

Multifunctional Flexible Conductive Materials for Supercapacitors and Biosensors

By

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ABSTRACT

Both natural polymers and synthetic polymers are great candidates to develop highly flexible stretchable advanced smart devices in order to fill up the highly demands on “Internet of Things”. However, many existing smart electronics are still limited by high production cost, low electric performance, heavy and rigid monofunctional devices, which calls for research and development of advanced conductive materials for smart electronics that are cost effective, light weight, highly flexible, stretchable yet tough, highly conductive and multifunctional for multiple purposes. For this thesis, three projects under the scope of flexible conductive materials for smart electronics were conducted. In the first project, a nanocellulose based small-scale flexible supercapacitor was developed. It allows high mass loading ratio of conductive materials such as polyaniline (PANI) and reduced graphene oxide (RGO) in a matrix of small volume. This feature will be beneficial for the development of lightweight and sustainable flexible energy storage device. To solve the problem of possible physical damages of nanocellulose-based supercapacitor during long-term charge-discharge processes, the second project was developed a flexible self-healable hydrogel supercapacitor by tannic acid treated GelMA-CNC (gelatin methacrylate-cellulose nanocrystal) hydrogels incorporated with PANI and RGO. It showed excellent electrochemical performance even after five cut-heal processes. To avoid the weak mechanical strength of natural polymers, in the third project, a double network tough and highly stretchable multifunctional conductive hydrogel was developed from polyacrylic acid (PAA) infiltrated with conductive agents (PANI and RGO). This versatile hydrogel can be developed into a number of different devices, including a supercapacitor, a wireless wearable strain sensor, an ammonia gas sensor and a nano energy generator that have demonstrated their promising applications in a smart farming system. Flexible smart devices were successfully developed in this thesis. They showed great potentials for a variety of applications in renewable energy storage, health care, and smart farming.

Key Words: Conductive Nanocellulose, conductive hydrogel, polyacrylic acid, Self-healable supercapacitors, PANI, RGO, Wireless Wearable sensors, Nano energy generator

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LIST OF ABBREVIATIONS

APS	ammonium persulfate
CNC	cellulose nanocrystal
CNT	carbon nanotube
CTE	coefficient of thermal expansion
CV	cyclic voltammetry
DN	double network
EDLC	electrical double-layer capacitors
EIS	electrochemical impedance spectroscopy
ESR	equivalent series resistance
FDA	Food and Drug Administration
FTIR	fourier transformed infrared
GCD	galvanostatic charge-discharge
GelMA	gelatin methacrylate
GO	graphene oxides
GNR	gold nanorod
IoT	internet of things
MBA	<i>N-N'</i> methylenebisacrylamide
NC	nanocellulose
NMP	<i>N</i> -methyl-2-pyrrolidinone
PAA	polyacrylic acid
PAAm	poly(acrylamide)
PAC	polyacetylenes
PAMPS	poly(2-acrylamido-2-methylpropane-sulfonic acid)
PANI	polyaniline
PEDOT	poly(3,4-ethylenedioxythiophene)
PDMS	Polydimethylsiloxane
PET	polyethylene terephthalate
PEN	polyethylene naphthalate

PI	polyimide
PPS	poly(p-phenylene sulfide)
PPV	poly(p-phenylene vinylene)
PPy	polypyrroles
PRP	polyacrylic acid – reduced graphene oxide – polyaniline
PSS	poly(styrene sulfonate)
PT	polythiophene
PVA	polyvinyl alcohol
PVdF	polyvinylidene fluoride
RGO	reduced graphene oxides
SC	supercapacitor
SEM	scanning electron microscope
TA	tannic acid
TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl
TENG	triboelectric nano energy generator
TMED	tetramethylethylenediamine

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CHAPTER I Introduction

1.1 General Overview

The digital revolution in the latter half of the last century facilitated a global community with people closely interlinked via the internet and the web, which is advancing towards the next generation. We are entering a new era of “Internet of Things (IoT)”, in which the internet-mediated interconnections have been expanding from people-people to people-things, and between things themselves [1-4]. In other words, communications no longer belong exclusively to living bodies, information can now be exchanged between humans and devices, and between devices themselves [4-6]. With the development of artificial intelligence, “smart” devices including computers, smart phones, sensors, actuators, robots, or nano-energy harvesters have been developed in a variety of fields such as smart home appliances, unmanned vehicles/aerial vehicles, medical sensors, robots and farm management. Such smart devices have been overturning the traditional way of communications as well as our lifestyles [5, 6].

While the functionality and capacity of the smart devices are expanding, their sizes are shrinking to meet the emerging demands for wearable devices, owing to the advancing of nano technologies. Nano-scale materials have enhanced reactivity, enhanced solubility, greater surface-to-volume ratios, unique magnetic/optical properties, and the versatility to be incorporated into a wide variety of structures including flexible and soft substrates [7, 8]. As compared with rigid electronic devices, flexible or soft electronic devices are usually smaller, thinner, more portable and energy efficient, and allow more freedom in the product design and development [7-9]. Despite of extensive research and development on flexible smart devices for IoT, there are still many challenges in the development of micro-scale and ultralight smart electronic devices with advanced features like non-toxic, flexible/foldable, self-healable, wearable, biocompatible or implantable [9-13], which calls for further research and development in multifunctional flexible smart devices with enhanced potentials in different applications.

1.2 Problem Statement

Most flexible substrates for electronics and sensors are based on polymer materials, including natural and synthetic polymers [12]. Synthetic polymers show great versatility for various applications since they can be synthesized from a wide range of chemicals and be tailored to yield a wide array of properties such as flexibility, adhesiveness, self-healable property, or stretchability [10-13]. Synthetic polymers have also gained popularity due to their processibility, consistency, and great mechanical properties, thus have been used in a variety of applications including wearable sensors, e-skins, and scaffolds [14, 15]. Despite of all the above advantages, synthetic polymers do exhibit disadvantages including non-degradable, lower biocompatibility and toxicity of breakdown products as compared to natural polymers [14, 15]. On the contrary, natural polymers are usually found in living creatures and plants such as silk, protein, cotton, linen, wool and DNA and are generally more biocompatible than synthetic polymers [10, 16]. They are abundance in nature and relatively easy to be isolated. Natural polymers can undergo enzymatic and hydrolytic degradation in the biological environment or landfill, therefore, are considered more environmentally sustainable than synthetic polymers [10, 16]. Most natural polymers have important functional groups like hydroxyl groups, carboxyl groups, or amine groups that allow chemical modifications to meet different technological needs. As a result, natural polymers have advantages for applications in medical devices such as biosensors, scaffolds, because they are less prone to produce toxic effects [11, 12, 14, 15]. Natural polymers, however, may face problems like instability, irreproducibility, changes in aesthetics upon storage, uncontrollable formulation characteristics and weak mechanical performances, therefore may limit their applications [11, 12, 14, 15]. With both advantages and disadvantages in different aspects, natural polymers and synthetic polymers are sometimes used in combination to meet demands of specific requirements for their end uses.

Among the various natural polymers, nanocellulose is considered as an excellent nature polymer substrate to fabricate flexible conductive materials. The ultra-high porosity of nanocellulose structures allows large number of conductive materials to be loaded on the substrate and facilitates ions transit through their pores (size varies from 30-50 nm to hundreds nanometers)

[17-19]. Low thermal expansion (0.1-1 ppm/K), another advantage of nanocellulose substrates, can efficiently reduce the thermal swelling/ shrinkage of energy storage components [20, 21], which will improve thermal stability of the devices. Although nanocellulose has excellent mechanical performances as a substrate, which are comparable to those of glass and aramid fibers [22], the overall mechanical strength may be decreased due to the incorporation of a large number of brittle conductive agents on the nanocellulose substrate. In order to load conductive materials (carbon materials and/or conductive polymers) onto/into the flexible substrate (nanocellulose), mixing and coating methods are usually used. A high-speed shear mixer can be used for mixing conductive materials into the nanocellulose substrate in water-based mixture and followed by a filtration system to obtain a nanocellulose based flexible conductive membrane [10, 16]. Another widely used method is *in situ* coating the conductive materials on the surface of the substrate. With this method, however, the conductivity and electrical performance of a flexible electrode is lower than the one obtained via mixing method because the conductive area is limited to the surface of the nanocellulose [10, 16]. Therefore, the mixing method shows great advantage on improving the electrical performance of the flexible electrodes. The mechanical property of some of the conductive agents like PANI is extremely brittle due to their conjugated backbones formed during polymerization, thus it needs to be incorporated within a substrate that has excellent mechanical strength for further fabricating electronic devices [10]. The nanocellulose based flexible conductive membranes can be assembled as “sandwich” like flexible supercapacitors with two flexible metal current collectors, and the core part in this flexible device is two nanocellulose flexible conductive membrane as the electrodes that are separated by a filter paper. However, low mechanical strength of the nanocellulose based flexible conductive membrane is still a limitation for their applications in smart electronic devices as it may lead to unstable electrochemical performances, cracks on the membrane electrodes caused by thermal swelling/shrinkage during long-term uses, low energy conversion efficiency, and short life cycles. Such limitations inspired the current study to explore the optimal ratio between the conductive materials and nanocellulose substrate in order to achieve both excellent electrical performance and outstanding mechanical performance.

In addition to membrane-based flexible conductive materials, conductive hydrogel is another promising candidate for flexible electronic devices due to their good electronic properties, tunable mechanical flexibility, stretchable and ease to process. In addition, unique characteristics such as self-healing, self-adhesive, and biocompatibility can be endowed to hydrogels to fulfill special demands [23-26]. For example, smart electrodes with self-healing ability can restore their physical integrity and maintain their electronic performance upon physical damages, which may overcome some challenges in nanocellulose based conductive membrane. Hydrogel substrates also have porous structures for loading conductive agents [27-29], including conductive polymers, metals nanoparticles/nanowires, carbon-based materials. The principal method of loading conductive agents onto/into the hydrogel substrate is similar to that of developing nanocellulose based flexible electrodes. The conductive materials should be evenly dispersed into the hydrogel during the cross-linking processes or they need to be evenly coated onto the surface of the hydrogel through *in situ* polymerization. Recently there have been significant advances in the development of hydrogel based smart electronics with unique electronic and mechanical properties. The hydrogel based flexible smart devices do not need complex procedures for assembling or packaging, and they can be developed into a variety of applications, such as “all-in-one” supercapacitors, electronic skin, strain sensors and self-powered devices. Still, several challenges exist [27-29] for the development of conductive hydrogels for smart electronic devices, such as uneven distributions of conductive agents, higher resistance, unstable sensing signals for long term uses, and the availability of multifunction to meet the demands of smart electronic devices.

1.3 Objectives

The objectives of the research for my thesis are to develop multifunctional flexible conductive materials that can be promising for smart electronic devices like supercapacitors and/or biosensors. Both natural and synthetic polymers are to be used in the projects for evaluations. Both membranes and hydrogel structures are to be used in the developments for assessments. The specific objectives are:

- 1). To develop a small scale ultra-light weight and flexible/foldable energy storage device (supercapacitor) composed of nanocellulose membranes as the substrate and polyaniline (PANI) /reduced graphene oxide (RGO) as the conductive agents, that has optimal electrochemical performance and thermal stability for long-term uses.
- 2). To develop a self-healable energy storage device (supercapacitor) composed of a hydrogel substrate of gelatin methacrylate (GelMA) and cellulose nanocrystal (CNC) and conductive agents of PANI/RGO.
- 3). To develop a multi-functional conductive hydrogel composed of a polyacrylic acid double network structure loaded with PANI/RGO that can be used a number of applications in smart farming including a self-powered energy source, an energy storage device (supercapacitor) and biosensors (ammonia gas sensor and plant growth sensors).

1.4 Layout & Highlights of Thesis

Following the first chapter of a brief introduction to the thesis, Chapter 2 will present a literature review on relevant research publications to our research topics. Chapter 2 is partially adapted from our publication: Hsu, H.H.; Zhong, W. Nanocellulose-Based Conductive Membranes for Free-Standing Supercapacitors: A Review. *Membranes* 2019, 9, 74.

In Chapter 3, we reported a metal-free, lightweight nanocellulose membrane-based PANI/RGO electrode with excellent flexibility and conductivity for assembling a sandwich-like free-standing supercapacitor. This Chapter is adapted from our publication: Hsu, H., et al. An Eco-Friendly, Nanocellulose/RGO/in Situ Formed Polyaniline for Flexible and Free-Standing Supercapacitors. *ACS Sustainable Chemistry & Engineering* 2019 7 (5), 4766-4776.

In Chapter 4, we developed a mussel-inspired biocompatible SCs with autonomously self-healing capability through a hybrid hydrogel system of gelatin methacrylate (GelMA), cellulose nanocrystal (CNC), and tannic acid (TA), which are all natural materials. PANI and RGO were loaded to endow excellent electrochemical performance. This Chapter is adapted from our publication: Hsu, H., et al. Mussel-Inspired Autonomously Self-Healable All-in-One Supercapacitor with Biocompatible Hydrogel. ACS Sustainable Chemistry & Engineering 2020 8 (18), 6935-6948.

In Chapter 5, we presented a first of its kind versatile polyacrylic acid (PAA) double-network hydrogel enhanced with PANI and RGO that has outstanding mechanical strength, stretchability and electrochemical performances. It can be developed into: 1) a clean energy harvesting device, 2) a supercapacitor for energy storage, 3) a plant growth sensor, and 4) an ammonia sensor. This multifunctional hydrogel shows a great potential for the development of smart systems for agriculture and smart farming. This Chapter is adapted from our manuscript that has been submitted and entitled “Self-powered and plant wearable e-skin as light fertilizer and sensor promoting and monitoring growth in smart farming”.

Chapter 6 is a general conclusion for the thesis and outlook for the future studies are also provided.

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CHAPTER II Literature review

2.1 Introduction

The arrival of the era of “Internet of Things” (IoT) is calling for advanced smart electronics including flexible wearable electronics that facilitate convenient and efficient communications between people, as well as between people and things [1, 2]. These things may vary from smart home appliances, smart furniture, smart textiles, smart phones and televisions, smart wearable electronics, smart health monitor devices, and unmanned vehicles/aircraft [3-6]. The interconnected smart electronic devices share resources and information between humans and objects. With their pervasive presence in the modern lives, such smart devices may recognize, quantify, and most importantly, may adapt themselves upon exposure to environmental changes [3-6].

To meet the demands for wearable smart devices, flexible conductive materials are expected to, be wearable, foldable, twistable, and stretchable [7, 8]. The flexible conductive materials may better fit the custom shapes of the devices at various scales [9]. These smart electronics may greatly extend our senses by being built into our clothes and accessories, attached to our skins and even implanted in our bodies [10]. The flexible conductive materials have found different applications, including energy storage devices, wearable sensors, biocompatible electronics, soft robots, and conformal human-machine interfaces [7, 8]. Such smart electronics, including wearables [11, 12], epidermal devices [13-16], and implantable electronics [17-20], are taking increasingly important roles in human health monitoring in biomedical applications, which will significantly change the future of healthcare as well as our relationships with electronics. Meanwhile, owing to the advancements in soft materials and flexible electronic technologies, tremendous progress has been achieved in plant wearable sensors for smart farming applications.

Recently, the rapid advances in novel materials, fabrication strategies, and innovative electronic constitution contribute to the development of versatile integration of multimodal smart devices, which can synchronously distinguish diverse stimuli from the complex environment, monitor multiple vital signs and serve as a power supply [21]. The challenges for developing such multifunctional smart devices include the developments of cost-effective materials and fabrication

technologies, and the necessity to develop flexible and light-weight self-powered systems to substitute bulky, rigid power sources which are incompatible with the emerging multifunctional electronic skin (E-skin) systems. A sustainable self-powered system can be achieved via harvesting the ubiquitous energy from the environment or the human body [22]. With the flexible features of smart electronic devices, they can be used for widespread applications, especially in energy storage devices and multifunctional wearable sensors with self-powered system.

2.2. Conductive Agents Incorporated in Flexible Substrates

Most conductive agents such as conductive and semi-conductive polymers, metallic particles, and carbon materials are brittle, therefore, are often used in combination with a soft and flexible substrate to fabricate flexible electronic devices. In order to enhance the electrochemical performance of the devices, amount of conductive materials is usually loaded onto the flexible substrate, which may decrease the mechanical strength and flexibility of the electrodes. It has been a challenge to keep a best balance between the electrochemical and mechanical performances of the composite electrodes of the devices. Generally, there are two major procedures to incorporate conductive components into the substrates to fabricate flexible devices: one is to coat conductive materials onto the top of flexible substrate matrix, and the other is to mix conductive agents into the flexible substrate. Schematic illustrations of the fabrication process of conductive flexible composite are shown in Figure 2.1.

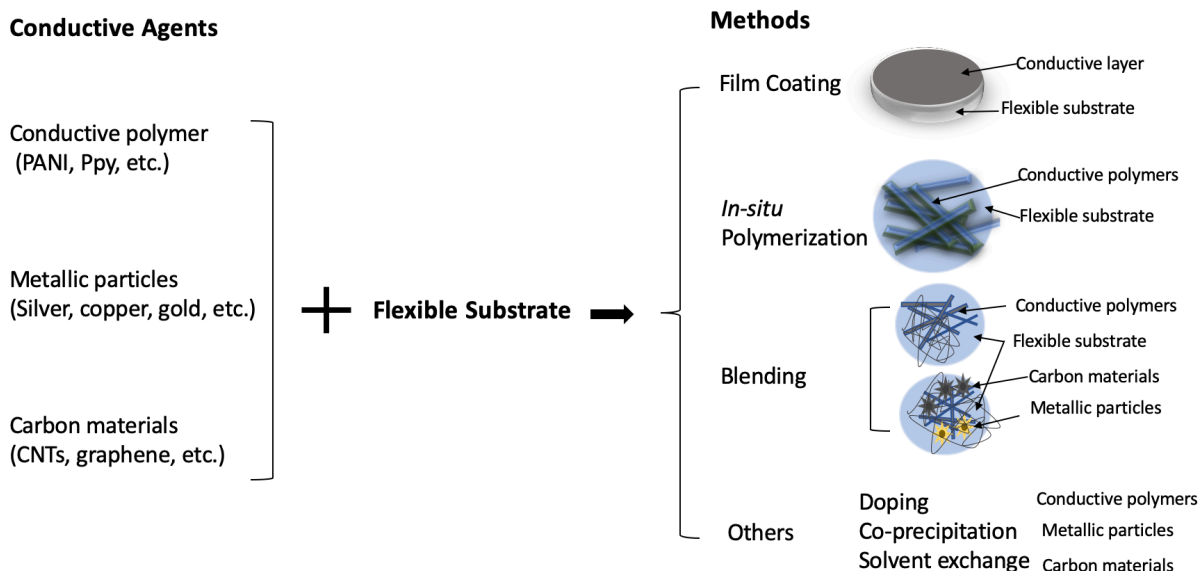


Figure 2.1 Schematic illustrations of the fabrication process of flexible conductive composite

Metallic particles such as silver nanowire, copper nanoparticles, or gold nanoparticles have a high intrinsic conductivity of about 10^5 S/cm, which is five times higher than that of carbon-based conductive materials [23, 24]. Both metallic particles and carbon materials are usually used for direct coating on the surface of the substrate, which is a simple and convenient method for producing flexible conductive composites. However, the increase of conductivity is positively associated with the loading of the metallic materials or thickness of the coating layer [25]. However, metallic particles are brittle and heavy, and therefore are difficult to be dispersed evenly onto the substrate.

Conductive polymers were introduced in 1977 [26] and found their applications in battery industries in 1980s as alternatives to metallic materials because of their good electrochemical performance, light weight, and low cost [27]. Polypyrroles (PPy), polyaniline (PANI), poly(p-phenylene vinylene) (PPV), poly(thiophene)s (PT), poly (3,4-ethylenedioxythiophene) (PEDOT), and poly (p-phenylene sulfide) (PPS) are widely used conductive polymers for fabricating electronic devices. Among the conductive polymers, PANI has been considered as the most promising conductive polymer because of its simple route of synthesis, controllable conductivity, and excellent electrochemical performance [28, 29]. *In situ* polymerization and blending are the two major procedures to incorporate conductive polymers into flexible substrate. The major advantages of *in situ* polymerization to incorporate conductive polymers into the substrate include

simple fabrication procedures with low cost and uniform three-dimensional (3D) network structures, which contribute to the good electromechanical performance of the final conductive composite.

Carbon materials include single wall/multiple wall carbon nanotubes, graphene oxide, reduced graphene, and graphite. Carbon materials generally have high conductivity and high tensile strength. Among them, carbon nanotubes have been known for their ultra-high tensile strength; graphene is a two-dimensional structure with an atomic thickness that offers extraordinary mechanical properties including a Young's modulus of 1 TPa, and an ultimate tensile strength of 130 GPa [30]. Blending usually allows more carbon particles to be incorporated into the flexible substrate as compared to surface coating, due to the carbon particles possibly becoming entrapped inside the substrate, leading to an improved conductivity of the conductive composite [31, 32].

Each of the above-mentioned types of conductive material have advantages and limitations. Metallic particles have higher conductivity, but lower electrons capacity as compared to conductive polymers and carbon materials. Although carbon materials have high surface areas, superior chemical stability, extraordinary mechanical properties, and power density, they have the drawbacks of low specific power capacitances and poor flexibility [33]. There are also concerns regarding the toxicity of some carbon materials such as carbon nanotubes [1-3], which are very popular ingredients for fabricating electrodes of flexible electronic devices. Conductive polymers can deliver as much as 10 times the energy but have relatively lower electrical conductivity compared to carbon-based materials [9]. Conductive polymers are also not stable because of the degradation of themselves and physical damages during charge-discharge cycles. Therefore, it has been a challenge to develop conductive materials with all the desirable properties for advanced flexible electronic devices.

Multiple conductive materials have been used in fabricating flexible conductive composite to optimize the electrochemical performance and overcome the drawbacks of a single component. For example, carbon materials and conductive polymers can be blended to improve both the stability and electrochemical performance. It has also been suggested that the electrochemical stability of PANI can be improved by incorporating reduced graphene oxide into PANI-based electrodes [34-

37]. This is because of the oxidation and reduction processes of PANI during charge–discharge cycles, in which part of the conductive polymerization product emeraldine PANI may convert to pernigraniline, which is a semiconductive polymer (Figure 2.2) [38-40]. This is because of the redox reactions of the ions transfer between two electrodes made from conducting polymers, which store charge via rapid reduction and oxidation reactions, are a particularly promising candidate [38-40]. This situation involves the electrodes' material deformation, including swelling, shrinkage, or cracking during charge and discharge cycles, which result in the poor working stability in the supercapacitors [41-44]. In addition, the degradation of PANI may be accelerated by the deformation of electrodes; thus, it can decrease the potential of working electrodes [9, 41-44]. Therefore, the combination of other materials with PANI provides synergetic benefits regarding electrochemical performance. Metallic material (Ag nanowire, Au) or carbon materials (GO/RGO, carbon nanotubes) can improve conductivity [43, 45]. Therefore, the combination of multiple conductive materials can improve the overall electrochemical property [24, 35, 36, 41, 43, 44].

