact	Wash off with soap and plenty of water;
Eye Contact	Rinse thoroughly with water for 15 minutes;
Swallowed	Do NOT induce vomiting. Never give anything by mouth if person is unconcious. Rinse mouth with water;
Any Case	Consult a physician, and provide the SDS of chemical;

Extingushing Measures

Extingushing Media	Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide
Extingushing Device	---

Figure 30. MSDS information

APPENDIX II

CURRICULUM VITAE

Candidate's full name: Xuesi Liu

Universities attended: 2003 September-2007 July, Bachelor of Engineering in Pulp and Paper, Tianjin University of Science and Technology

Publications: None

Conference Presentations: International Mechanical Pulp Conference: Metso BCTMP Concept for Lowest Energy and Chemical consumption