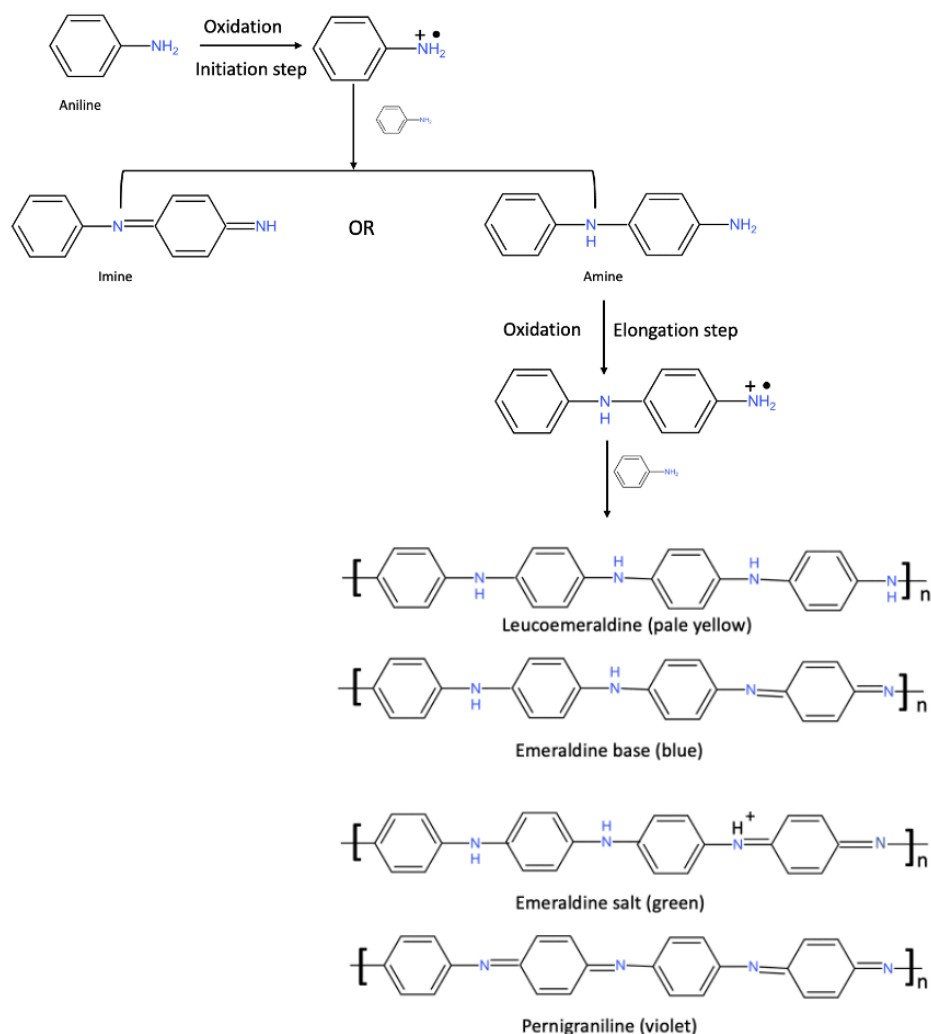


Figure 2.2 The polymerization processes of PANI and pseudocapacitance processes of PANI during charge–discharge cycles.

2.3 Polymers Substrates for Developing Flexible Conductive Materials

Most of the substrates for developing flexible conductive materials are composed of polymers. The incorporation of conductive agents into the polymer substrates may lead to the development of smart materials that show advanced features like self-healing capacity, and conformational changes in response to such environmental stimuli as temperature, ionic strength, pH, or light [46-48]. These substrate polymers include natural polymers and synthetic polymers that can be in different forms like membranes or hydrogels [49].

2.3.1 Natural Polymers VS. Synthetic Polymers

Much attention has been given to the development of synthetic polymers for electronic devices, consumer products, and medical devices [49-51]. Synthetic polymers showed great advantages in their versatility and capable of being tailored for a wide variety of applications. Synthetic polymers can be synthesized with a wide range of chemical linkages that can greatly affect their chemical and mechanical properties such as flexibility, adhesiveness, self-healing capacity, or stretchability [49-51]. For example, poly-hydroxy acids such as poly(glycolic acid), poly(l-lactic acid), and their copolymer poly(lactide-co-glycolide) are the most widely used synthetic polymers for health care applications [52, 53]. The polymers have gained popularity due to their processibility, consistency, adequate flexibility and great mechanical properties. They are already used in variety of applications including wearable sensors, e-skins, and scaffolds [52, 53]. Synthetic polymers exhibit a number of advantages, however, they also have disadvantages, especially that they are less biocompatible and biodegradable than natural polymers. The toxicity of their breakdown products and tissue biocompatibility of the synthetic polymers are the major issue in determining the applications of the devices [52, 53].

Natural polymers can be found in living creatures or plants such as silk, protein, cotton, linen, wool and DNA (Figure 2.3) [49, 54]. These polymers have such advantages including natural abundance, relative ease of isolation and room for chemical modification to meet the needs for specific applications [49, 54]. Natural polymers can undergo enzymatic and hydrolytic degradation in the biological environment or landfill [49, 54]. Some natural polymers have important functional groups that are suitable for applications in medical devices such as biosensors and are less prone to produce toxic effects [50-53].

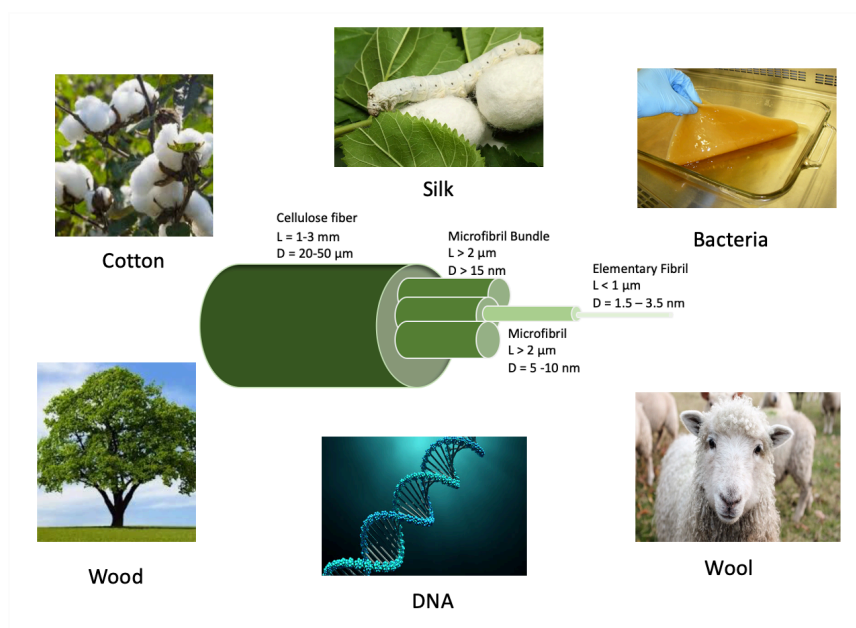


Figure 2.3 Natural sources of cellulose fibers

Comparing natural and synthetic polymers, the former face many problems like instability, irreproducibility, changes in aesthetics on storage, and uncontrollable formulation characteristic, while synthetic polymers are usually more stable and controllable in properties and higher in mechanical properties[50-53]. On the other hand, natural polymers are more biocompatible, biodegradable and sustainable [50]. With those features, natural polymers are excellent candidates for developing flexible devices for health care, medical or agricultural applications. Natural polymers include cellulose, chitosan, gum, alginate, pullulan and amylose (starch) (Figure 2.4), have been used for a variety of flexible conductive devices [52, 53].

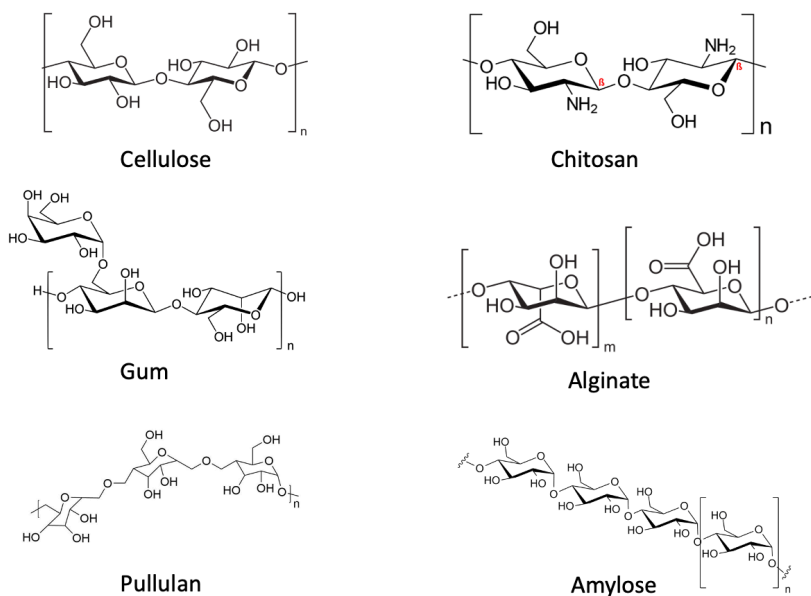


Figure 2.4 Chemical structure of cellulose, chitosan, gum, alginate, pullulan and amylose (starch).

2.3.2 Nanocellulose Based Flexible Conductive Membrane

Cellulose nanomaterials have been explored for their use in electronics and functional devices because of their sustainability, high strength, flexibility, transparency and low thermal expansion [55, 56]. Cellulose membrane-based electrodes have low thermal expansion, which is desirable in electronic components that generate heat. Coefficient of thermal expansion (CTE) for cellulose materials and their composites has been measured and reported for various cellulose based films [55, 56]. The thermal expansion of cellulose has been measured to be as low 0.1 ppm/K, and the CTE for films and composites containing cellulose nanomaterials has been reported to be as low as 1 ppm/K [57-60]. Bacterial cellulose typically has a lower CTE than plant-derived cellulose nanofibers, and modified bacterial cellulose was shown to have a thermal expansion of 1 ppm/K [57]. These values are favorable compared to existing polymeric materials, which can have CTE values up to hundreds of ppm/K [60]. Because low thermal expansion is important for electronics printed or deposited onto flexible substrates, cellulose materials may offer favorable properties and potentially improved performance over other polymer films [57-60]. Cellulose-based flexible conductive membranes can overcome issues with piezoceramics such as brittleness, low energy

conversion efficiency, inability to operate under long life cycles without the issues of depolarization, and the lack of flexibility to operate under strong ambient vibrations [57-60].

With the development of nanotechnology, the isolation method of nanocellulose from natural plants is becoming a heated topic in the field of advanced materials. The advantageous features of nanocellulose include not only all of the excellent features of cellulose, but also includes low density and high mechanical strength, Young's modulus, and surface-to-volume ratio compared to cellulose and synthetic materials [61]. The advanced features of nanocellulose membranes show great potential in many applications, such as wound dressing, membrane-based oil/water filters, and energy storage devices. Specifically, nanocellulose shows great potential to be used as substrates for loading conductive materials and fabricating lightweight flexible composite membrane electrodes with high electrochemical performance. These nanocellulose-based composite membrane electrodes can be assembled into energy storage devices with light weight, small size, flexibility, longer life cycles, and good electrical performance [62-64]. Nanocellulose-based composite membrane electrodes can also be fabricated by a simple filtration system [43, 44, 65, 66] with conductive components incorporated via blending or *in situ* polymerization. Specifically, nanocellulose suspension and conductive component suspension or solvent can be mixed and subsequently transferred to a filtration system, in which the liquid(s) are allowed to pass through the filter and a well-mixed conductive materials/nanocellulose composite membrane is left behind on the filter. An air-dried composite membrane can be later peeled from the filter membrane for further use [37, 43, 44, 65, 66].

With the fast growth of the world market for sensors, a variety of sensors are highly demanded for environment pollution prevention, health management, and biomedical applications. Biosensors that are made by nanocellulose-based conductive membrane for health management and tissue engineering are attracting extensive research interest [67]. Nanocellulose, as a great flexible and ultra-thin substrate, can support electronic components to fabricate biomedical sensors to be integrated onto or into the human body [68, 69]. Nanocellulose-based biomedical sensors for home uses such as glucose and cholesterol sensors can help patients better manage their chronic diseases. Some other biomarkers including gases, proteins, DNA, pathogens, or toxic compounds can also

be detected by nanocellulose-based sensors [68, 69]. A recent study used functionalized cellulose nanocrystals coated with polyvinylpyrrolidone to fabricate a conductive film as a biosensor that can distinguish similar chemical compounds [68]. The highly sensitive nanocellulose-based sensor showed great potential for detecting biomolecules in the human body. Another study fabricated a conductive film with a 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO)-oxidized nanocellulose hydrogel based on graphene quantum dots to monitor the fluorescent quenching that can be used for laccase enzymes detection [70]. This nanocellulose-based sensor can increase the signal regarding the intensity of the fluorescent without shifting the wavelengths [70]. Besides, a TEMPO-oxidized nanocellulose biosensor can be used to detect biomolecules, C-phycocyanin, and copper ions [71].

Moreover, nanocellulose-based supercapacitors can provide high power conversion efficiency with low cost and have subsequently become one of the most promising devices to replace conventional energy storage devices [72, 73]. Most flexible supercapacitor electrode films are made by polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), which are not easily degraded and can lead to serious environmental concerns [72, 73]. Another example is nanocellulose-based PEDOT:PSS-PPy nanopapers which showed higher flexibility than the nanopapers containing only polypyrrole [74]. Abundant studies have been conducted to develop flexible conductive membranes by using conductive polymers such as PANI, PPy, and PPV along with nanocellulose to assemble composites that have both good electrochemical and mechanical properties [74, 75]. Carbon materials or other metallic particles can be incorporated along with conductive polymers to fabricate nanocellulose-based flexible conductive membranes to achieve the expected performance. On the other hand, some flexible electrode membranes were made by coating metallic particles on top of cellulose or printing papers. However, this type of electrode membrane did not maintain good specific capacitance when compared to the one made by conductive polymers [25, 30, 76]. Adding conductive polymers significantly improves the specific capacitance and stability of the hybrid electrodes [77-80]. In sum, the nanocellulose-based conductive membrane with excellent flexibility can be widely applied in wearable electronics to fill up the increasing demand for consumer electronics.

To develop a high performance flexible conductive membrane by using conductive polymers, an acidic environment is usually required during the in-situ polymerization of PANI or PPy to optimize the growth of these polymers and consequently ensure well-dispersed conductive polymers in the nanocellulose substrate. Acids that have often been used for such purposes include hydrochloric acid, sulfuric acid, and dodecylbenzenyl sulfonic acid [24, 42, 81, 82]. However, it is difficult to have a suitable solvent for most conductive polymers when using a coating method to fabricate high-performance conductive nanocellulose films. Neither is coating nor electrodeposition applicable for loading conductive polymers onto nanocellulose films, because of the thermal degradation of the polymers at the elevated temperature. As a result, in situ polymerization is becoming the most popular way to incorporate conductive polymers into nanocellulose hybrids [27, 32]. However, the drawbacks of in situ polymerization include its complicated processes and environmental concerns: the time-consuming reactions involve multiple steps and operation procedures.

2.3.3 Flexible Conductive Hydrogels

Conductive hydrogel is another excellent candidate for developing flexible smart devices due to its unique properties such as superior softness, high water contents, responsiveness, biocompatibility and bioactivity. It has been widely used in E-skin, bio-actuators or implantable sensors [83-88]. Conductive hydrogels are composed of intrinsic conductive materials and cross-linked polymer networks. The polymer networks provide the substrate while the incorporated conductive materials endow their electrical conductivity [83-88]. Various strategies have been developed to fabricate conductive hydrogels for flexible electronic devices, including polymerization of the conductive monomers on a prefabricated hydrogel, mixing the conductive agents into the hydrogel during crosslinking, and self-assembling the modified conductive materials [83, 85, 86]. The resulted conductive hydrogel is a hydrogel network in which the conducting materials are entrapped [83, 85, 86]. In the process of fabricating conductive hydrogels, conductive materials like conductive polymers, metals nanoparticles/nanowires, carbon-based micron/nano materials and ions, have been used and studied [83-88].

Several types of conducting polymers, including poly (3,4-ethylenedioxy thiophene) (PEDOT), polypyrrole (PPy), and polyaniline (PANI) (Figure 2.5) become promising candidates in hydrogel electronics due to their favorable mechanical and electrical properties, electrochemical stability, biocompatibility, and processability for chemical modification [85, 89]. The conducting polymers can either form interpenetrating networks with nonconducting polymer networks or polymerized out layer on prefabricated hydrogels [89-91]. For example, Poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT: PSS) conductive hydrogels particularly provide a promising electrical interface with biological tissues for recording and stimulation, in which the coexistence of ionic and electrical conduction ensures a low interfacial impedance [90]. Existing methods to prepare PEDOT:PSS hydrogels mostly rely on mixing or in situ polymerization of PEDOT:PSS within non-conductive hydrogel templates to form interpenetrating polymer networks [90]. A soft and stretchable polymer network within the loosely-crosslinked PEDOT:PSS network led to a conductive hydrogel with low PEDOT:PSS content (1.1 wt%), high conductivity ($>10 \text{ Sm}^{-1}$), and high stretchability ($>100\%$) [90]. However, the evenly dispersed PEDOT:PSS on the hydrogel is still a challenge that need to be solved. A few strategies have been developed to convert pure PEDOT:PSS solutions into well dispersed and connected networks, including increasing ionic strength, lowering pH, and adding ionic liquids and co-solvents [89, 91]. Recently, a study showed that the addition of volatile dimethyl sulfoxide in aqueous PEDOT:PSS solutions followed by controlled dry-annealing, and subsequent rehydration can yield pure PEDOT:PSS hydrogels, which exhibited high electrical conductivity (2000 S m^{-1}), high stretchability ($>35\%$ strain), but low Young's modulus (2 MPa), superior mechanical, electrical and electrochemical stability, and tunable isotropic/ anisotropic swelling in wet physiological environments [92].

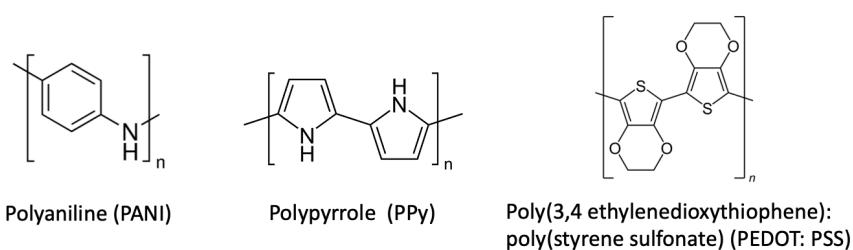


Figure 2.5 The chemical structures of some conductive polymers.

Metals such as nanowires, nanorods, nanoparticles, are excellent nanomaterial candidates for developing flexible and wearable electronics because they have high electrical conductivity, interesting optical, catalytic properties, facile fabrication and modification processes [93-96]. However, the research on conducting hydrogels by adding metal-based materials is rarer. Recently, gold nanorod (GNR) incorporated gelatin-based hydrogels have been successfully synthesized by UV crosslinking the mixture of centrifuged GNRs and gelatin methacrylate (GelMA) prepolymer solution [97]. The GelMA-GNR hydrogel exhibited electrically and mechanically enhanced material characteristics as compared to pure GelMA hydrogel, which provide suitable matrices for specific applications in cardiac tissue engineering [97]. Metal-based conductive hydrogels have also been prepared by in situ polymerization of hydrogel monomer and reduction of metal ions using reducing agent. Silver nanoparticle entrapped polyacrylic acid-methylol urea hydrogel has been fabricated by in situ free-radical polymerization of acrylic acid and reduction of silver ions. In the process of the polymerization, methylol urea acted as a cross-linking and reducing agent at room temperature [98]. The conductivity showed significant enhancement in conductivity with increasing concentration of Ag^+ and the electrical conductivity of such hydrogel up to 0.572 S cm^{-1} [98]. However, great efforts should be made for fabricating metal-based conductive hydrogels with excellent properties including electrical conductivity, mechanical and tried to use novel materials such as liquid metal to prepare novel metal-based conductive hydrogels.

Beside conductive polymers and metal nanowires, carbon-based materials are also considered to be promising conductive materials for fabricating conductive hydrogels, due to their unique properties of high electrical conductivities, excellent environmental stability and low production cost [85, 89]. Among various carbon-based materials, CNTs and graphene have been widely explored in materials science, and been intensively used as conductive filler in the conductive hydrogels for flexible and wearable electronics [99-103]. Blending with various polymer and self-assembly after modification are the two most common ways for preparing carbon-based conductive hydrogels. Generally, graphene, with its conjugated structure, cannot be dispersed uniformly in

water, which limits its applications in fabrication of conductive hydrogels [99-103]. Hydrophilic polymers modification is an efficient way to promote graphene dispersion in water. A partially or fully reduced graphene oxide can uniformly disperse in the polyacrylamide hydrogel network and serve as electronic pathways, contributing to the good conductivity of the hydrogels [104]. The unreduced GO with oxygen-containing groups can interact with polyacrylamide chains via hydrogen bonds and electrostatic interactions. Such non-covalent interactions imparted toughness and high stretchability to the conductive hydrogels [104]. In addition to graphene, CNTs also have been widely introduced into hydrogel systems for their tubular structure and superb electrical property. For example, a CNT incorporated gelatin methacrylate (GelMA) hydrogels were prepared through in situ polymerization by UV irradiation. CNTs homogeneously embedded in the hybrid hydrogel can be attributed to the GelMA coated CNTs uniformly dispersed in the prepolymer solution [105].

2.4 Advanced Functions of Flexible Conductive Materials

Appropriate mechanical and electrochemical performances are two basic requirements for flexible conductive materials to be used in flexible electronic devices. Still there have been extensive research and development to further enhance the properties of flexible conductive materials to endow multiple desirable functions to the end products. These advanced functions include self-healing capacities, ultra-high mechanical properties, and 3D printability [88, 106-110].

2.4.1 Self-healing Capacity

A self-healing material is a so called “smart materials” that can automatically restore some or all of its functions after suffering external mechanical damages or harsh environments such as high temperatures or irradiation. Depending on the self-healing mechanism, self-healing behavior can be induced by an external stimulus like heat, self-healing agent or autonomous interactions of the constituting molecules via dynamic chemical bonds or noncovalent interactions [88, 106-110].

The self-healing mechanism with an agent is usually achieved via a self-healing agent loaded in a microcontainer, which will release its cargos to repair the broken region upon damages [88, 106-

110]. The main drawback of such a mechanism is that the self-healing agent is consumed during the self-healing process. As a result, the self-healing behavior cannot occur for an unlimited number of times [107]. Self-healing behavior using heat as the stimulus can be accomplished multiple times.

For autonomous self-healing, dynamic chemical bonds such as the C–N bonds (acylhydrazone bond and imide bond), B–O bonds (phenyl borate ester), C–C/C–S bonds (reversible free radical reaction), Diels–Alder (cycloaddition reversible reaction), disulfide bonds and dynamic noncovalent interactions such as multiple hydrogen bonds, ionic interactions, host–guest interactions and hydrophobic interactions have been studied for preparing self-healing materials (Figure 2.6) [106, 108, 109]. The self-healing capability of the materials can not only prolong the service life of the products, but also increase the reliability of the products in use and reduce the waste of resources.

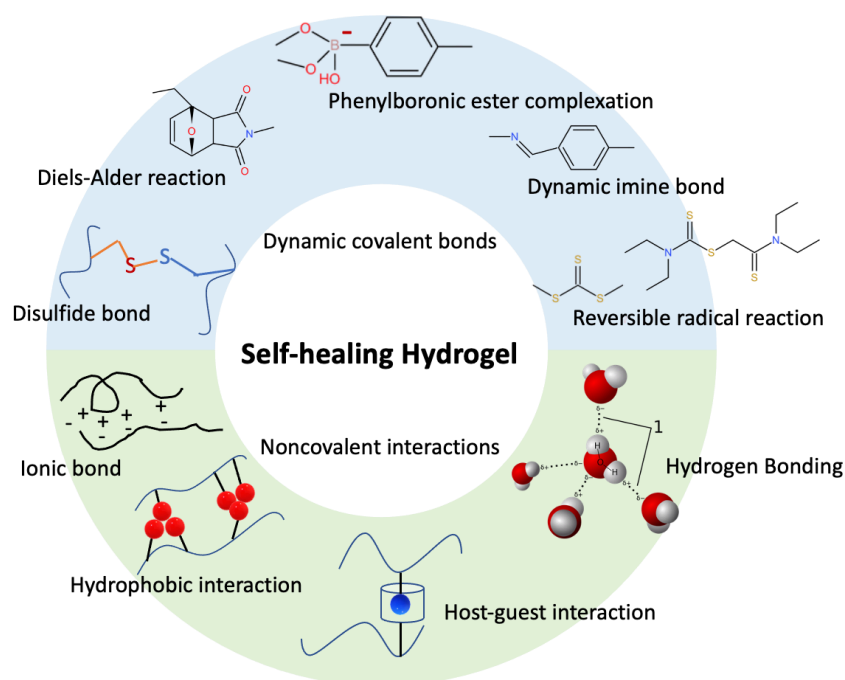


Figure 2.6 Mechanisms of self-healing hydrogels

2.4.2 Ultra-high Mechanical Properties

Exceptional mechanical performance is another important yet difficult task to achieve for flexible materials. Most polymer hydrogels have weak chemical crosslinking and heterogeneous networks, which may lead to poor capability in dissipating energy during loadings. As a result, the

hydrogels usually fracture at low strain and show very low fracture strength or toughness [89, 111, 112].

To improve the mechanical performance of hydrogels, strategies based on homogeneous networks, double networks, nanocomposites, and micelle crosslinks (Figure 2.7) have been widely developed in the past few decades to produce hydrogels with outstanding strength, toughness, self-healing and recovery properties [89, 111, 112]. Double network hydrogels have been reported to produce hydrogels with extremely high strength and toughness, which are promising for the preparation of tough conductive hydrogels to meet a broad spectrum of demands for wearable and implantable flexible devices [89, 111, 112]. Double network (DN) hydrogels are composed of two interpenetrating polymer networks with contrasting mechanical properties: One network is densely cross-linked and brittle, while the other network is sparsely cross-linked and flexible [111, 112]. Upon loadings, the internal fracture of the brittle network dissipates substantial amounts of energy at large deformations, while the second network provides hidden elasticity to maintain the integrity of hydrogels. For example, a double network hydrogel comprised of poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS) and poly(acrylamide) (PAAm) networks were developed with a rigid and densely crosslinked PAMPS network which host the free radical polymerization of AAm to form a loosely crosslinked second network interpenetrating with the first one [112]. Such double network hydrogels show a very high compressive strength at 17.2 MPa, which is more than 20 times of that for each single network [112]. The inter/intramolecular interactions and structures within and between two networks are important for optimizing their mechanical properties. Functionalization of one or both networks enables diverse manipulation of the properties and functionalities of tough polymer hydrogels.

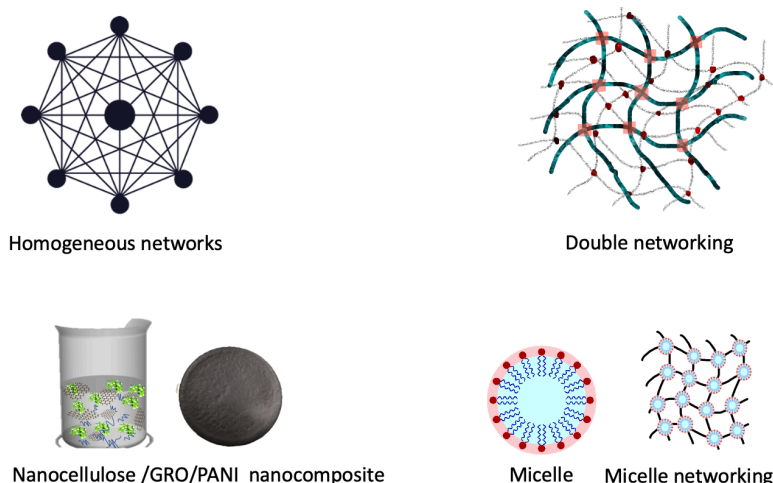


Figure 2.7 Examples of hydrogel networks

2.4.3 3D Printability

Some conductive flexible hydrogels can be fabricated by three-dimensional printing with custom shapes or structures. 3D pre-gel inks with appropriate viscosity and shear-thinning property have been used to print 3D structures that sustain stretching and compression loads [105, 113-115]. Various technologies, including bio-plotting, light-based printing and ink-jet printing, have been utilized to fabricate 3D structures from electrically conductive hydrogels or electrically conductive hydrogel precursors [105, 113-115]. In 3D bio-plotting, conductive hydrogels or precursors are deposited through a nozzle on a substrate [113]. The shear thinning behavior of the printing ink enable smooth flow under the applied pressure forces, and facilitate material deposition in the desired patterns. A key challenge of such an approach is to ensure the shape stability of the printed structures, after the recovery of the sheared hydrogel or the crosslinking of the printed structure post printing [105, 114]. In light-based printing approaches such as stereolithography, direct laser writing, a light-reactive hydrogel precursor is either illuminated by a travelling beam of UV light or laser or by a projected pattern on the hydrogel precursor to induce curing in specific regions to form crosslinked patterned areas [105, 114]. Often a z-displacement of the precursor reservoir is performed to allow layer-by-layer deposition in the z-direction to fabricate 3D structures. Acrylate polymer based chemistry has been frequently used for such processes as photo crosslinked hydrogels. In inkjet or piezo printing, conductive hydrogels or precursors are deposited on a printing stage by deformation of a piezo element, leading to the deposition of small droplets [105,

114]. This approach can meet specific needs on the hydrogel shapes to fit more applications on smart electronics.

2.5 Applications of Flexible Conductive Materials

2.5.1 Flexible Energy Storage Device

Existing energy storage devices, including batteries and supercapacitors, are generally too rigid and heavy to provide sustainable power to a variety of flexible and wearable electronic products in modern society. Therefore, there is high demand for future energy storage devices with light weight, flexibility, excellent electrochemical performance and mechanical properties. A nanocellulose-based paper battery has recently attracted attention for its applications in smart and wearable electronic devices [116, 117]. The electrochemical performance of the nanocellulose-based paper battery is comparable to that of a conventional battery, while it is eco-friendly and degradable and shows a great potential to replace the conventional batteries [116-118]. The conventional battery electrodes usually consist of a polymer binder of electrodes such as polyvinylidene fluoride (PVdF), which requires a toxic organic solvent such as N-methyl-2-pyrrolidinone (NMP) during fabrication processes [116-118]. On the other hand, a nanocellulose-based paper battery doesn't require complicated process and hazardous solvents. A nanocellulose paper-based lithium battery (Figure 2.8), in which nanocellulose provides a 3D porous structure incorporated with carbon nanofibers and LiFePO_4 to maintain an excellent cycling capacity (85%) even after 1000 cycles [119]. Another recent study used nanocellulose-modified polyethylene separators in the lithium battery to improve the cycling stability of a high-energy density lithium battery [120]. The nanofiber layer was thermally stable and flexible with hydrophilic property and was coated with polyethylene on both sides to fabricate a tri-layer separator to enhance the cycling stability and safety of the lithium battery [120]. These studies showed that nanocellulose-based batteries have great potential to solve the stability and safety concerns of existing lithium batteries.

Capacitor is another type of promising energy storage devices, have attracted considerable interest due to their high power density, rapid charge and discharge rates and long lifetimes. Supercapacitors (SC) has been developed based on the conventional capacitors (Figure 2.8). Like

flexible lithium-ion batteries, flexible supercapacitors have also been developed to meet the growing demands for flexible electronic devices [9, 63, 64, 121, 122]. In general, there are two types of supercapacitors, the electrical double-layer capacitors (EDLC) and the pseudocapacitors. Both types of SCs can be fabricated by using nanocellulose membranes as the substrate. A typical EDLC consists of two metal plates (collectors), two electrodes membranes, one separator, and an electrolyte (Figure 2.8) [9, 63, 121, 122]. Electrical energy is stored in EDLCs by physically separating positive and negative charges without faradaic reactions. A pseudocapacitor, on the other hand, involves a reversible surface redox reaction on the surface of the electrodes' materials. Pseudocapacitors generally have poor capability and low electrochemical conductivity as compared to EDLCs [121, 123, 124].

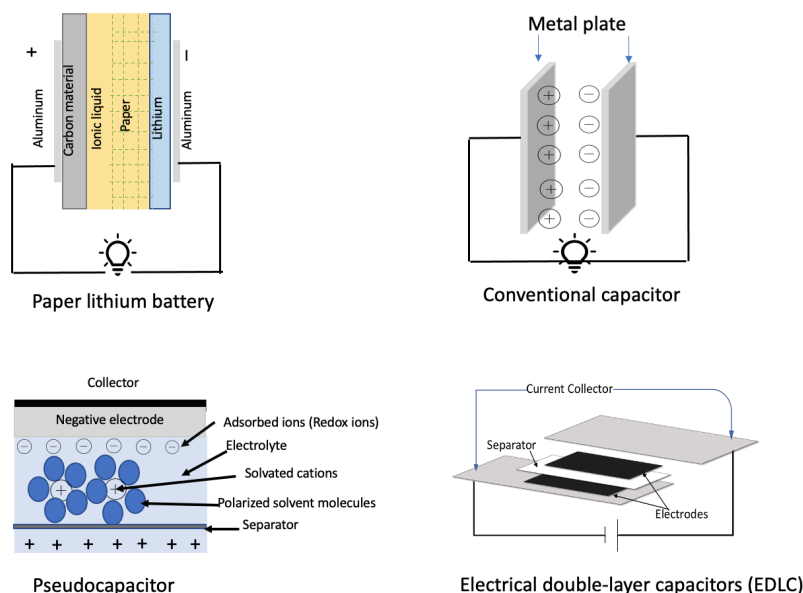


Figure 2.8 The schematic of paper lithium battery, conventional capacitor, pseudocapacitor, and electrical double-layer capacitors (EDLC).

Conductive hydrogels have also been extensively studied for flexible supercapacitors. A flexible supercapacitor based on functionalized hydrogels incorporated with reduced graphene oxide was prepared by chemical reduction with hydro quinones as the reducing and functionalizing molecules [121, 123, 124]. In another study, sulfuric acid-polyvinyl alcohol (H_2SO_4 -PVA) gel was used as the electrolyte to develop a flexible conductive hydrogel-based supercapacitor, which exhibited a specific capacitance of 441 F g^{-1} at 1 A g^{-1} [125]. In addition, hydrogel based supercapacitor with

self-healing property was developed by using single wall nanotube and polyvinyl alcohol (PVA) that exhibit self-healing via hydrogen bonding. The material showed 80% healing efficiency on specific capacitance [125, 126].

2.5.2 *Sensors*

Sensors are one of the promising applications of conductive flexible materials [84]. Flexible strain sensors (Figure 2.9) have experienced growing demands due to their applications in personalized health monitoring, human motion detection, structural health monitoring, smart garments, and robots [21, 22, 84, 87, 88, 103, 110, 112]. The structure of a strain sensor usually includes sensing component, electrodes and electrical wires (Figure 2.9). The performance of the sensing component plays a critical role in the sensor. The working mechanism of flexible strain sensor is to transform the deformation into the change in material resistances, which can be further represented by the changes in current at a constant voltage [103, 111]. The sensing performances of a strain sensor can be evaluated in terms of gauge factor, strain range, durability, static and dynamic stability, response time and the linearity between strain and relative change in resistance. Suitable materials and assembly methods are very important for obtaining flexible sensing components with a wide strain range, high sensitivity and stability [103, 111]. In the development of mechanical sensors, conductive hydrogels were usually used as sensing elements, which were fabricated by the incorporation of conductive fillers in a hydrogel matrix [127]. Because of the high electrical conductivity, conductive polymers and carbon materials were typically used as fillers to fabricate conductive hydrogels with good flexibility and sensitivity [127]. Such sensors usually work by detecting the resistance changes caused by shape variations upon the application of external forces [110]. Self-healing capability allows restoration of the sensors to their original states after damages, endowing these sensors with enhanced durability and extended lifetime. Self-healable, wearable human motion soft sensors have been fabricated for healthcare monitoring [89, 111].

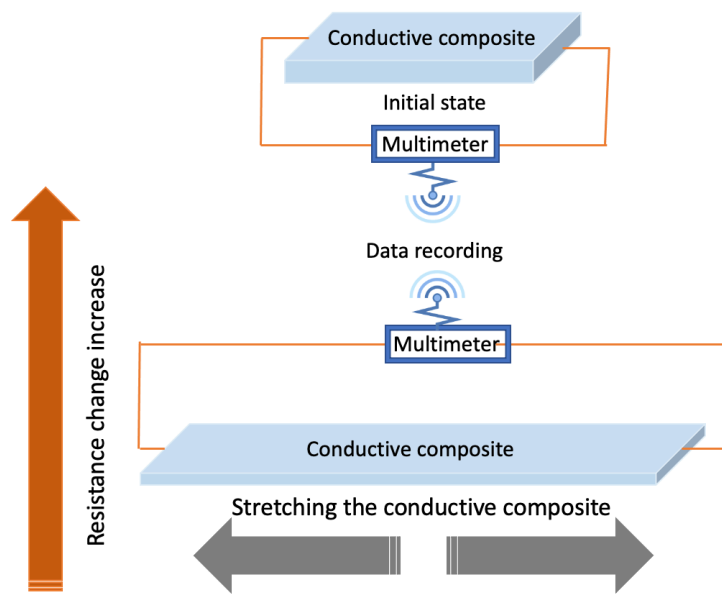


Figure 2.9 The schematic of a strain sensor working mechanism.

Flexible touch panels are sensors that have gained tremendously interests as future electronic component to provide an easy and intuitive interface for human-machine interaction and E-skin [128-130]. To date, several sensing mechanisms for panels have been developed, including capacitive, acoustic wave, resistive and infrared ray. Among them, capacitive and resistive sensing have become the most used in flexible touch panels. The most critical part of both resistive and capacitive flexible touch sensing systems is conductive materials with flexibility and high sensitivity [128-130]. At present, indium tin oxide is the dominant conductor materials for touch sensing due to its sufficiently low resistance and high transparency. However, its stiff and brittle properties limit its further applications in flexible touch devices because the future touch panels are expected to be stretchable or at least flexible in order to interact with human body [128]. Hydrogels are soft, stretchable, and possibly transparent, making them promising for fabrication of touch panels. Hydrogel can serve as ionic conductor because it contains large amounts of water. Therefore, conductive hydrogels with dissolved ions can serve as the crucial component for the next generation of touch panels for E-skin due to their stretchability, high ionic conductivity and biocompatibility [7, 106, 131].

2.5.3 Flexible Self-powered Device

Flexible self-powered electronics can be developed from flexible conductive materials such as conductive membranes and conductive hydrogels. The flexible self-powered electronics can be applied to biosensor networks and energy harvest systems for the next generation IoT applications [3]. Such flexible self-power devices may substitute the conventional bulky power devices with innovative electronic devices featured by portability, light weight, and conformal contact capability [15]. For example, self-powered wireless sensors can be implanted in organs to monitor the biological vital signs based on real-time/bilateral data transmissions without requiring extra surgery for battery replacement [132]. A tough and self-powered hydrogel was developed from polyacrylonitrile hydrogel incorporated with ferroelectric poly(vinylidene fluoride) for artificial skin fabrications [131].

In addition, the properties of piezoelectric and triboelectric materials and their incorporation into biomaterials such as collagen, chitin, gelatin, cellulose, have drawn tremendous attentions to develop new biocompatible devices composed of piezoelectric or triboelectric biomaterials [132]. However, the performance of the self-powered devices can be degraded by external humidity and mechanical abrasion. Although these limitations have been improved by designs of specific packaging or device structures, they have not been fully resolved. There are still various fundamental and engineering problems in the field of these devices [132-134].

2.6 Summary

There has been an increasing demand for the next-generation wearable electronic devices based on flexible conductive materials. Flexible membrane based conductive materials and hydrogel based conductive materials are two most promising candidates for this field. Both of synthetic polymers and natural polymers are excellent candidates to develop flexible conductive materials. Natural polymers are attractive due to their biocompatibility, low toxicity and environmental sustainability. However, natural polymers may be low in mechanical strength and versatility for modifications, which are advantages for synthetic polymers.

Cellulose is an abundant natural polymer for the development of flexible substrates for electronic devices. A combination of nanocellulose substrate and conductive agents in a composite structure has been extensively studied as a strategy to obtain synergetic effects on flexibility and electrochemical performance. Approaches for such combination, including coating and blending, doping, in situ polymerization, and inkjet printing, have been widely used to develop nanocellulose based conductive membrane materials. However, it is difficult to achieve a well-dispersed morphology of the conductive agents on the nanocellulose substrate; as well, the ratio of nanocellulose and conductive agents still need to be optimized to maintain good mechanical performance and electrochemical property.

The advances in the fabrication of conductive hydrogels and their applications in flexible electronic devices have been reviewed. Various electrical conductive components including conductive polymers, metallic nanomaterials, carbon-based materials and ions have been used to endow conductivity to hydrogels. Due to their excellent biocompatible, tunable electrical conductivity, flexible and stretchable mechanical properties, conductive hydrogels offer tempting possibilities in flexible device applications, for example, touch panels, flexible energy storage devices, and flexible sensors. However, there are still challenges in developing conductive hydrogels with facile fabrication technology and appropriate performance for viable applications. Most current conductive-hydrogel-based flexible devices have much lower performance in efficiency and sensitivity when compared with their classical counterparts. Besides, conductive hydrogels contain pure water solvent, and will inevitably freeze at subzero temperatures and dry under hot environment, which severely limits their practical applications at extreme temperatures. Thus, designing hydrogels with high conductivity, extreme-temperature tolerance and stable mechanical properties will promote development in flexible electronic devices. Finally, the preparation of conductive hydrogels with high conductivity and high mechanical strength remains a challenge, which is quite important for their application in flexible devices. Further investigations to explore efficient and simple synthetic methods are needed to reduce resistance and increase mechanical strength. Overall, the future of flexible conductive electronic devices will be largely dependent on how effectively we can balance the functionality and stability.

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CHAPTER III

An Eco-friendly, Nanocellulose/RGO/*in-situ* Formed Polyaniline for Flexible and Free-standing Supercapacitors

Abstract

There have been extensive demands for eco-friendly, light-weight, flexible and high performance supercapacitors for advanced applications like wearable electronics, hybrid electric vehicles and industrial grid storage. In this work, a metal-free nanocellulose-based PANI/RGO electrode with excellent flexibility, mechanical strength and conductivity was developed and assembled into sandwich-like supercapacitors. Reduced graphene oxide (RGO) was mixed into aniline during the *in-situ* polymerization of PANI to improve conductivity of the composite electrode. This eco-friendly metal-free nanocellulose based electrodes were fabricated via filtrations driven by a vacuum and assembled into sandwich structures. The ratios between nanocellulose, PANI and RGO were optimized to achieve both high electrochemical performance and good mechanical properties. The composite electrode has a large active materials mass loading ratio of 16.5 mg/cm², and the assembled supercapacitor gives small impedance at 3.90 Ω , suggesting an excellent conductivity. This work shows a great potential of the developed flexible and light-weight nanocellulose composites in the fabrications of supercapacitors that can be used in a variety of biomedical applications including e-skins.

Key Words: Nanocellulose, polyaniline, reduced graphene oxide, flexible electrodes, supercapacitor.

3.1 Introduction

Supercapacitors, as compared to conventional capacitors, are outstanding in electrochemical performance and have greater potentials in such advanced applications as wearable electronics, hybrid electric vehicles and industrial grid storage [1-4]. The electrochemical performances of supercapacitors include capacitance, power density, energy density, cycle life and stability, which are highly dependent on the materials used for the electrodes [5]. However, flexibility, light-weighted, and micro-sized supercapacitors with proper electrochemical performance are still in great demands. Conductive polymer such as polyaniline (PANI) showed great promises in developing high-electrochemical performance electrodes for supercapacitors and batteries. Polyaniline shows not only excellent faradaic pseudocapacitance, good conductivity, but also simple polymerization method and low cost [6, 7]. However, PANI is a brittle material due to the conjugated backbone after polymerization, which limits its applications in high performance electrodes [6, 7]. Moreover, PANI undergoes significant swelling and shrinking which may lead to cracking during charge-discharge cycles, therefore limits the specific capacitance and power density of PANI-based electrodes [5, 8]. These limitations call for an improved design for the PANI-based electrodes with improved mechanical and electrochemical performances.

In recently years, flexible substrates have been used to fabricate composite films to improve the mechanical properties of the PANI-based electrodes. Among these flexible substrates, nanocellulose has many features including highly porous structure, low density, high specific strength, great flexibility, bio-degradability and abundance in nature [9-12]. The ultra-high surface-to-volume ratio of the porous nanofiber structure allows large amount of conductive particles to be physically entrapped, which contributes to large energy storage capacity and high power delivery in a small electrode unit [13]. Nanocellulose is both strong and flexible with a tensile strength of about 1.7 GPa and a Young's Modulus ranging from 100-130 GPa, which is comparable to that of glass and aramid fibers [14]. Nanocellulose is therefore a promising substrate to improve the mechanical properties of PANI electrodes.

On the other hand, the poor electrochemical stability of PANI electrode can be overcome by adding reduced graphene oxide (RGO) to develop a nanocellulose-based PANI-RGO electrode composite. RGO is a nanostructure carbon material that has been widely used for developing electrodes for supercapacitors due to its excellent conductivity [15, 16]. Specifically, RGO can be mixed with PANI to enhance both electrochemical and mechanical properties of the electrodes [8]. The exact mechanism of such a synergetic result is not fully understood, though possible explanations are that the two materials are joined together via

covalent grafting or noncovalent mixing/absorption [6, 7]. Kang, et al. fabricated a graphene oxide/polyaniline composite electrode with improved electrochemical performance due to a network composed of PANI grown seamlessly on the surface of graphene oxide and served as conductive link between interlayers of graphene oxide [15]. Manoj et al. developed a polyaniline-graphene oxide-based electrode for high-performance supercapacitors. This composite electrode showed a specific capacitance of 132 F g⁻¹ at a current density of 5 A g⁻¹. The cells were found to have remarkable cycling stability with a retention of 84.8% of the initial capacity after 1000 cycles [17].

Despite of the extensive work on developing polyaniline and graphene based high performances supercapacitors, some research gaps still need to be filled up. Firstly, cellulose as a biodegradable natural material needs to be studied in depth for its possible applications in energy storage devices. However, there have not been many studies on cellulose-based supercapacitors as compared to the amount of work done on supercapacitors based on synthetic polymers. Secondly, among the existing work on nanocellulose-based supercapacitors, not all aspects of performance of the materials have been fully studied. Mechanical data, for example, are missing for some of the reports. Thirdly, a common limitation of nanocellulose-based supercapacitors is the small mass loading ratio of conductive materials on the nanocellulose substrates, which gives large resistance and may negatively affect the charge-discharge efficiency of a supercapacitor. The data from some recent studies on the nanocellulose-based supercapacitor are summarized in Table 3.1.

Table 3.1 A summary on performance of nanocellulose-based electrodes

Active Materials	Thickness (μm)	Mass loading (mg cm ⁻²)	Specific Capacitance (F g ⁻¹)	EIS (Ω)	Tensile strength (MPa)	Ref.
CNT ¹	15	1.7	200	10	N/A	[18]
rGO ²	100	0.11	212	8	N/A	[19]
PPY ³ +rGO	2-3	1.85-3.54	408	4.5	N/A	[20]
PANI ⁴ +PVA ⁵ +Au	80	N/A	350	25	1.2	[21]
PANI+graphite	N/A	2.0	355.6 (F cm ⁻²)	32.3	N/A	[22]
PANI+PPY+graphite	N/A	N/A	N/A	N/A	23.7	[23]
PANI+rGO	N/A	N/A	N/A	210	1.2	[24]
PANI+SWCNT ⁶	0.05	N/A	0.33 (F cm ⁻²)	N/A	N/A	[25]
PANI+GNP ⁷ +PVA	10	N/A	421.5	1.77	2.6	[26]
PANI+ExG ⁸ +AgNO ₃	N/A	16.0	200.0	4.87	N/A	[5]
PANI+RGO	40	16.5	79.71	3.10	8.83	current work

1. Carbon nanotube; 2. Reduce graphene; 3. Polypyrrole; 4. Polyaniline; 5. Polyvinyl alcohol; 6. Signal wall carbon nanotube; 7. Graphite nanoplatelets; 8. Exfoliated graphite

N/A: data not available

To achieve a high specific capacitance in an assembled SC, a large and bulky electrode is required if the loading mass of the active materials is low, therefore, may not meet the demands

for light-weight and small-size energy storage devices with large power/energy density [12, 27]. Furthermore, metal particles were usually used as an active material in order to increase the conductivity of the electrodes [28-32] despite of their toxicity [33-35]. There is also a big environmental concern on the metal or metal oxide materials that have been used in energy storage devices, because they are non-degradable and toxic [36-38]. Nowadays there have been extensive research interests towards fabrication of greener energy storage devices to meet eco-friendly requirement.

In this chapter, we develop a metal-free nanocellulose-based PANI/RGO composite film electrode for supercapacitors with large mass loading of active materials on the substrate (Figure 3.1). The assembled supercapacitors can therefore achieve high specific capacitance in a small size. The flexible composite film electrode can be fabricated through facile and scalable steps. The mechanical and electrochemical properties of the electrodes are optimized with different ratios of PANI, RGO and nanocellulose substrate to achieve the best results. In this design, nanocellulose provides a highly porous and flexible loading substrate; PANI contributes to a high pseudocapacitance, while RGO improves the cyclic stability and specific capacitance. The composite film also has improved power density at a high current, making it a promising material for small size and high performance supercapacitors for various advanced applications.

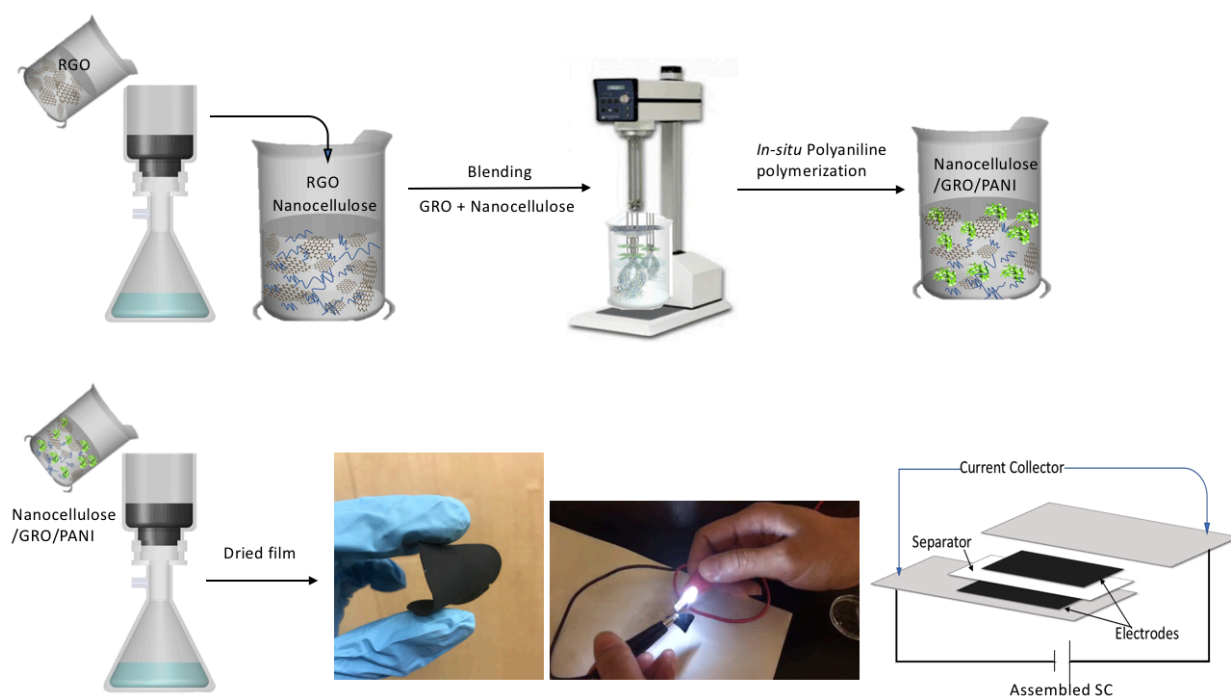


Figure 3.1 Scheme for fabrication of the nanocellulose/PANI/RGO flexible film electrodes and assembling of the supercapacitors.

3.2 Materials & Methods

3.2.1 Materials

Clean hemp fibers were provided by Schweitzer-Mauduit (SWM) International (Winnipeg, Canada). Graphene oxide was purchased from Tanfeng Tech. (Suzhou, China). All other chemicals were purchased from Sigma Aldrich Canada (Oakville, ON) and used without further purification unless stated otherwise.

3.2.2 Nanocellulose Isolation

Clean hemp fibers (1.89 g) were grounded using a household grinder (coffee grinder) for about 50s, then bleached in 8% H₂O₂ for 48 hours and then in KOH (50 mg/ml) for another 48 hours [39, 40] to remove lignin and hemicellulose. The bleached cellulose was dispersed in water (1g/L), and processed using a high shear lab mixer (Sliverson L5M-A, MA, United States) at 8000 rpm for 2 hours to disintegrate fibers.[41] Big fiber loops were separated from nanocellulose by centrifugation at 1400 rpm, and the supernatant containing nanocellulose and nanoparticles were centrifuged at 4000 rpm for 20 minutes. The nanocellulose was subsequently collected from the settlement. A dry nanocellulose film was made by filtering the cellulose-water suspension through a glass filtration device with a nylon filter paper (pore size of 0.45 μ m).

3.2.3 Preparation of PANI/RGO Nanocellulose Composition Film

Nanocellulose was dispersed into 1 M sulfuric acid and blend using a high shear lab mixer. Graphene oxide (2 mg/mL) was dispersed into distilled water followed by sonication for 2 hours to achieve even dispersion [5, 15, 42]. Sodium hydroxide (1 M) and sodium borohydride (0.1 M) were added into graphene oxide and water mixture and stirred for 2 hours followed by heating for 1 hour at 90 °C [43]. The mixture was then washed with distilled water and filtered through a nylon filter paper using a glass filtration system. The obtained wet reduced graphene oxide was subsequently added into the nanocellulose mixture, followed by blending at 6500 rpm for about 1 hour until the mixture was well dispersed. Aniline and ammonium phosphate sulphate (APS) were added into the mixture and stirred for 20 minutes to allow polymerization to occur evenly in the mixture. The polymerization took about 4 hours. The nanocellulose based PANI/RGO electrode film was finally obtained by filtering the mixture through the nylon filter paper (pore size of 0.45 μ m) in the filtration system. All composite electrode samples were fabricated in a disk-shape with the diameters of 5.4 ± 0.1 cm, the surface areas were 22.89

$\pm 0.86 \text{ cm}^2$. The surface area of electrodes for assembling in the supercapacitor device was 3 cm^2 ($2 \times 1.5 \text{ cm}$). The compositions of electrodes were shown in table 3.2. Due to the mechanical performance of nanocellulose based conductive membranes are very sensitive to the ratios of nanocellulose, polyaniline and reduced graphene oxide, a total of 19 samples were developed for this study. The composition of the samples are shown in Table 3.3. Most of them did not show any valid data on either electrochemical tests nor mechanical tests. Only six samples were successfully obtained valid data on both electrochemical tests and mechanical tests, which were labeled in Table 3.2.

Table 3.2 The Composition Ratios of Electrode Film

Sample Thickness ^b	Cellulose	RGO	Aniline	RGO/Cellulose	Aniline/ cellulose	Aniline/RGO	Electrode Wt ^a	
	(mg)	(mg)	(μL)	(mg mg^{-1})	($\mu\text{L mg}^{-1}$)	($\mu\text{L mg}^{-1}$)	(mg)	(μm)
NC/PANI	21.70	-	300.00	-	13.82	-	23.20	35.00
NC/PANI/RGO-1	21.00	90.00	290.00	4.29	13.81	3.22	32.40	50.00
NC/PANI/RGO-2	23.00	90.00	290.00	3.91	12.61	3.22	35.90	45.00
NC/PANI/RGO-3	24.00	94.50	304.50	3.94	12.69	3.22	36.40	40.00
NC/PANI/RGO-4	26.00	135.00	300.00	5.19	11.54	2.22	30.60	45.00
NC/PANI/RGO-5	24.00	135.00	300.00	5.63	12.50	2.22	32.70	40.00

a. The average weight of one piece of electrode, geographic area: 3 cm^2

b. The thickness was measured based on each electrode that used for assembling in SCs

Table 3.3 The Composition of Samples

Sample Number	Aniline (μL)	RGO (mg)	Nanocellulose (mg)	Aniline/Nanocellulose ($\mu\text{L}/\text{mg}$)	Aniline/RGO ($\mu\text{L}/\text{mg}$)	Resistance (Ohm)	Sample Status	Sample Name in Thesis
C1	100	0	10	10.0	0	N/A	Fragmentation	N/A
C2	100	0	20	5.0	0	2-3M	High resistance	N/A
C3	150	0	20	7.5	0	1M	High resistance	N/A
C4	200	0	20	10.0	0	1.5-3K	High resistance	N/A
C5	300	0	20	15.0	0	200	Weak membrane	N/A
C6	300	0	21.7	13.82	0	200-300	Data Available	NC/PANI
C7	300	10	21.7	13.82	30	N/A	Weak membrane	N/A
C8	300	50	21.7	13.82	6	N/A	Weak membrane	N/A
C9	280	90	20	14	3.11	190-250	Not stable during test	N/A
C10	280	90	20	14	3.11	50-80	Not stable during test	N/A
C11	280	100	20	14	2.8	N/A	Fragmentation	N/A
C12	0	90	10	0	N/A	1000	Low capacitance	N/A
C13	290	90	21	13.81	3.22	80-100	Data Available	NC/PANI/RGO-1
C14	290	90	23	12.61	3.22	190-220	Data Available	NC/PANI/RGO-2
C15	304.5	94.5	24	12.69	3.22	130-180	Weak membrane	N/A
C16	304.5	94.5	24	12.69	3.22	700-980	Data Available	NC/PANI/RGO-3
C17	300	135	26	11.54	2.222	1.6-2.8k	Data Available	NC/PANI/RGO-4
C18	300	135	24	12.50	2.222	300-450	Data Available	NC/PANI/RGO-5
C19	300	180	24	12.50	1.667	90-100	Fragmentation	N/A

3.2.4 Characterization

The surface morphology of nanocellulose-based PANI/RGO film was examined under a scanning electron microscope (SEM) (JEOL, JSM-5900LV) at an accelerating voltage of 10 kV. Fourier transformed infrared (FTIR) spectra were recorded on a Thermo Nicolet iS10 FTIR Spectrometer.

3.2.5 Electrochemical Test

Two electrodes (3 cm^2) were cut from the air dried composite film. A supercapacitor with a sandwich configuration (Figure 3.1) was assembled using two pieces of aluminum foil as the current collectors and a non-conductive filter paper (Whatman, grade 5) as the separator in between the two electrodes. 1 M sulfuric acid was used as the electrolyte. The supercapacitor was sealed by parafilm to prevent moisture evaporation. The average dry weight of each

electrode was about 40 mg. The electrochemical properties of the assembled SCs were investigated using an electrochemical workstation. The electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency ranging from 105 to 0.01 Hz, 10 mV AC amplitude and zero DC amplitude. The Galvanostatic Charge/Discharge (GCD) measurements were performed from 0 to 0.8 V at a constant current ranging from 5 to 50 mA. The cyclic voltammetry (CV) curves were recorded from 0-0.8 V at scan rates ranging from 0.002 to 1 V s⁻¹. The capacitance of a single electrode that was assembled for SC can be calculated from GCD curves as a function of the discharging slope after the IR drop:[5]

$$C = 2I\Delta t/(\Delta V - V_{IR}) \quad (1)$$

where I is the discharge current; Δt represents the time span of a full discharge; ΔV is the potential change after a full discharge; V_{IR} indicates the potential drops at the initial discharge stage, which is mainly attributed to the intrinsic resistance of the electrode materials and the resistance of the electrolyte. Mass-specific or area-specific capacitance of a sample can be determined by dividing the C by its mass or area.

The equivalent series resistance (ESR) was calculated using:[5]

$$ESR = V_{IR}/2I \quad (2)$$

Energy density (E) and power density (P) can be estimated according to the equations:[44]

$$E = \frac{1}{2} \times C_{device, specific} \times \Delta V^2 = \frac{1}{2} \times \frac{C_{device}}{mT} \times \Delta V^2 = \frac{1 \times \Delta t \times \Delta V}{2mT} \quad (3)$$

$$P = E/\Delta t \quad (4)$$

where m is the total mass of the device [44]. The mass loading (in mg cm⁻²) was calculated as the total weight of an electrode divided by its geometric area [5].

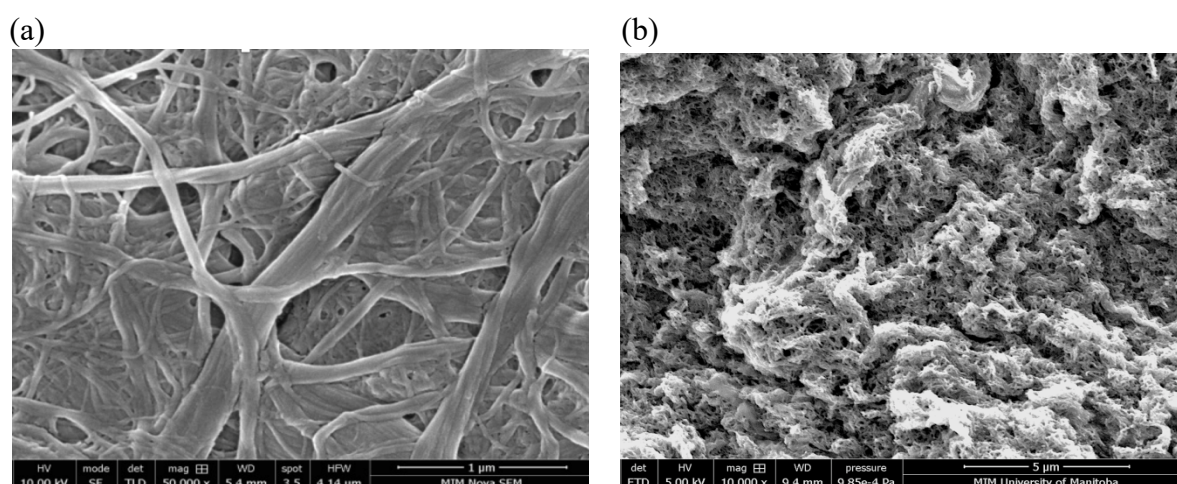
3.2.6 Mechanical Testing

The mechanical properties of samples were measured using an Instron 5965 mechanical analyzer. The tensile tests were performed on nanocellulose-based PANI/RGO composite film electrodes with a size of 5cm × 2cm at a speed of 10 mm min⁻¹ until breaking. The Young's modulus was calculated as the slope in the initial linear region from the stress-strain curves [45].

3.3 Results and Discussion

A schematic illustration shows the main procedures of fabricating the SC electrodes (Figure 3.1). The compositions of the nanocellulose-based composite films are shown in Table 3.2. Figure 3.2 (a-h) shows the SEM micrographs of the surfaces of the samples: nanocellulose film,

nanocellulose/PANI composite film, nanocellulose/RGO composite film and five nanocellulose/PANI/RGO composite films. The micrographs for the nanocellulose film (Figure 3.2a) shows the fiber size of nanocellulose is around 50-100 nm. For the nanocellulose/PANI film, a layer of evenly grown PANI can be observed on the surface of the nanocellulose substrate (Figure 3.2b), which may be achieved due to a reduced polymerization rate of PANI at a low temperature (4 °C). As a result, there are not many nanocellulose fibers that can be observed at the surface of the composite film. For the nanocellulose/RGO film, Figure 3.2c shows that the RGO layers are wrinkled and connected together through the nanocellulose fibers, indicating that RGO layers of a good quality were formed [46, 47]. Such a structure increases the space in the porous structure of the composite, and consequently improves the ions transports mobility and improves the conductivity of the film. For the nanocellulose/PANI/RGO film, Figure 3.2d shows that the RGO layers are coated on the well-grown interconnected PANI and connected with nanocellulose fibers. Figure 3.2d-h shows the five composite electrode films (NC/PANI/RGO-1 to 5) with RGO layers that were coated on the well-grown interconnected PANI and connected with nanocellulose fibers. The SEM images confirm the successful fabrication of nanocellulose based PANI/RGO composite film electrodes for supercapacitors.



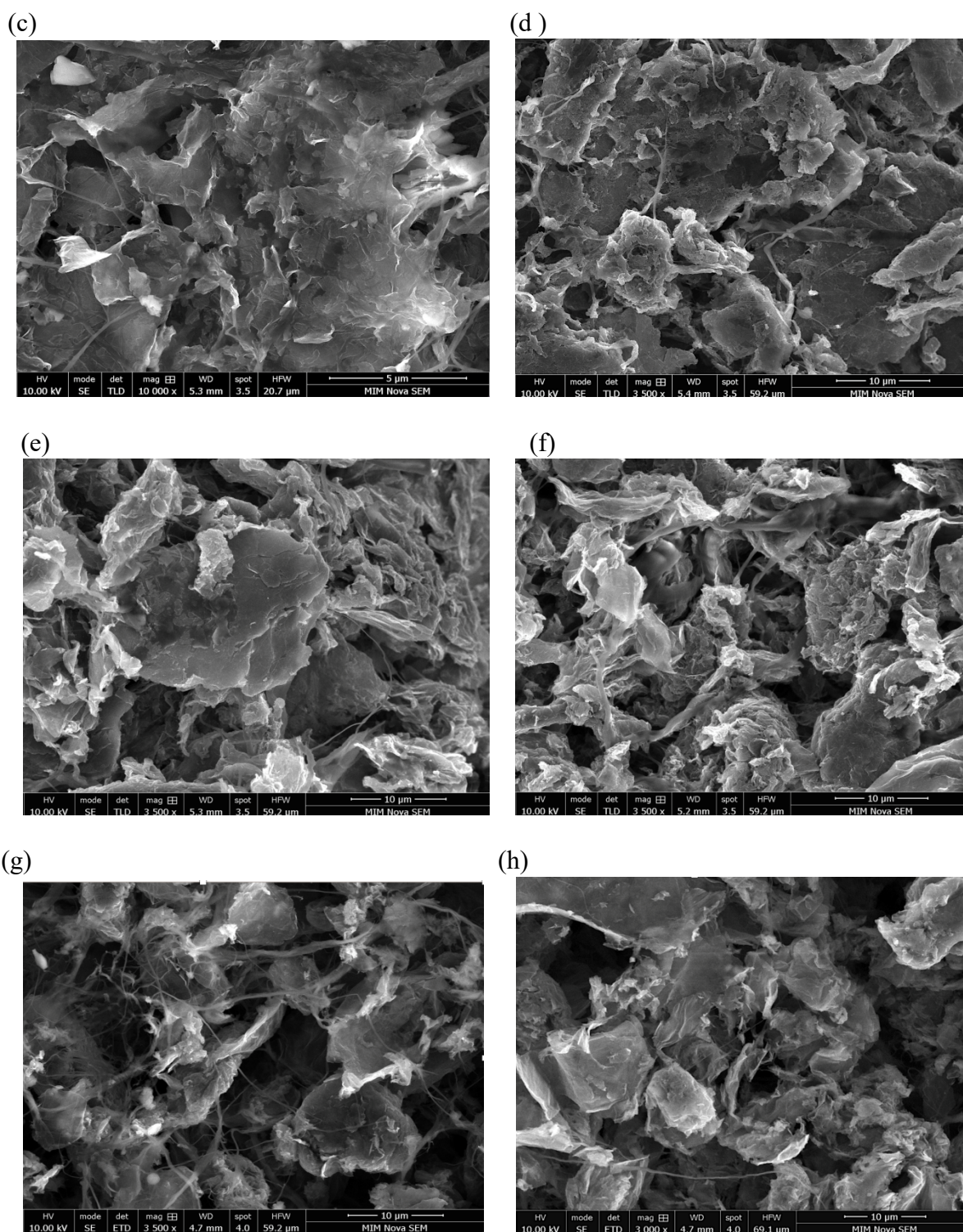


Figure 3.2 SEM micrographs of the nanocellulose film and nanocellulose-based PANI/RGO composites. (a) Nanocellulose; (b) NC/PANI; (c) NC/RGO; (d) NC/PANI/RGO-1; (e) NC/PANI/RGO-2; (f) NC/PANI/RGO-3; (g) NC/PANI/RGO-4; (h) NC/PANI/RGO-5.

FTIR spectra are shown in Figure 3.3. The FTIR spectra for all samples present typical peaks of cellulose (chemical structure shown in Chapter 2, Figure 2.4) at 896 cm^{-1} (C-H

bending), 1031 cm^{-1} (C–O stretching), 1162 cm^{-1} (C–O stretching), 1429 cm^{-1} (alkane C–H bending), 1640 cm^{-1} (O–H bending of absorbed water), 2897 cm^{-1} (C–H stretching), and 3333 cm^{-1} (O–H stretching) [5, 48, 49]. PANI gives typical peaks at 798 cm^{-1} (aromatic C–H out-of-plane bending), 1123 cm^{-1} (aromatic C–H in-plane bending), 1298 cm^{-1} (aromatic amine C–N stretching), 1485 cm^{-1} (benzenoid ring C=C stretching), 1566 cm^{-1} (quinoid ring C=C stretching), and 3437 cm^{-1} (N–H stretching), indicating that PANI in the emeraldine salt state [5, 48, 49]. These peaks can be observed on the spectra for PANI, nanocellulose/PANI and nanocellulose/PANI/RGO, indicating that PANI has been successfully coated on the nanocellulose substrate. RGO shows peaks at 690 cm^{-1} (C–H bending), 1402 cm^{-1} (C–H bending), and 3138 cm^{-1} (O–H stretching) [5, 48, 49]. Also PANI is adsorbed onto RGO through the amino groups of aniline by alkane bending (1429 cm^{-1}), C–H stretching (2897 cm^{-1}), and O–H stretching (3333 cm^{-1}), indicate both PANI and RGO have been successfully loaded on the nanocellulose substrate [50].

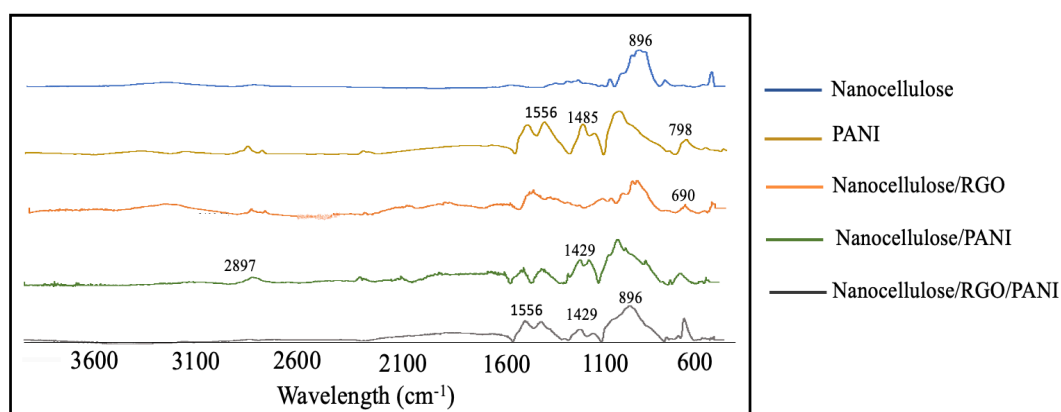
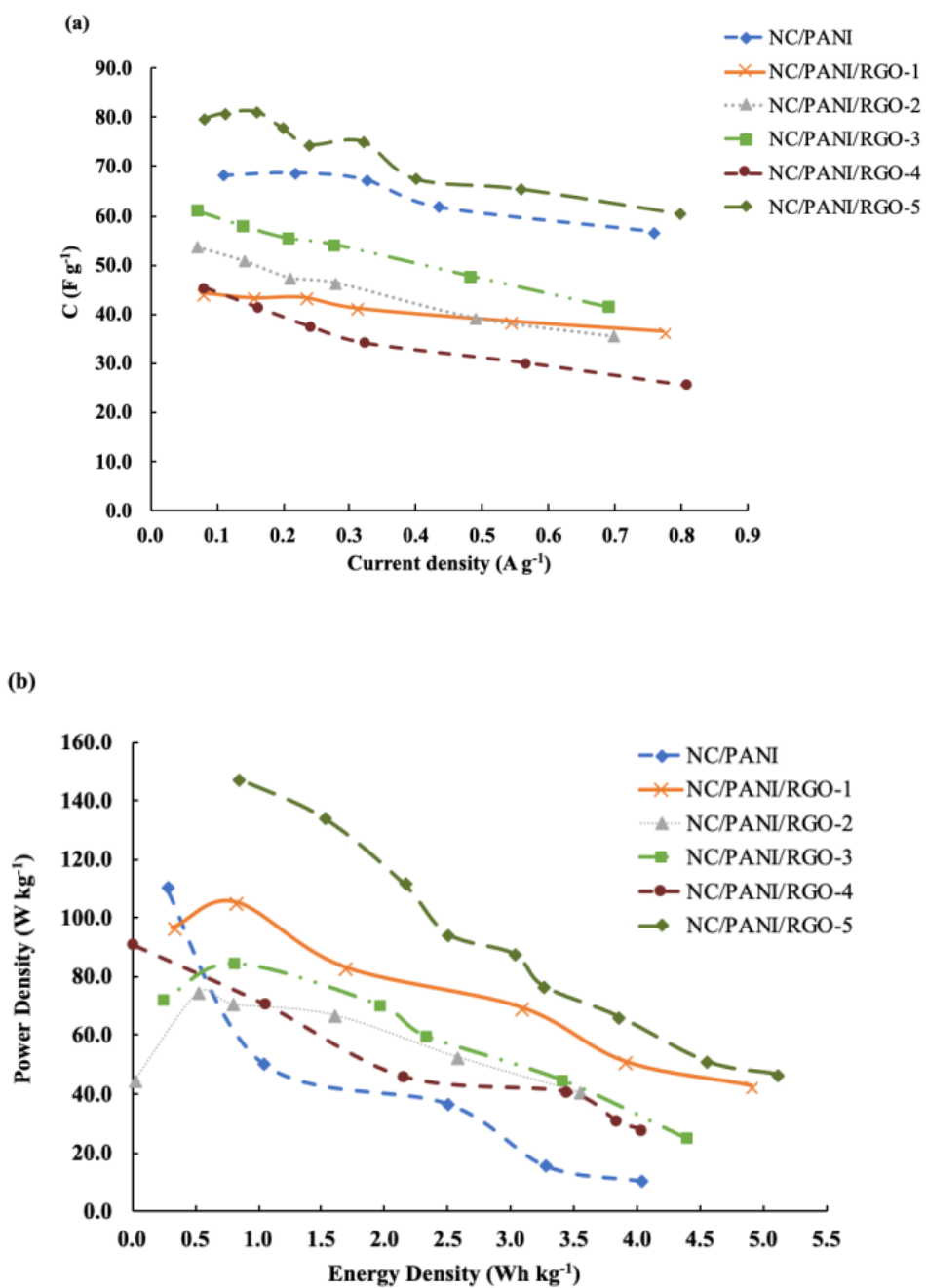
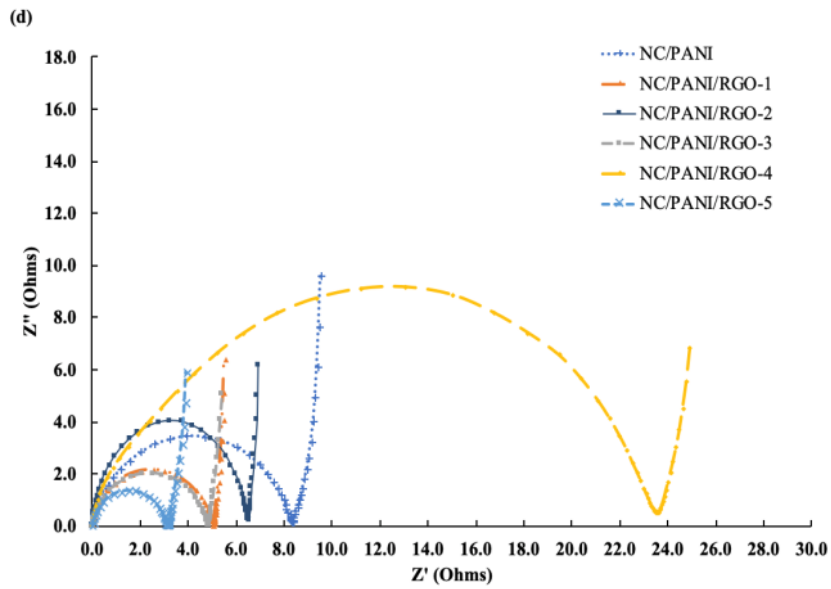
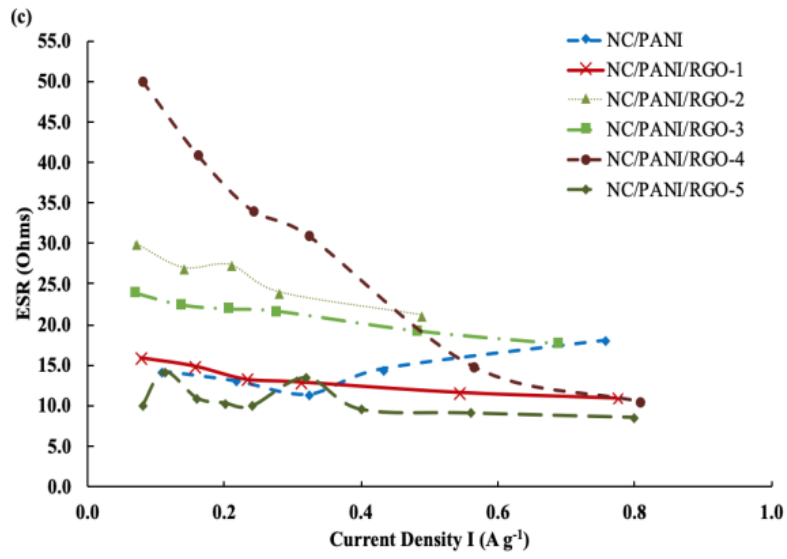
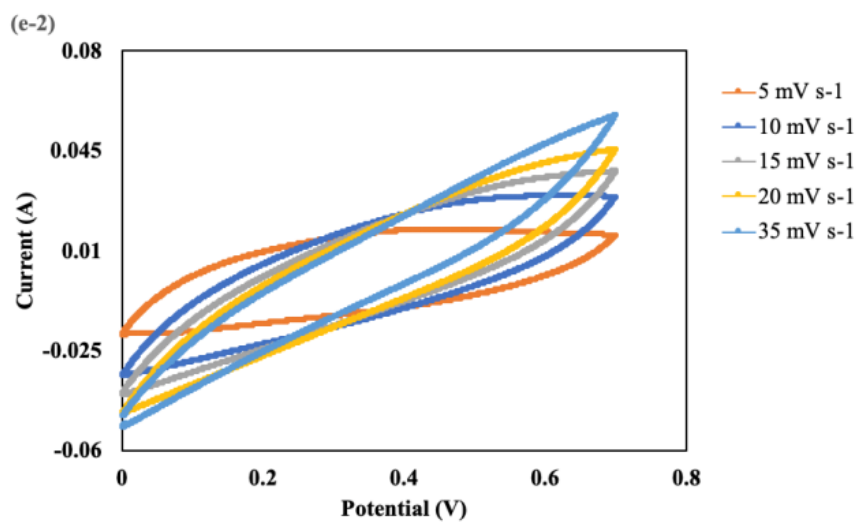
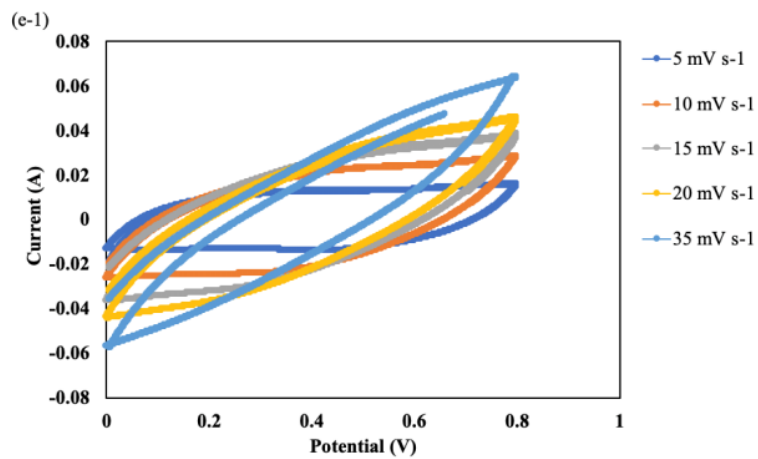


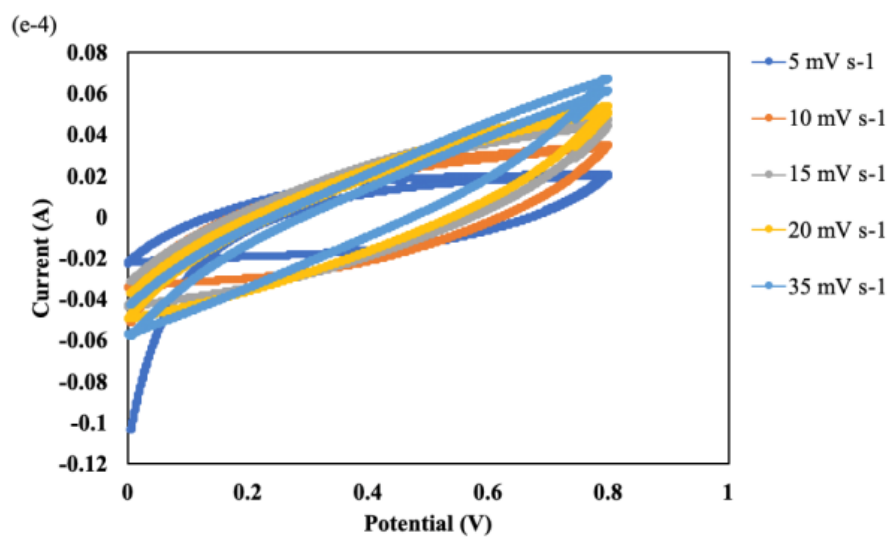
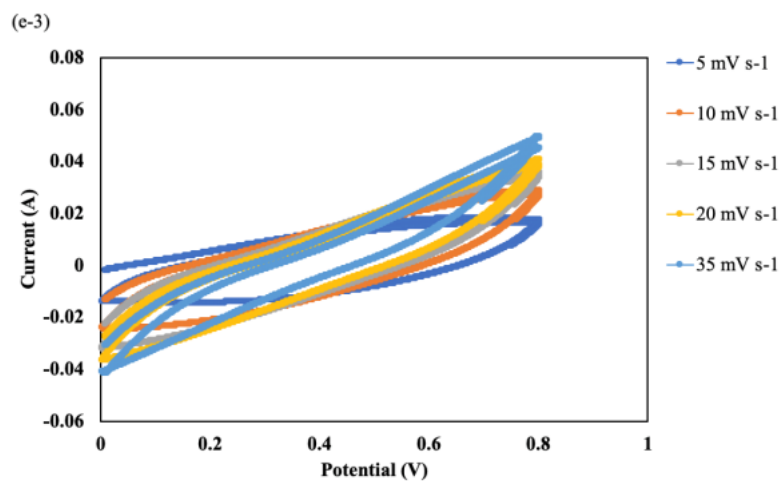
Figure 3.3 FTIR spectra of nanocellulose, nanocellulose/PANI, nanocellulose/RGO, nanocellulose/RGO/PANI.

The electrochemical performances of the assembled SCs with these electrode composite films were evaluated in terms of capacitance (Figure 3.4a), powder density and energy density (Ragone plots) (Figure 3.4b), equivalent series resistance (ESR) (Figure 3.4c) and electrochemical Impedance Spectroscopy (EIS) (Nyquist plots) tests in two electrode systems (Figure 3.4d). Different Cyclic Voltammetry scan rates of each sample (Figure 4e 1-6). These properties were mass-specific, based on the mass of electrodes used for assembling the sandwich-like SCs.









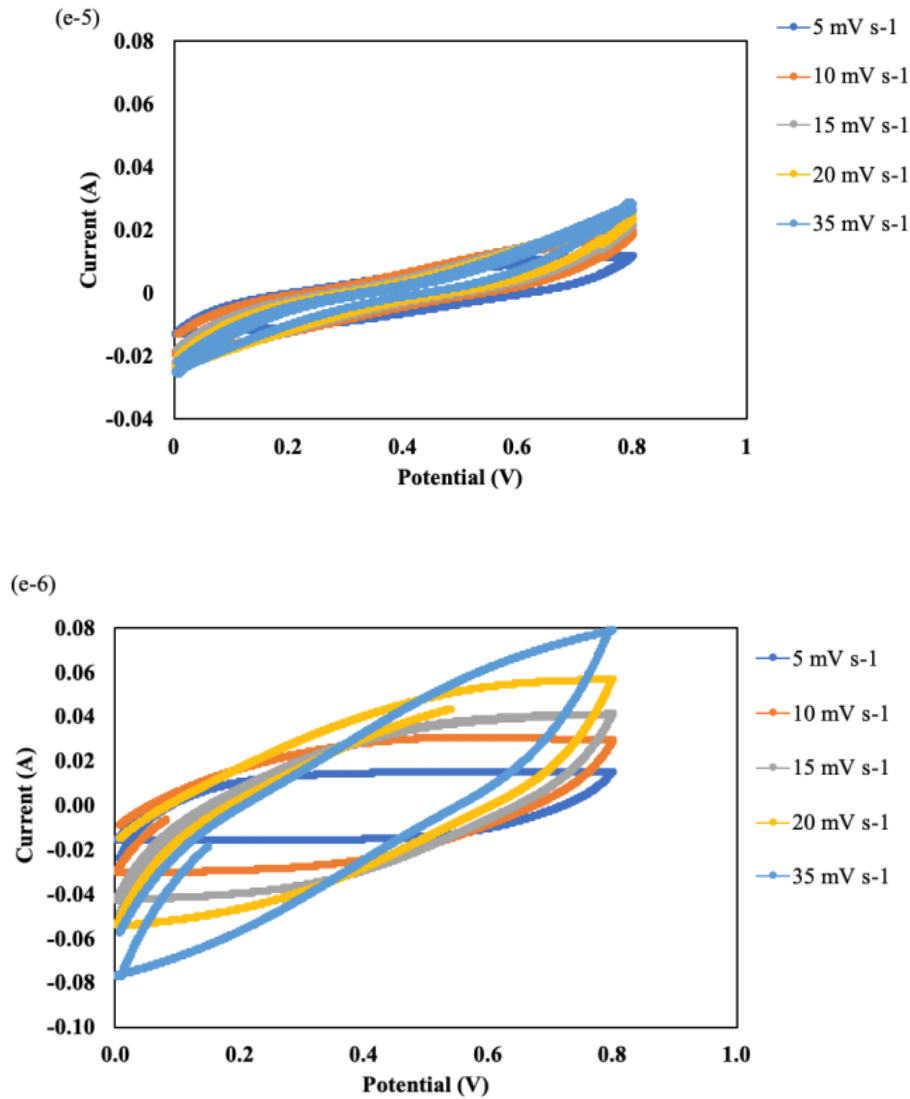


Figure 3.4 Electrochemical performance of all SC samples based on NC/PANI/RGO composite films. (a) Mass-specific capacitance versus current density; (b) Ragone plots; (c) Equivalent Series Resistance; (d) Nyquist plots; (e1-6) Cyclic voltammetry at different scan rates: NC/PANI (e-1); NC/PANI/RGO-1 (e-2); NC/PANI/RGO-2 (e-3); NC/PANI/RGO-3 (e-4); NC/PANI/RGO-4 (e-5); NC/PANI/RGO-5 (e-6).

Sample NC/PANI is a control sample containing PANI but no RGO. As compared to films containing both PANI and RGO, the assembled supercapacitor with NC/PANI shows significantly larger V_{IR} drop and shorter charge-discharge time with potential window scanning from 0 to 0.8V (Figure 3.5a-b). A larger V_{IR} drop means more energy wasted during the charge-discharge cycles, which is not desirable for energy storage devices [51, 52].

As shown in Figure 3.4a, the highest capacitance is observed in sample NC/PANI/RGO-5 (79.71 - 60.49 F g⁻¹). Figure 4a also shows a high capacitance (60 -70 F g⁻¹) for sample NC/PANI; The Ragone plots (Figure 3.4b), however, shows that NC/PANI has a very sharp

initial drop (110.45 W Kg^{-1} to 50.65 W Kg^{-1}) on power density with the increase in energy density, indicating instability of the SC device. Also, NC/PANI shows both the lowest power density (10.40 W Kg^{-1}) and the lowest energy density (4.03 Wh Kg^{-1}) when compared to other samples, indicating that the amount of energy stored and transferred per unit volume in SCs based on NC/PANI is less than in SCs based on NC/PANI/RGO samples.

Cyclic Voltammetry (CV) was also performed for each sample at different scanned rate from 5 to 35 mV s^{-1} to check how it varies the capacitance. It can be seen that, with an increase in the CV scan rate, the oxidation peaks of CV scans shift to the right, and the reduction peaks of CV scans shift to the left. The more significant in the shifts of oxidation and reduction peaks in CV scans, the more significant redox reactions may take place in pseudocapacitance based conductive materials like PANI [7, 17, 53]. A larger area enclosed by a CV curve usually indicates a better specific capacitance at a scan rate [7, 17, 53]. The best result of CV scans was found in sample NC/PANI/RGO-5, as indicated by the largest area enclosed by the CV curves, followed by sample NC/PANI. In Figure 3.4e (1-6), NC/PANI/RGO-5 showed significant redox behaviors as compared to other samples. Sample NC/PANI/RGO-2 and 3 behaved similarly in CV scans; Sample NC/PANI/RGO-4 did not show significant shifts during CV scan, suggesting that there was no significant redox behavior of pseudocapacitance in the sample when different CV scan rates were applied. The specific capacitance of NC/PANI/RGO-4 is the lowest when compared to others, because of the smaller area of CV curve in this composite. Results of CV scans for the samples agree with the capacitance results in Figure 4a.

In summary, all the NC/PANI/RGO samples generally have better balance between energy and power density than the NC/PANI, and therefore are more suitable for energy storage applications. A possible explanation is that the pseudocapacitance processes of PANI during charge-discharge involve such material deformation as swelling, shrinkage and cracking, leading to a poor stability during energy release in a device [26, 54]. In addition, the deformation of the composite material may also accelerate the degradation of PANI, which may result in a low working potential of PANI electrode [12, 26, 54]. Therefore, PANI has usually been used in combination with other materials like metal or carbon materials to decrease the V_{IR} drop and improve its overall electrochemical property [15, 17, 32, 54]. During charge-discharge cycles, part of the emeraldine PANI (conductive) may be converted to pernigraniline (semiconductive) due to the reduction of the ions during their transfer between electrodes [55-57]. This agrees with recent studies on PANI-based electrodes or supercapacitors which suggest that the stability of PANI can be improved by adding RGO [15,

17, 58]. A synergistic effect between PANI and RGO in double-layer energy storage devices may arise from the PANI which provides a source of high pseudocapacitance and the RGO which improves the conductivity of the electrodes [26, 59-61].

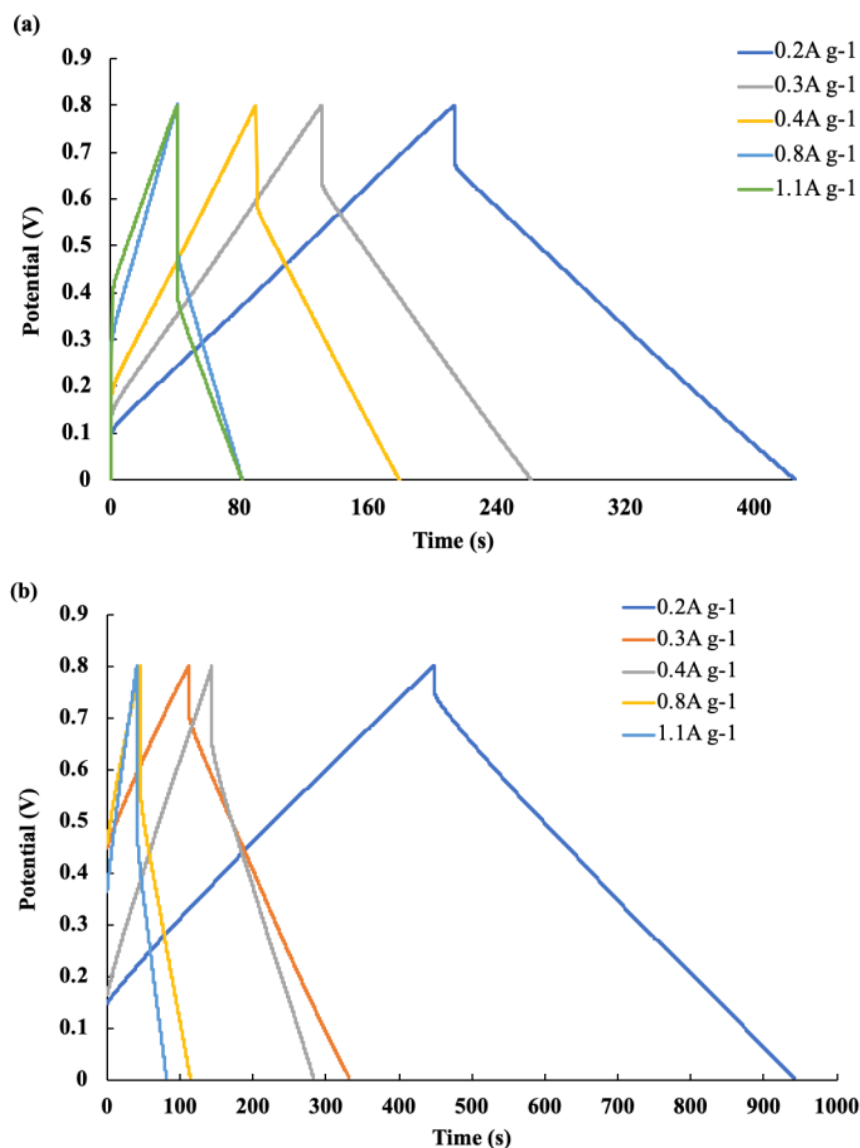


Figure 3.5 Galvanostatic charge-discharge curve by current density (0.2 A g⁻¹ to 1.1 A g⁻¹), with potential window scanned from 0-0.8V.
(a) Galvanostatic charge-discharge curve of sample NC/PANI,
(b) Galvanostatic charge-discharge curve of sample NC/PANI/RGO-5.

The electrode films NC/PANI/RGO-1, 2, and 3 have the same aniline/RGO ratio of 3.2 $\mu\text{l mg}^{-1}$, but different ratios of aniline/cellulose and RGO/cellulose as shown in Table 3.2. Their properties were compared to exam the impact of nanocellulose content on the performance of the composite film. As shown in Figure 3.6(a) and (b), the performance of the composite film

is sensitive to the nanocellulose contents. When the ratio of RGO/PANI is fixed, an increase in the nanocellulose content (as represented by the reducing ratio of aniline/cellulose) was found to cause an increase in the resistance (ESR) on an assembled supercapacitor, but a decrease in the power density of the device. On the other hand, the samples' mechanical behaviours are more clearly to be understood by testing the ultimate tensile stress and Young's Modulus than compression tests. The results showed the more nanocellulose contents in the samples, the higher breaking stress and Young's Modulus values of the samples. Among the three samples, NC/PANI/RGO-1 has the lowest nanocellulose content and consequently the lowest Young's Modulus (0.2 MPa) and breaking stress (2.18MPa). Despite of its good electrochemical performance, NC/PANI/RGO-1 is fragile and very difficult to handle and assemble into a supercapacitor. NC/PANI/RGO-2 has higher nanocellulose content than NC/PANIRGO-1, and consequently has better mechanical but poorer electrochemical performance than NC/PANI/RGO-1, as shown in Figure 3.4 (a-d). Among sample NC/PANI/RGO-1,2 and 3, NC/PANI/RGO-3 shows reasonable performance both mechanically (breaking stress at 4.75 ± 2.28 MPa, Young's Modulus at 0.6 ± 0.35 MPa) and electrochemically (minimal ESR at 11.8 Ω and maximum power density at 84.25 W Kg⁻¹).

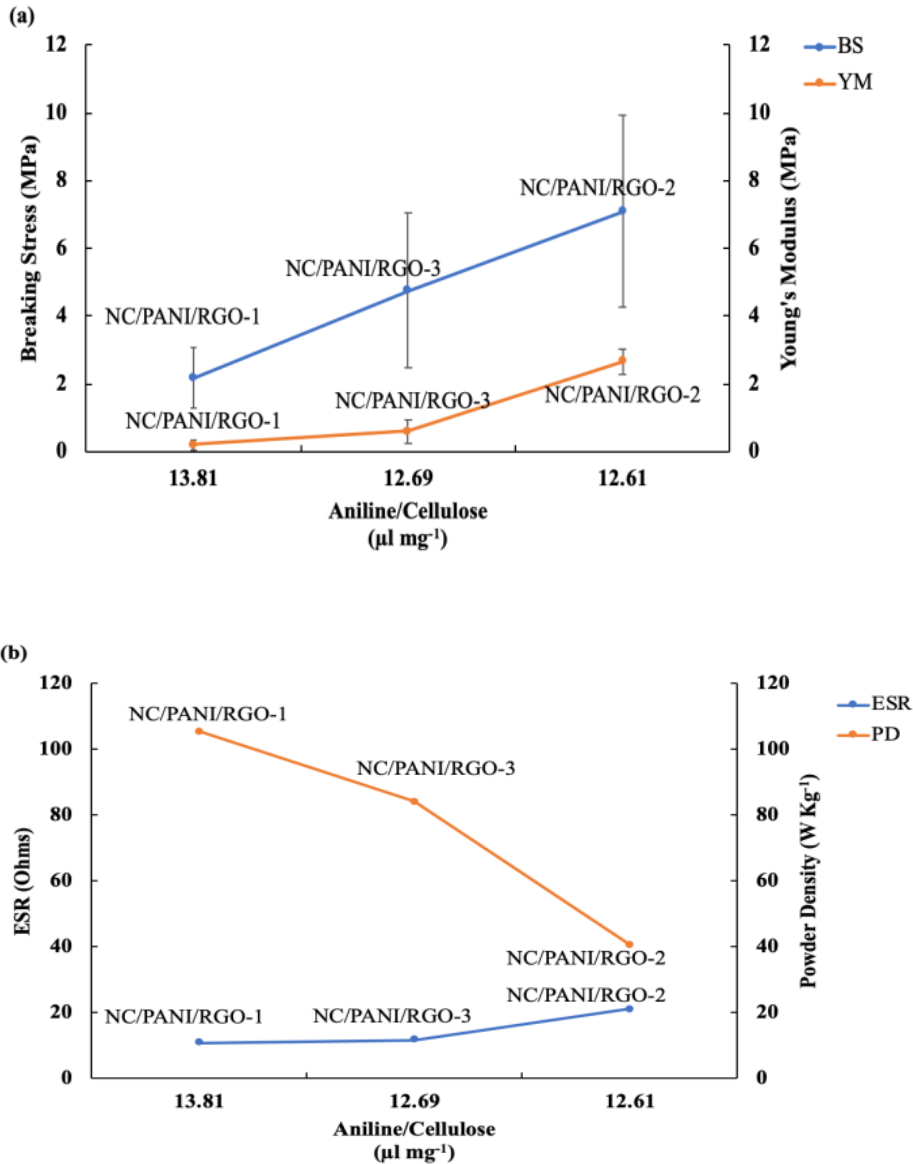


Figure 3.6 Mechanical performance Vs. electrochemical performance of sample NC/PANI/RGO-1,2,3. (a) Mechanical stresses of NC/PANI/RGO-1,2,3. (b) ESR, powder density and the ratio of aniline/cellulose with a fixed ratio of PANI/RGO.

To further optimize the electrochemical performance of the composite film, the ratios of RGO/nanocellulose were raised in NC/PANI/RGO-4 and 5, which have the same ratio on aniline/RGO (2.22). The assembled supercapacitor with NC/PANI/RGO-4 has a very large EIS (23.90 Ω) and ESR (45.05 Ω) (Figure 3.4 c-d), indicating a high resistance and a poor electrochemical performance due to high nanocellulose content. NC/PANI/RGO-4 is therefore not considered a good electrode for an assembled supercapacitor despite of its high Young's Modulus (4.83 MPa) (Figure 3.7). On the other hand, the supercapacitor is assembled with

NC/PANI/RGO-5 show a lowest EIS (3.13Ω), and the ESR ($8.60 \Omega - 10 \Omega$) is lower than other samples during different discharge currents were applied (Figure 3.4c-d).

NC/PANI/RGO-3 and NC/PANI/RGO-5 both contain the same amount of nanocellulose (24 mg). But NC/PANI/RGO-5 has a higher amount of RGO than CN/PANI/RGO-3 (Table 3.2), thus NC/PANI/RGO-5 has a better electrochemical performance (Figure 4a-d). Supercapacitor containing NC/PANI/RGO-5 shows lower resistance on both ESR (8.6Ω) and EIS (3.13Ω) when compared to NC/PANI/RGO-3. Lower resistance means better conductivity and smaller V_{IR} drop during charge-discharge cycles (Figure 3.5). The smaller the V_{IR} drop, the smaller energy waste that will be produced during charge-discharge cycles, which improves overall electrochemical performance [51]. Among all electrode film samples, NC/PANI/RGO-5 has the highest loading ratio (wt/wt) of conductive materials on the substrates (Table 3.2) and lowest resistance. Supercapacitor assembled with NC/PANI/RGO-5 also shows the highest power density (147.53 W Kg^{-1}) and energy density (5.09 Wh Kg^{-1}) along with reasonable mechanical properties (Figure 3.7). The ratios of RGO to aniline in NC/PANI/RGO-5 is the highest, RGO has been found to improve the mechanical performance on PANI/cellulose composite [15, 58]. Therefore, we conclude that the best sample in the current study is NC/PANI/RGO-5 which shows the best electrochemical performance and acceptable mechanical performance to maintain both strength and flexibility of the assembled SC.

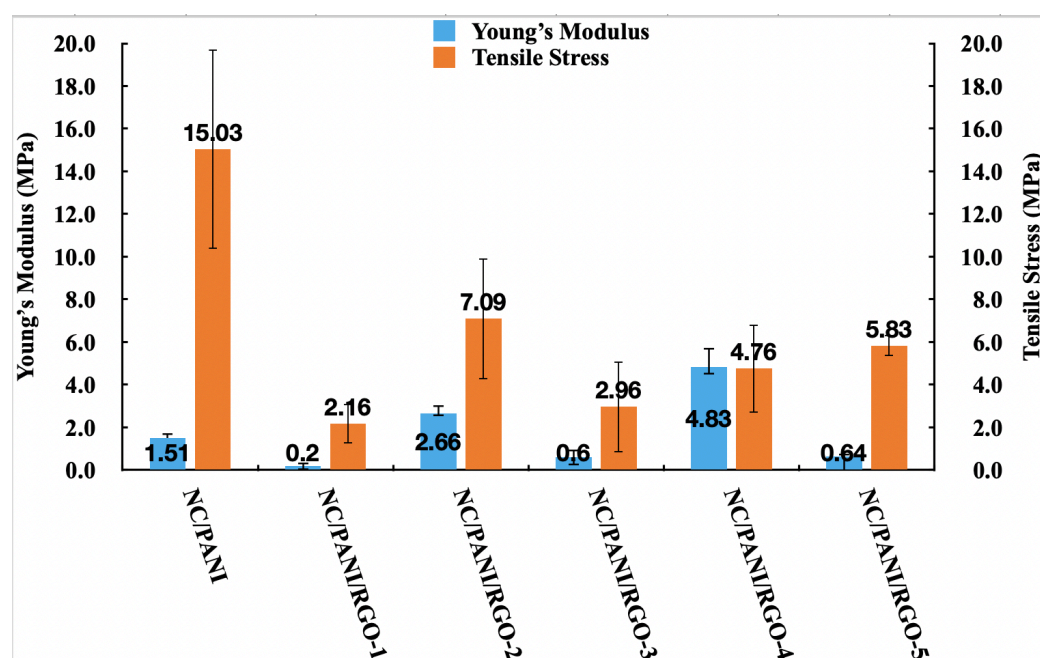


Figure 3.7 Tensile strength and Young's modulus of composite film electrode samples.

The electrochemical performance of a supercapacitor depends on the amount of conductive materials that can be loaded on the electrodes. A higher ratio of mass loading in a limited area of substrates is therefore very important. In the current study, composite electrode films with a large mass-loading of active materials (PANI and RGO) were enabled by the highly porous structure of the nanocellulose substrates to optimize their electrochemical properties. Moreover, the porous nanocellulose substrate can largely increase the absorption of aqueous electrolyte by the film in an assembled supercapacitor and contributes to a good electrochemical performance. Table 3.1 lists the mass loading on cellulose substrates and their electrochemical/mechanical performance from a few previous studies. This work shows the highest loading ratio of active materials. A high mass loading ratio in a flexible electrode usually contribute to good energy storage capacity which are desirable for most applications in wearable electronics. The film electrode developed in the current study also demonstrates very low resistance and excellent mechanical properties as compared to other work (Table 3.1). The nanocellulose/PANI/RGO composite film developed in this study is therefore promising for supercapacitors due to its high conductivity enabled by a large mass loading ratio of conductive materials on the flexible and highly porous nanocellulose substrate.

As shown in Figure 3.8b-d, nanocellulose in the NC/PANI/RGO composite films provides a flexible substrate for the electrode to allow easy handling and assembling into a supercapacitor; while a composite electrode film containing no nanocellulose substrates can get cracks when dried out (Figure 3.8a), which is not suitable for further assembly into a supercapacitor device.

To further verify the flexibility of the composite electrode film, the cyclic voltammetry tests on bended samples were conducted following previous similar studies [20, 42, 61]. As showed in Figure 3.8 (e, f, h), the assembled SC devices were bended into different angles (120° and 90°), scanned by a cyclic voltammetry tester at 10 mV s^{-1} with an operation potential window from 0 to 0.8 V. As shown in Figure 3.8, there is no significant difference in the cyclic voltammetry curves between the flat sample and samples bended at different angles (120° to 90°), indicating the flexibility of the developed composite electrode films for supercapacitors. Three red LED lights powered by three fabricated SCs (containing NC/PANI/RGO-5) in series (Figure 3.8g). Each assembled SC was charged under 10 mA up to 0.8 V for about 5 minutes to get fully charged. All three red LED were on with full brightness for 2 minutes after they were connected to the SCs, and gradually faded out after 2.5 minutes (The videos are available in the publication web).

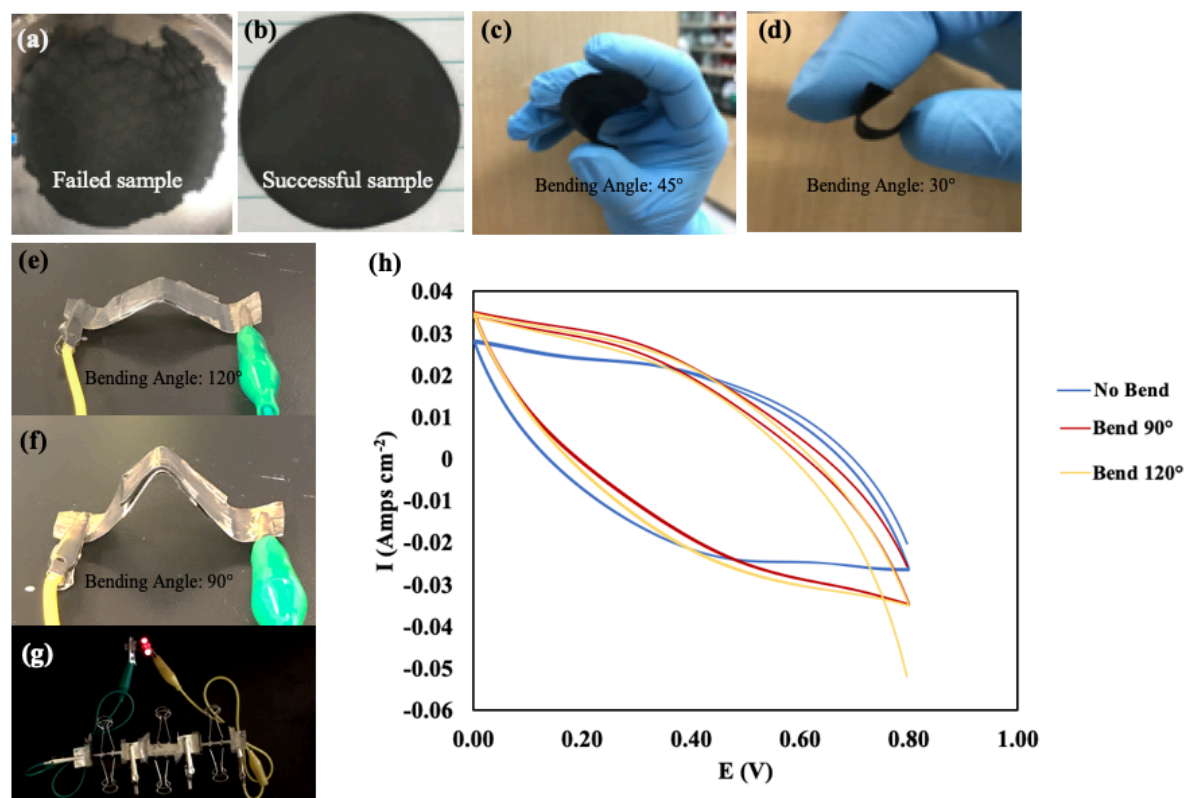


Figure 3.8 The flexibility of the composite electrodes film. (a) A failed sample containing only PANI/RGO that was brittle and cracked; (b) A NC/PANI/RGO composite film; (c-d) Bended composite electrode films; (e-f) The assembled SC with NC/PANI/RGO electrode films bended at 120° (e) and 90° (f) for cyclic voltammetry scanning; (g) Three assembled SC in series connection to 3 LED lights; (h) Cyclic voltammetry scans at 10 mV s^{-1} on the assembled SC with NC/PANI/RGO electrode film bended at 90°, 120° and no bending.

3.5 Conclusion

An eco-friendly metal-free nanocellulose-based flexible and lightweight supercapacitor with a high mass loading ratio of active materials and good mechanical properties has been developed in this chapter. PANI and RGO were incorporated into the nanocellulose substrate as the conductive materials to fabricate a composite film for electrodes with high specific capacitance and high conductivity. To achieve an optimal balance between electrochemical and mechanical performances of the electrode film, the ratios between nanocellulose, PANI and RGO were adjusted in the fabrication the electrode film. Composite films with different component ratios were evaluated in terms of specific capacitance, energy density, power density, ESR, and EIS. In general, a high content in nanocellulose contributes to higher mechanical properties (both strength and flexibility) but leads to a low electrochemical

performance. The nanocellulose/PANI/RGO flexible composite film developed in this work has a high conductivity enabled by the large mass loading ratio of PANI and RGO, therefore is a promising material for developing supercapacitors for advanced applications in various areas from energy storages to biomedical devices including e-skin.

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CHAPTER IV

A Mussel-inspired Autonomously Self-healable All-in-one Supercapacitor with Biocompatible Hydrogel

Abstract

Flexible and self-healable supercapacitors (SC) show great potential in developing smart energy storage devices for health care electronics, which call for the development of non-toxic, biocompatible and biodegradable electronics based on natural materials. Most self-healable mechanisms need external stimuli and long healing time, which limits their practical applications. Herein, we developed a mussel-inspired biocompatible SC with autonomously self-healing capability through a hybrid system of gelatin methacrylate (GelMA), cellulose nanocrystal (CNC) and tannic acid (TA). Mussel-inspired TA on GelMA-CNC hydrogels were optimized by concentrations and timings to evaluate stress, Young's modulus, toughness, and compressive tests for further developing electrochemical performance on the hydrogel electrode with Polyaniline (PANI) and reduced graphene oxide (RGO). This SC shows an impedance of 5.67 Ω and 6.38 Ω after one healing processing. The specific capacitance, energy density and power density of the SC reached 1861.21 mF cm⁻³, 20.65 mW cm⁻³, and 595.59 mWh cm⁻³, and retained 96%, 100% and 82%, respectively, of their original values after one cut-healing process. This study demonstrates remarkable potential in advanced smart and biocompatible energy storage devices.

Keywords: *flexible and biocompatible supercapacitor, mussel-inspired self-healing electrode, all-in-one supercapacitor, gelatin methacrylate, cellulose nanocrystal*

4.1 Introduction

The rapid progress of biocompatible hydrogel supercapacitors (SCs) featured with robust flexibility and self-healing capability is potentially accelerating the evolution of integrated electronic devices for health care applications, such as wearable devices, flexible and healable sensors, and artificial muscles or actuators [1-5]. The electrochemical performance of flexible SCs may be compromised in real life applications if they work in a continuously deformed status, or if there are damages or cracks in the electrodes caused by redox reactions in the brittle conductive materials during long-term charge and discharge cycles [6]. To overcome such limitations, self-healing SCs have been developed to enable automatic healing/repairing of cracks to prevent structural fractures and to restore the structural integrity and electrical properties of the devices after mechanical damages[7]. Briefly, self-healing mechanisms include chemical and physical self-healing. Chemical self-healing mechanism is normally complicated, it may involve supramolecular chemistry, dynamic covalent chemistry, photo initiator or microcapsule techniques (The details can be found in Chapter 2, Figure 2.6) [8, 9]. Compared with chemical approach, physically repairing is mild and feasible, which mostly consists of non-covalent bonds, such as hydrogen bonding, Van Der Waals force, guest-host interaction, hydrophobic interaction (Table 4.1).

Developing of self-healable SCs for medical uses that based on natural polymers are highly attractive to researchers recently [3]. Natural polymers are non-toxic, therefore exhibit great potentials in biomedical applications such as implantable devices and tissue engineering scaffolds. Natural polymers can be easily disposed by landfill, and eventually turn into carbon dioxide, water, and some other inorganic compounds [10]. Most existing self-healable SCs (listed in table 4.1) are composed of synthetic polymers which may be toxic to human body or cause skin irritations [11]. They are mostly non-degradable and may cause serious environmental concerns and high handling costs [12]. Therefore, synthetic polymers may have limited applications in health care sectors. In order to meet the demands of both the medical electronics market and the goal of sustainability, “from nature to nature”, self-healable biodegradable energy storage devices based on natural polymers with excellent electrochemical performance and mechanical properties are highly desired [10].

In this chapter, we developed an all-in-one configured autonomously self-healable hydrogel supercapacitor based on natural polymers including mussel-inspired tannic acid (TA), gelatin methacrylate (GelMA) and cellulose nanocrystals (CNC). Mussel-inspired tannic acid treated hydrogel was further coated with polyaniline (PANI) and reduced graphene oxide (RGO) via

in-situ polymerization to fabricate an all-in-one configured flexible and autonomously self-healable supercapacitor (Figure 4.1).

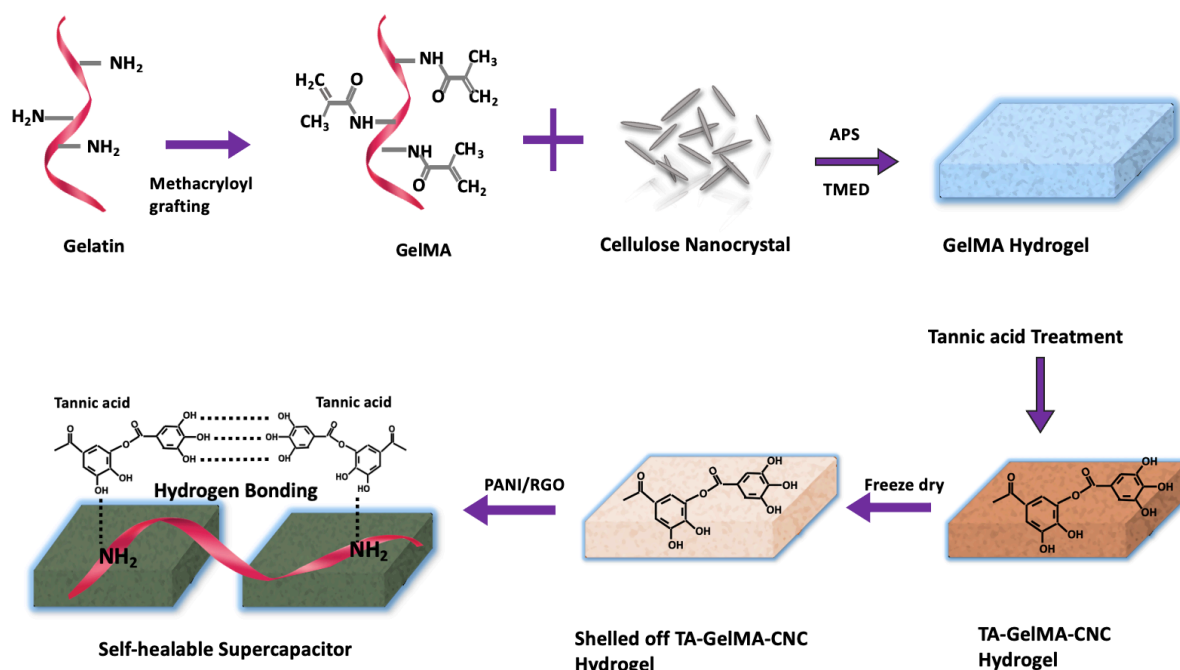


Figure 4.1 Schematic illustration of fabricating an all-in-one self-healing SC, and the internal mechanism of the self-healing.

Gelatin has been approved by Food and Drug Administration (FDA) as a biodegradable and biocompatible natural polymer, which shows great potentials in smart energy storage devices for medical care [13-15]. Gelatin has frequently been used in tissue engineering because it is similar to collagen in its capacity to minimize the immunogenicity in human body [16]. Thus, this biocompatible hydrogel supercapacitor has great potential to be used in health care. Several recent studies have been reported on the electrical signal promoted wound healing, which will promote the healing of chronic wounds, such as diabetic foot ulcers [17-20]. This study is a pioneer work to develop natural polymer-based supercapacitor that can maintain a good electrochemistry and mechanical performance. Moreover, gelatin hydrogels are highly hydrophilic due to the presence of a large number of hydrophilic pendant groups, which contribute to high retention of water in the polymer matrix, leading to an enhanced ionic conductivity [21]. Modification of gelatin by grafting methacryloyl moieties on amine groups generates gelatin methacrylate (GelMA), which significantly improves the compressive and elastic moduli of gelatin hydrogels [22, 23]. To further improve the mechanical strength of the

GelMA hydrogel, cellulose nanocrystal was incorporated into the GelMA hydrogel in the current study. CNC have been found to enhance mechanical strength of hydrogel due to their high crystallinity and strong intramolecular bonding [24-27]. Tannic acid is a plant-derived natural polyphenol compound which is rich in ester-linked pyrogallol and catechol groups. It has been reported that tannic acid showed biocompatibility *in vivo* when used in scaffolds for medical applications [28-30]. Tannic acid can bind with collagen or gelatin by multi-point hydrogen bonding and hydrophobic interactions [31-34]. The hydrogen bonding is formed between tannic acid and GelMA to generate GelMA-based self-healable double-network (DN) [23]. It is therefore imperative to fabricate SCs that are automatically healable, both physically and electrochemically, without external stimuli, and biocompatible [35, 36]. This study further explores the mechanism in the development of mussel-inspired biocompatible supercapacitors.

Table 4.1 Summary of self-healing electric devices from recent studies

Compositions	Self-healing mechanism	Resistance	Healing Conditions	Healing time	Electrical healing efficiency on Specific Capacitance	Tensile stress MPa	Strain %	Ref.
CNT ¹ /PBS ²	B–O bond	N/A	R. T. ¹³ with pressure	10 s	98%	1.75	250	[37]
CNT/PBDMS ³	B–O bond	2.1 Ω m	R. T. with pressure	N/A	N/A	N/A	N/A	[38]
CNT/AgNW ⁴ / PDMS ⁵ –MPU ⁶ _{0.4} –IU ⁷ _{0.6}	Dynamic bonding	25 Ω	R. T.	12h	> 90%	N/A	100	[39]
Nickel particles/ supramolecular polymer RGO/SAP ⁸	Hydrogen bonding	N/A	R. T. with pressure	15 s	90%	1	20	[40]
	Hydrogen bonding	267 Ω m	R. T. with pressure	30 s	100%	N/A	N/A	[41]
Graphite/bPEI ⁹	Hydrogen bonding	N/A	R. T. with pressure	10 s	98%	6	35	[42]
SWCNT ¹⁰ /PANI- PVA ¹¹ -H ₂ SO ₄	Hydrogen Bonding	13.2 Ω	R. T.	10s	80%	470	380	[43]
PANI/PVH ¹² - H ₂ SO ₄	Hydrogen Bonding	0.23 Ω	R. T	20min	96%	62.3	88.6	[44]
Current work	Hydrogen bonding	5.67 Ω	R. T.	4-6 h	96%	17.42 KPa	63	

Abbreviations:

1. CNT: carbon nanotube; 2. PBS: polyborosiloxane; 3. PBDMS: polyborondimethylsiloxane; 4. AgNW: silver nanowire; 5. PDMS: poly(dimethylsiloxane); 6. MPU: 4,4' -methylenebis (phenyl urea) unit; 7. IU: isophorone bisurea unit; 8. SAP: superabsorbent polymer; 9. bPEI: branched polyethylenimine; 10. SWCNT: single wall carbon nanotube; 11. PVA: polyvinyl alcohol; 12. PVH: copolymer of vinylimidazole and hydroxypropyl acrylate; 13. R.T. room temperature

4.2 Materials and Methods

4.2.1 GelMA-CNC Hydrogel

GelMA-CNC hydrogel was synthesized by methacryloyl grafting following a well-developed method [23]. Specifically, 10% (w/v) gelatin was completely dissolved in Dulbecco's phosphate-buffered saline (DPBS) at 40 °C with magnetic stirring. After that, MA (0.8 ml MA/1 g gelatin) was added to the gelatin solution and stirred at 50 °C for 2 h. The reaction was stopped by diluting the solution volume to 4-fold, and GelMA solution was dialyzed against deionized water with 12-14 Da cut-off at 50 °C for 1 week. Then the solution was lyophilized until a white porous foam was produced. GelMA powder was dissolved in 0.1M H₂SO₄ with 10% (w/v) concentration at 40 °C for 30 mins, then Sodium cellulose nanocrystals (CNC) (12% wt in water) (Cellulose Lab, Canada) was added into GelMA solution and well homogenized. The ratio of CNC to GelMA is 1 to 9 (w/w). GelMA-CNC hydrogel was formed by adding APS (5.7 mg ml/L) and TEMED (2.9 mg ml/L) into GelMA-CNC solution at room temperature. Cylindrical GelMA-CNC hydrogel samples 3.5 cm in diameter and 3.0 mm in height were prepared for further tests.

4.2.2 TA-GelMA-CNC hydrogels

The fabrication process of TA treated GelMA hydrogel is as follows in Table 4.2, however, not all of the treatments of GelMA-CNC hydrogels could obtain a proper quality for further fabrication procedures. Thus, the four concentration of TA solution was made as (w/w) 40 %, 60 %, 80 % and 100 %; GelMA-CNC hydrogels were immersed in 40 %, 60 %, 80 %, 100 % TA solution with 12 hours, 24 hours, 48 hours, and 72 hours respectively [23]. After soaking with TA, TA-GelMA-CNC hydrogels were frozen at -20 °C for 4 hours, and then freeze dried at -47°C overnight. The TA shells on the GelMA hydrogels can be easily peeled off after freeze drying for PANI and RGO coating in the next step.

4.2.3 Preparation of the All-in-One Configured TA-GelMA-CNC Supercapacitor:

RGO and PANI were *in situ*-polymerized and deposited onto both sides of the TA-GelMA-CNC hydrogels which served as the electrolyte separator. Specifically, 100 mg RGO aqueous solution (0.1 wt %) was added into 10 mL 1 M H₂SO₄ solution, which was sufficiently dispersed using ultrasonic dispersion instrument until RGO was homogeneously dispersed into the solution. Then, 300 µl aniline monomer was added into the blended solution with constant stirring in ice-water

bath for 10 min. On the other hand, 375 mg APS was dissolved in 10 mL 1 M H₂SO₄ solution, cooled at 0 °C, and dropped into the above as-prepared homogenous solution of RGO and aniline monomer under vigorously stirring. The TA-GelMA-CNC hydrogels were immersed into the obtained blended solution for polymerization at 4 °C for 8 hours, and subsequently washed with deionized water for several times to remove residual aniline monomers and APS, yielding the all-in-one TA-GelMA-CNC SC with both surfaces deposited with RGO and PANI nanocomposites electrodes. The edges of an obtained sample were trimmed into the size of 25mm * 20mm * 2.5 mm and assembled into an all-in-one configured supercapacitor by connecting their two opposite ends with aluminum foils as current collectors.

Table 4.2 The tannic acid (TA) Treatment for Self-healable Supercapacitor Samples

Time (hr) / TA Concentration	10%	20%	40%	60%	80%	100%
6	Not significant self-healing	Not significant self-healing	Not significant self-healing	PANI/RGO not coated well	PANI/RGO not coated well	Fragment hydrogel
12	Not significant self-healing	Not significant self-healing	PANI/RGO not coated well	Data Available	PANI/RGO not coated well	Fragment hydrogel
24	Not significant self-healing	Data Available	Data Available	Data Available	Data Available	Data Available
48	Not significant self-healing	Dehydrated in TA	Fragment hydrogel	Data Available	Dehydrated in TA	Dehydrated in TA
72	Dehydrated in TA	Dehydrated in TA	Fragment hydrogel	Data Available	Dehydrated in TA	Dehydrated in TA

4.2.4 SEM characterization

The lyophilized hydrogels samples were placed on a wafer for gold coating. The morphologies of samples were characterized by a JEOL JSM-5900LV scanning electron microscope.

4.2.5 FTIR characterization

Fourier transformed infrared (FTIR) spectra (Thermo Nicolet iS10 FTIR Spectrometer) was used to investigate the intermolecular interactions among GelMA, CNC, TA, RGO and PANI. The spectra were obtained from lyophilized samples of GelMA, GelMA-CNC, TA-GelMA-CNC at room temperature.

4.2.6 Electrochemical Test

An all-in-one TA-GelMA-CNC supercapacitor (Figure 4.2) was assembled by sandwiching the hydrogel between two pieces of aluminum foil as the current collectors and sealed by parafilm to prevent moisture evaporation. The electrochemical properties of the assembled SCs were investigated using an electrochemical workstation. The electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency ranging from 10^5 to 10^{-2} Hz, 10 mV AC amplitude and zero DC amplitude. The Galvanostatic Charge-Discharge (GCD) measurements were performed from 0 to 0.8 V at a constant current ranging from 1 to 10 mA. The cyclic voltammetry (CV) curves were recorded from 0 to 0.8 V at scan rates ranging from 0.002 to 1 V s⁻¹. The capacitance of a single electrode that was assembled for SC can be calculated from GCD curves as a function of the discharging slope after the IR drop:[45]

$$C = 2I\Delta t/(\Delta V - V_{IR}) \quad (1)$$

where I is the discharge current; Δt represents the time span of a full discharge; ΔV is the potential change after a full discharge; V_{IR} indicates the potential drops at the initial discharge stage, which is mainly attributed to the intrinsic resistance of the electrode materials and the resistance of the electrolyte. Volume-specific capacitance of a sample can be determined by dividing the C by its volume.

The equivalent series resistance (ESR) was calculated using: [45]

$$ESR = V_{IR}/2I \quad (2)$$

Energy density (E) and power density (P) can be estimated according to the equations:[46]

$$E = \frac{1}{2} \times C_{device, specific} \times \Delta V^2 \quad (3)$$

$$P = E/\Delta t \quad (4)$$

4.2.7 Rheology characterization

All rheology experiments were conducted on a TA Discovery Hybrid Rheometer. The hydrogels (8 mm in diameter and 1 mm in thickness) were loaded on the parallel plate, the diameter of the parallel plate is 20 mm. During oscillation frequency experiments, the samples were measured in the frequency ranging from 0.1 to 100 rad s⁻¹ with a constant strain of 0.5% at 21°C.

4.2.8 Mechanical Testing

The mechanical properties of samples were measured using an Instron 5965 mechanical analyzer. The tensile tests were performed at a speed of 10 mm min⁻¹ until breaking. Sample sizes were 25

mm (length) $\times$ 20 mm (width) $\times$ 2.5mm (thickness). All samples were tested with three replications. The Young's modulus was calculated as the slope in the initial linear region from the stress-strain curves [23]. Compression and cyclic compression experiments were carried out on samples with a diameter of 8 mm and a height of 10 mm under a maximum compression strain of 50% at a speed of 10 mm min⁻¹. The total number of 50 cycles were tested during cyclic compression test.

4.3 Results and discussion

4.3.1 Fabrication of the SC

The scheme of fabricating the all-in-one TA-GelMA-CNC supercapacitor was shown in Figure 4. 1. Modification of gelatin by grafting methacryloyl moieties on amine groups generates gelatin methacrylate (GelMA); CNC was added into GelMA solution (1 to 9 w/w) before GelMA polymerization to mechanically reinforce the hydrogel [24-27]. Ammonium Persulfate (APS) was used as an initiator, tetramethylethylenediamine (TMED) was used as a catalytic agent for crosslinking the GelMA hydrogel. The hydrogel was then immersed into tannic acid to endow self-healing property (TA-GelMA-CNC hydrogel) [31, 47]. PANI and RGO were then coated onto the TA-GelMA-CNC hydrogel to enable electrical conductivity. PANI is a brittle pseudocapacitive polymer. It may deform (swelling, shrinkage or cracking) during charge-discharge cycles and impact the overall electrochemical performance of SCs. Several studies suggested PANI mix with carbon materials may enhance the stability on overall electrochemical performance [48-53]. Our previous study on a nanocellulose based SC composed of PANI and RGO also showed that RGO enhances the electrochemical stability of PANI [6]. Therefore, this protocol has been applied in the current study to fabricate a hydrogel-based supercapacitor that has a stable electrochemistry performance.

GelMA-based self-healable double-network hydrogels were fabricated via pre-crosslinking GelMA and the subsequent formation of hydrogen bonds between hydroxyl groups in tannic acid [23]. Healing in such hydrogels can be achieved automatically without chemical crosslinking and external stimuli (Figure 4.1). Insoluble gelatin-tannin precipitated complexes were formed via gelatin-tannin reactions, owing to the binding between phenolic hydroxyl groups in tannins and the peptide carbonyl groups in gelatin [54, 55]. Such insoluble gelatin-tannin precipitated complexes not only formed on the GelMA hydrogel surface, but also penetrated into the inner

structure of the hydrogels. The insoluble complex layered up on the hydrogel surface can make it difficult to obtain an even surface coating of PANI and RGO through *in-situ* polymerization [31, 47]. Such a tough surface layer of gelatin-tannin insoluble complex was therefore peeled off after freeze drying to prepare the hydrogel surface for further coating of PANI/RGO (Figure 4.2a-b). The PANI/RGO nanocomposites electrodes were then deposited via *in situ*-polymerization onto the surface of the freeze-dried hydrogel with part of PANI/RGO penetrated into the freeze dried hydrogel (Figure 4.2c). The excess PANI/RGO was rinsed with water, leaving behind a stable layer of PANI/RGO incorporated onto the hydrogels. Electrochemical performance tests were conducted including Electrochemical Impedance Spectroscopy (EIS) Nyquist plots; Equivalent Series Resistance (ESR); volume-specific capacitance versus current density; power density and energy density in Ragone plots. The results suggest that the device can maintain excellent electrochemical performance with lower resistance (5.67Ω), even after cut-healing process, the specific capacitance can still remain at 96%.

Conventional supercapacitors usually have a layered configuration composed of two electrodes with a polymer electrolyte sandwiched in between (the configuration structure was shown in Chapter 2, Figure 2.8) [35, 36, 56]. The sandwich-like multilayer configuration can be apt to delaminate due to the displacement during physical deformation or damage, which may also cause the disconnection on the interface between the electrodes and separator [44, 57, 58]. Supercapacitors with an all-in-one configuration (Figure 4.2c and d), on the other hand, combine fast charge-carrier transportation, robustness and excellent integrity may potentially overcome the drawback of multilayered supercapacitors. However, there have been only a few reports on the development of all-in-one self-healable SC [44, 57]. To the best of our knowledge, the current study is the first report on the development of all-in-one configured autonomously self-healable hydrogel SC based on natural polymers.

The self-healable TA-GelMA-CNC hydrogel was assembled into an all-in-one configured supercapacitor by connecting their two opposite sides with aluminum paper as current collectors, and the TA-GelMA-CNC hydrogel itself served as the electrolyte separator. Four assembled SCs in series were charged at 10 mA for 5 minutes and can light a LED light for about 4 minutes (Figure 4.2d).

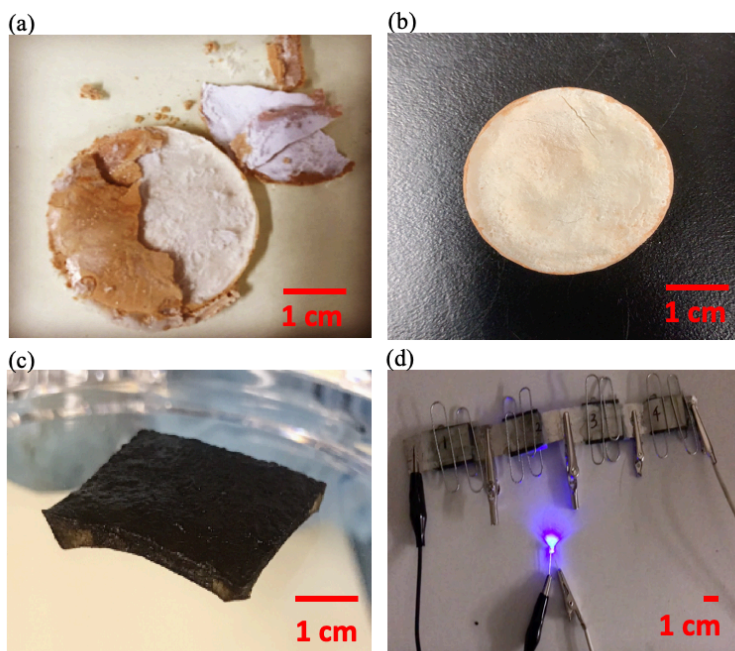


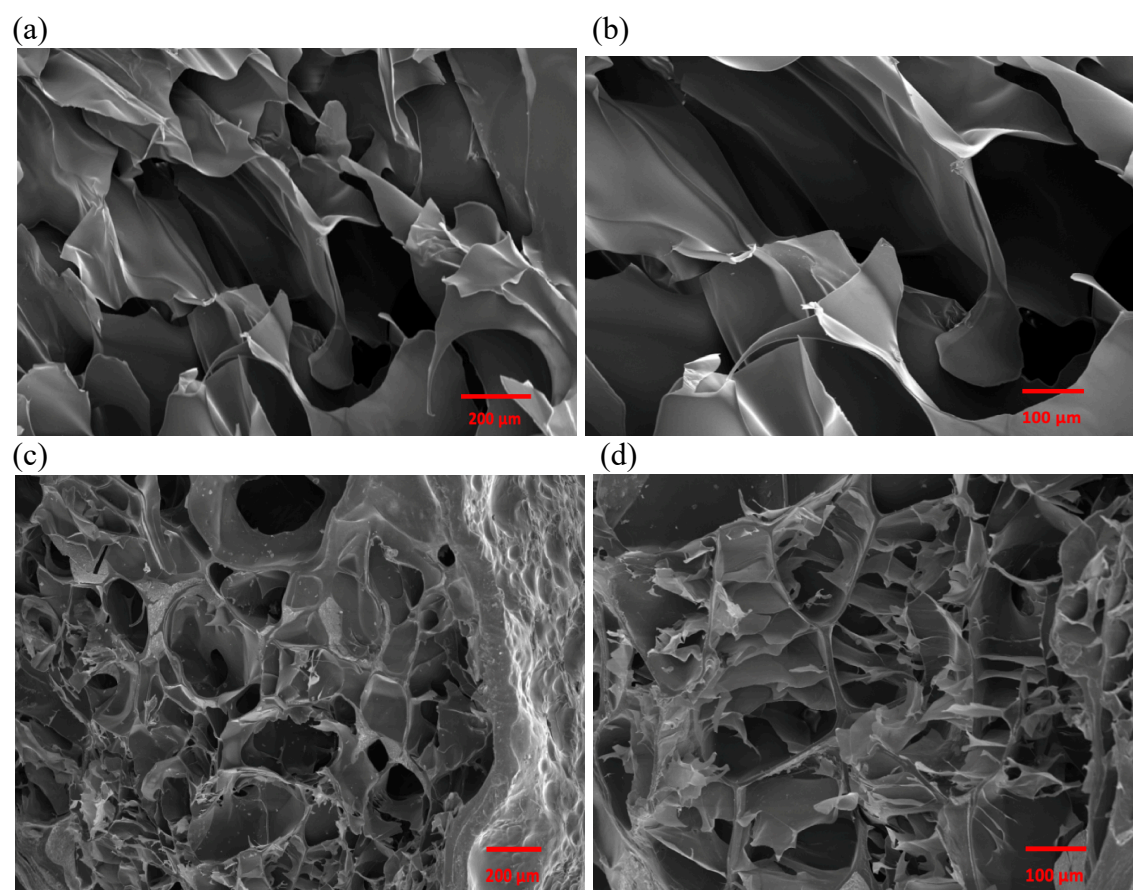
Figure 4.2 Photos of all-in-one TA-GelMA-CNC supercapacitor fabrication. (a) A shell composed of insoluble gelatin-tannin precipitated complexes on the GelMA-CNC hydrogel surface, which can be peeled off after freeze drying; (b) GelMA-CNC hydrogel with shell removed; (c) PANI/RGO coated TA-GelMA-CNC hydrogel; (d) Four all-in-one self-healable TA-GelMA-CNC SCs assembled in series to light up a LED light for about 4 minutes.

4.3.2 Morphology

Figure 4.2c shows the cross-sectional configuration of the all-in-one self-healable TA-GelMA-CNC SC. A thick layer of conductive PANI and RGO was deposited on top of the TA treated GelMA-CNC hydrogel. The conductive agents can also penetrate deeply into the TA-GelMA-CNC hydrogel which has a porous structure due to freeze drying.

SEM micrographs for hydrogel cross sections (Figure 4.3a-h) show porous 3D network structures for all lyophilized hydrogels, including GelMA hydrogels (Figure 4.3a-b); GelMA-CNC hydrogels (Figure 4.3c-d) and TA treated GelMA-CNC hydrogels (Figure 4.3e-h). SEM micrographs for hydrogel surface exhibit evenly coated PANI/RGO on the surface of TA-GelMA-CNC samples (Figure 4.3i-j). It can be seen that large pores are evenly distributed in GelMA hydrogels. The diameters of the pores in GelMA can reach several micrometers. It is also shown that the incorporation of CNC may reduce the pore sizes of the hydrogels (Figure 4.3c-d). CNC has been used as nanofillers for the reinforcements of polymeric materials due to their high aspect

ratio and modulus [26]. CNC served as macro crosslinkers can contribute to the structural integrity and mechanical enhancement of the GelMA hydrogel [26, 59]. Still the pore size is evenly distributed in GelMA-CNC, which is beneficial for further coating of conductive agents. TA treated GelMA-CNC shows a denser porous structure and much thicker walls between the pores because of the penetration of tannin into GelMA-CNC hydrogel to form a water insoluble gelatin-tannin precipitation complex [54, 55]. This phenomenon agrees with the findings in a recent study on a self-healing and adhesive gelatin hydrogel treated by TA [47]. Overall, such hierarchically porous structure is an excellent substrate for further fabrication of supercapacitors with high ions transport mobility rate and consequently excellent electrochemical performance [45, 49].



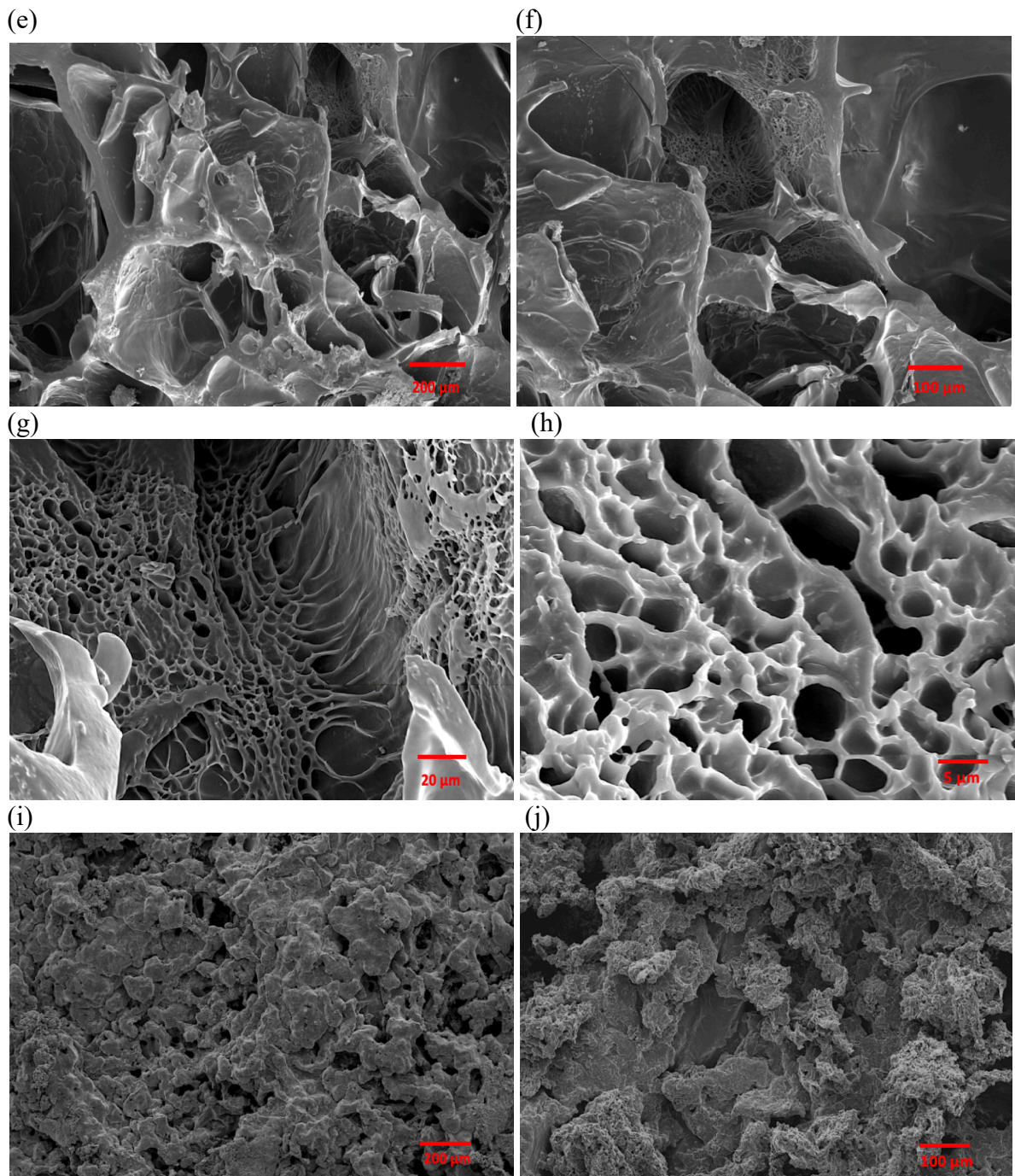


Figure 4.3 SEM micrographs of cross sections of GelMA hydrogel(a-b); GelMA-CNC hydrogel(c-d); GelMA-CNC-TA hydrogel(e-h); The surface SEM images of GelMA-CNC-TA hydrogel coated with PANI/RGO(i-j).

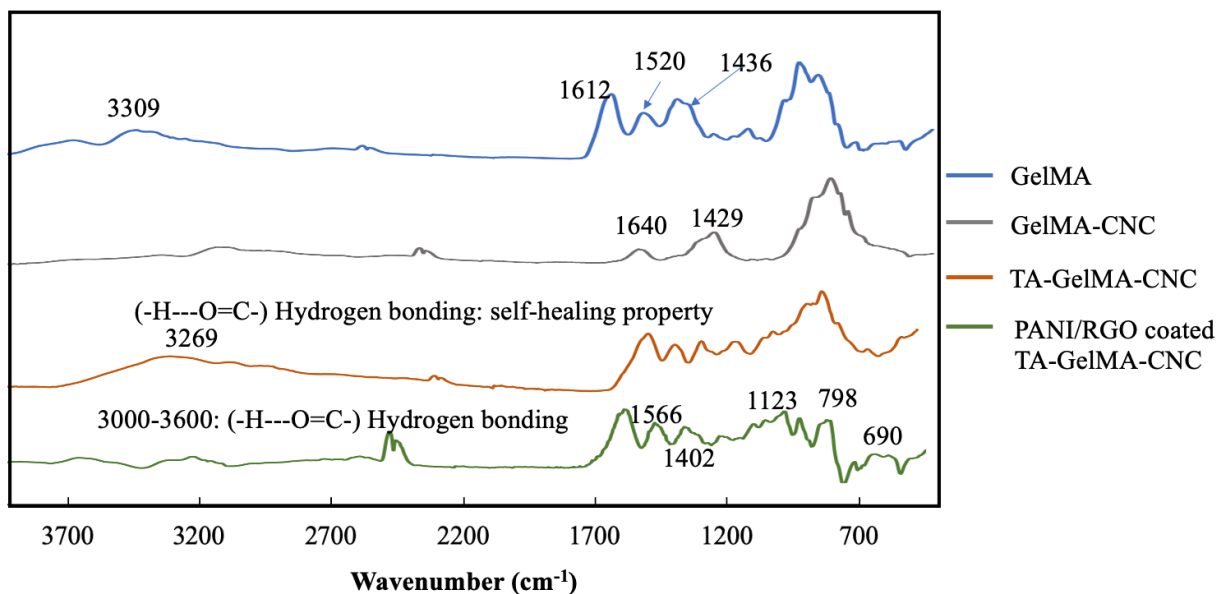


Figure 4.4 FTIR spectra of GelMA, GelMA-CNC, TA-GelMA-CNC, and PANI/RGO coated TA-GelMA-CNC.

FTIR spectra of GelMA, GelMA-CNC, TA-GelMA-CNC, and PANI/RGO coated TA-GelMA-CNC are shown in Figure 4.4. The peaks in the spectrum of GelMA include amide I, II, III groups at 1612 cm^{-1} , 1520 cm^{-1} , and 1436 cm^{-1} respectively [60]. GelMA-CNC presents typical peaks at 896 cm^{-1} (C–H bending), 1031 cm^{-1} (C–O stretching), 1162 cm^{-1} (C–O stretching), 1429 cm^{-1} (alkane C–H bending), 1640 cm^{-1} (O–H bending of absorbed water), 2897 cm^{-1} (C–H stretching) [45, 61, 62]. TA-GelMA-CNC showed a typically wave at around $3000\text{--}3600\text{ cm}^{-1}$ are closely related to the formation of hydrogen bonds due to the wavenumber of amine N–H and galloyl O–H shift in this range. The peak value 3309 cm^{-1} (GelMA) shifted to 3269 cm^{-1} (GelMA-TA) indicated the formation of H-bonding [63]. The results also provide evidence that there was no covalent bonding formed. PANI gives typical peaks at 798 cm^{-1} (aromatic C–H out-of-plane bending), 1123 cm^{-1} (aromatic C–H in-plane bending), 1298 cm^{-1} (aromatic amine C–N stretching), 1485 cm^{-1} (benzenoid ring C=C stretching), 1566 cm^{-1} (quinoid ring C=C stretching), and 3437 cm^{-1} (N–H stretching), indicating PANI in the emeraldine salt state [45, 61, 62]. RGO shows peaks at 690 cm^{-1} (C–H bending), 1402 cm^{-1} (C–H bending), and 3138 cm^{-1} (O–H stretching) [45, 61, 62].

4.3.3 Impact of TA concentrations on performance of the SC

To investigate the impact of TA concentrations on electrochemical performance of the SC, the self-healable GelMA-CNC hydrogels were treated with 40 %, 60 %, 80 % and 100 % TA respectively for 24 hours. The results were shown in Figure 4.5a, c-e. The electrochemical performances of the self-healable GelMA-CNC SCs treated with tannic acid of different concentrations were evaluated in terms of Electrochemical Impedance Spectroscopy (EIS) (Nyquist plots) tests in two electrode systems (Figure 4.5a); equivalent series resistance (ESR) (Figure 4.5c); specific capacitance (Figure 4.5d) and powder density and energy density (Ragone plots) (Figure 4.5e).

The Nyquist plots (Figure 4.5a) shows that the smallest EIS at $5.67\ \Omega$ can be achieved in GelMA-CNC hydrogel supercapacitors that were treated with 40 % and 60 % TA for 24 hours. With a further increase in the concentration of tannic acid, the EIS increased dramatically for the sample treated with 80 % TA ($28.69\ \Omega$) and for the sample treated with 100 % TA ($36.78\ \Omega$). The results of ESR tests shown in Figure 4.5c agree with the EIS results. ESR values for all samples decreased gradually with increased current density. The most stable and lowest ESR ($7.2\ \Omega$) can be found in the SC that is treated with 60 %TA. The highest initial ESR ($105\ \Omega$) can be observed in the SC that is treated with 100 %TA. In general, both EIS and ESR increased with higher concentrations of tannic acid treatment. However, a higher resistance was found in the SCs which are treated by 40%TA when compared to the sample treated with 60 %TA.

The results of specific capacitance based on volume were shown in Figure 4.5d. Electrochemical performance can be evaluated by weight, area and volume [64]. Normally, the electrochemical performance of free-standing SCs were calculated by the cell weight or electrodes area; hydrogel based free-standing supercapacitors could use volume as the unit for electrochemical performance evaluation[65-67]. This may be because of water evaporation from hydrogels therefore the data may not be accurate [65-67]. Additionally, the active materials can be penetrated into the hydrogel, therefore measuring the electrochemical performance by electrodes area may not be suitable [64-67]. In the present study, the electrochemical performance therefore is evaluated based volume. For such all-in-one supercapacitors with porous substrates, the weight of electrolytes may also be taken account when the gravimetric capacitance is calculated [68-70]. Therefore, all of the electrochemical evaluation results in this current study were calculated based on volume-specific to keep accuracy of the data. The specific capacitance of all self-healable SC

samples decreased with an increase in the current density from 1.6 to 8.0 mA cm⁻³. The highest specific capacitance (1861.21 mF cm⁻³) at a current density of 0.8 mA cm⁻³ is shown in the self-healable SC that was treated by 60 %TA. The specific capacitances for samples treated with 40 % and 60 % TA were drastically decreased and that for sample treated with 100 %TA was found to be the lowest. When the applied current density was raised to 8.0 mA cm⁻³, the highest specific capacitance (858.06 mF cm⁻³) was found again in the SC sample which was treated with 60 %TA, while the lowest specific capacitance was still found in the SC sample that was treated with 100 %TA.

Ragone plots (Figure 4.5e) on the power density and energy density gave similar results as specific capacitance. The highest power density (595.59 mW cm⁻³) and energy density (20.65 mWh cm⁻³) were demonstrated by the self-healable SC sample that was treated with 60% TA. The SC sample that was treated with 80%TA shows a lower energy density at 10.67 mWh cm⁻³, while the SC sample that was treated with 100%TA shows the lowest power density at 99.93 mW cm⁻³. Also, the SC samples that were treated with 40%TA and 80%TA both show a sharp drop in power density while the energy density is increased. Such a sharp drop on power density will reduce the lifetime of the energy storage devices including supercapacitors, batteries and fuel cells. Therefore, GelMA-CNC hydrogels SC samples treated with 40 % and 80 % TA are not suitable to fabricate supercapacitors.

In general, the all-in-one self-healable SC that was treated with 60 % TA shows the best electrochemical performance.

4.3.4 The impact of TA treating time on the performance of the SC

After comparing the overall electrochemical performance among the self-healable GelMA-CNC SCs treated with TA of different concentrations, we chose the best TA concentration (60 %) for a further investigation on the impact of treating time on electrochemical performance of the SCs. TA treating time of 12hrs, 24hrs, 48hrs, and 72hrs were tested and the results were compared as shown in Figure 4.5b, f-h.

It can be seen that the EIS value (Figure 4.5b) experienced a decline from the sample with 12hr treating (9.5 Ω) to the sample with 24hr treating (5.67 Ω), then increased with the increase in TA treating time, from the sample tread with TA for 48 hrs (22.15 Ω) to 72 hrs (27.68 Ω). The lowest EIS is found in the hydrogel treated by 60 % TA for 24 hours.

ESR results (Figure 4.5f) show a similar trend with the EIS results. ESR generally decreased with an increase in current density from 0.8 to 8.0 mA cm⁻³. The highest ESR (70 Ω) is found in SC that was treated by 60 % TA for 72h, while the lowest ESR (30 Ω) is found in SC that was treated for 24 hrs at a current density of 0.8 mA cm⁻³.

The specific capacitance is shown in Figure 4.5(g). The maximum specific capacitance (1861.21 mF cm⁻³) is observed in SC that was treated with 60% TA for 24 hrs at a current density of 0.8 mA cm⁻³. The specific capacitance decreased with an increase in the current density in all SC samples. When applied the current density at 8.0 mA cm⁻³, the highest specific capacitance (858.06 mF cm⁻³) is still found in the SC sample that was treated with 60 % TA for 24 hrs and is significantly higher than other SC samples.

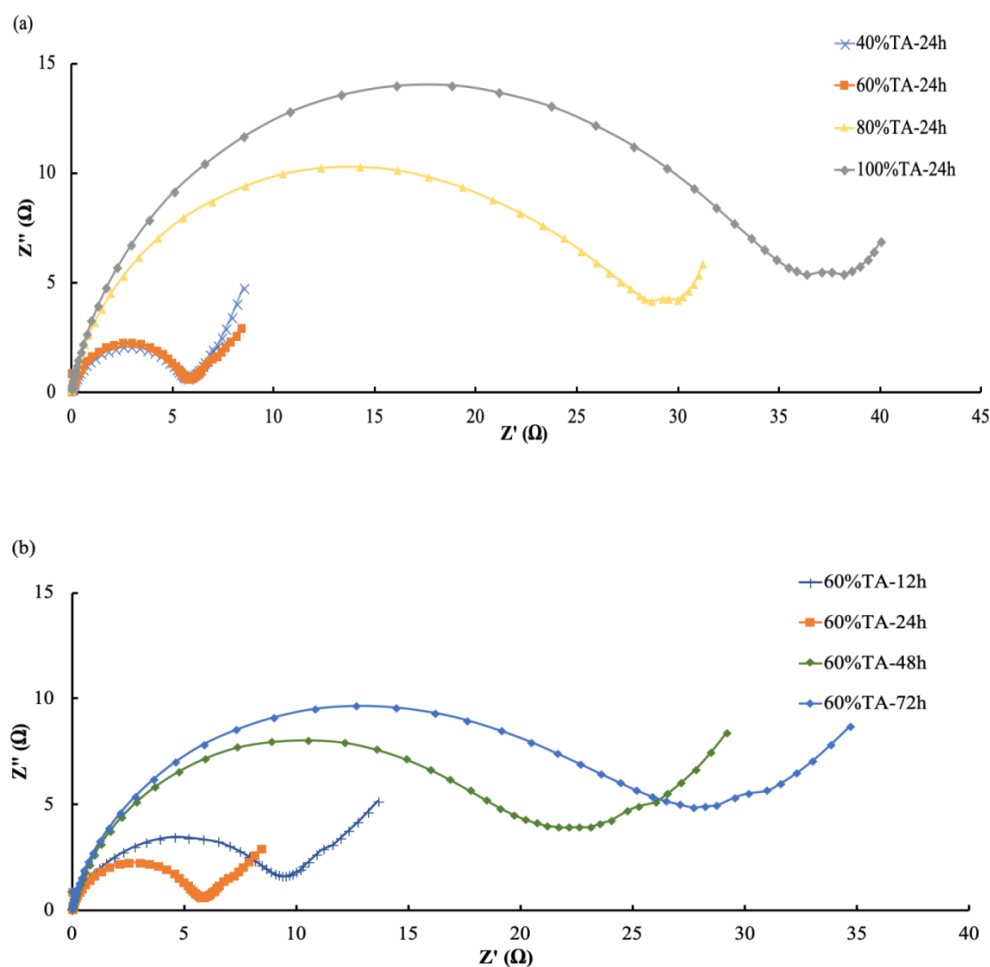
Finally, the power density and energy density results were shown in Ragone plots (Figure 4.5h). The SC samples that were treated with 60 % TA for 12 hrs, 48 hrs and 72 hrs show a significant low value in power density when compared to the SC sample that was treated with 60%TA for 24hrs. The maximum power density (595.59 mW cm⁻³) and energy density (20.65 mWh cm⁻³) are both found in the SC sample that was treated with 60 %TA for 24 hrs.

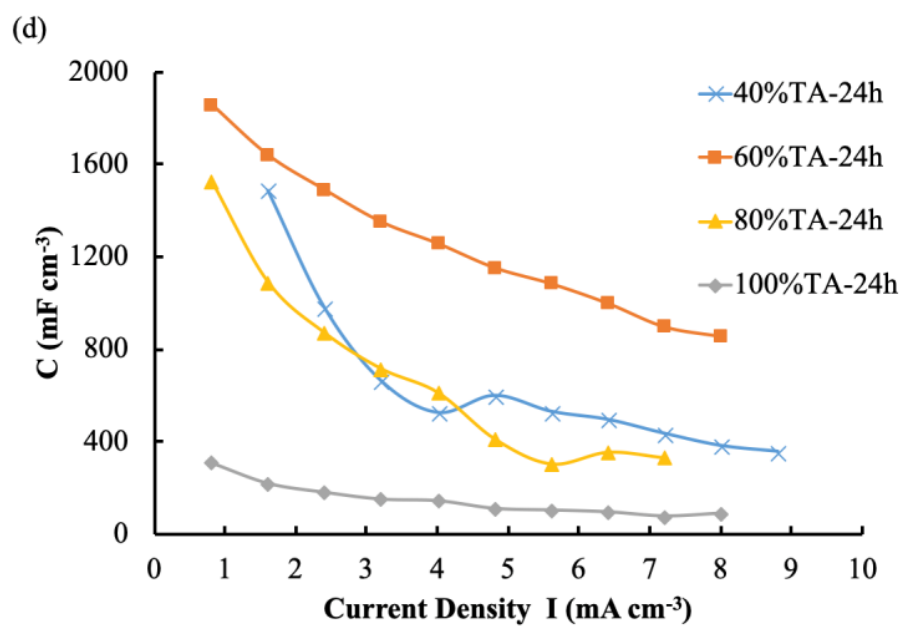
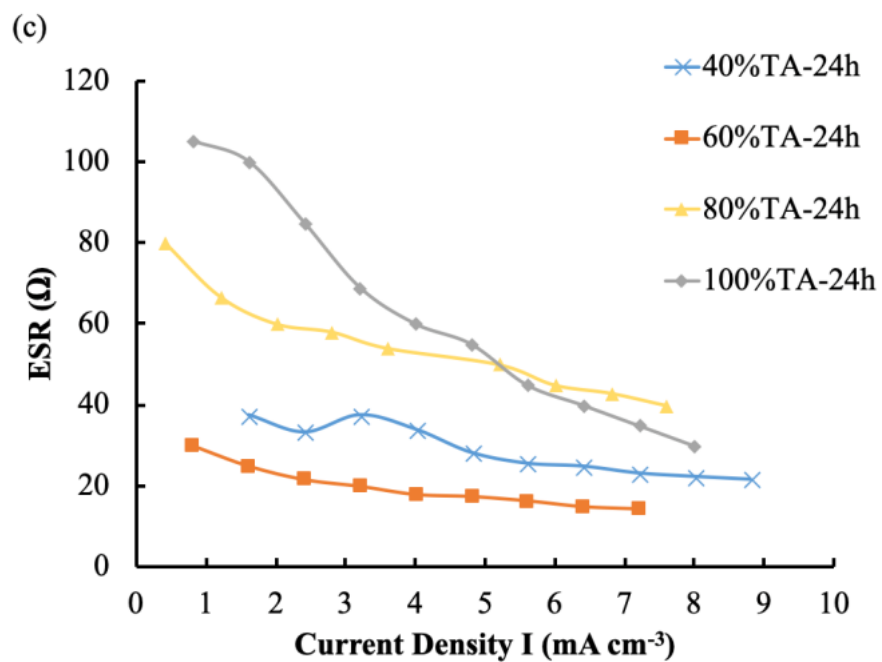
In general, we found that a treatment by 60 % TA for 24 hours produces supercapacitors with best electrochemical performance. The developed supercapacitors show comparable performance with similar studies (shown in Table 4.1). It should be noted that in current work the SC devices were developed from natural polymers, which is different from all other listed work with SC devices fabricated from synthetic polymers, which may have better mechanical properties but limit their applications in the biomedical field such as tissue engineering or implantable sensors.

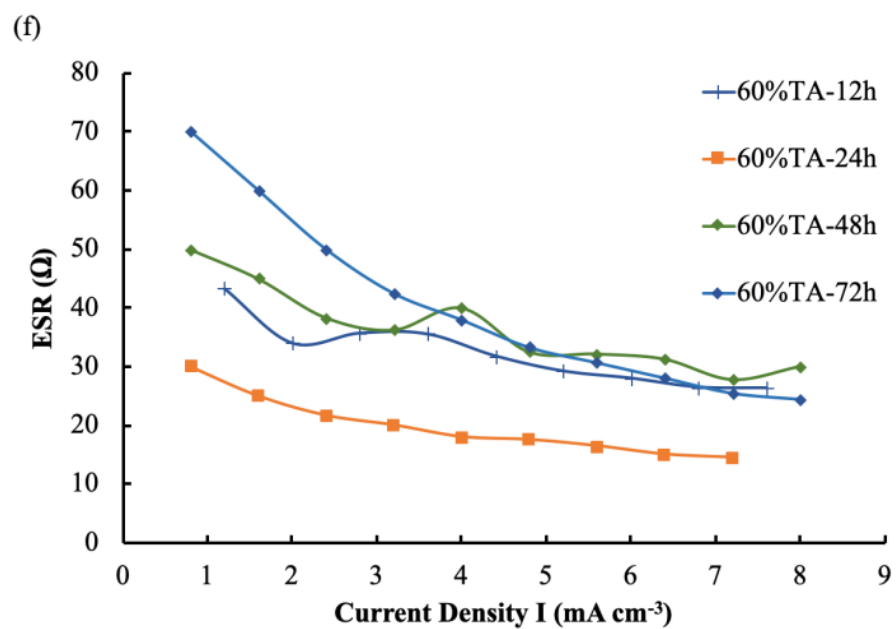
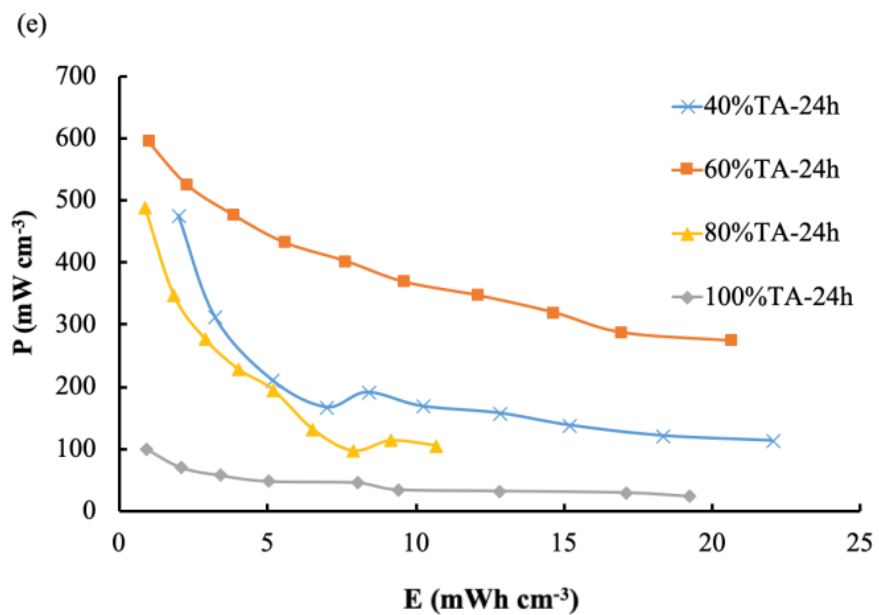
After the TA treatment, protein-tannin interactions result in both water soluble and insoluble precipitated complex that deposited on the GelMA-CNC hydrogel. Water insoluble complex was formed by strong hydrogen bonding between phenolic hydroxyl group of tannin and carbonyl group of gelatin [54, 55]. The condensed sticky layer formed by water insoluble gelatin-tannin precipitated complex may significantly block the pores in the hydrogel and hamper the diffusion of tannic acid and conductive agents [47, 71]. To prepare the hydrogel for more efficient coating of conductive agents via *in-situ* polymerization to fabricate supercapacitors, the condensed sticky layer on the surface of GelMA-CNC hydrogels was peeled off after freeze drying. Still, the water insoluble gelatin-tannin precipitated complex may form deeply in the hydrogel and cannot be removed by surface peeling due to the penetration of tannin in the hydrogel during soaking

treatment. The water insoluble gelatin-tannin precipitated complex can increase the thickness of the porous structure and decrease the pore size of the GelMA-CNC hydrogel. As the concentration of TA for treatment increase from 60 % to 100 %, the GelMA-CNC hydrogel showed plasticized property (Figure 4.7a, b): the hydrogel treated with 100% TA demonstrated a wider plastic zone than the one treated with 60 % TA. This results agree with a study by Zhang et al, in which a large amount of gelatin-tannin water insoluble precipitated complex was formed by being treated with highly concentrated TA, probably because that a highly concentrated TA may enhance the grafting and branching reactions between gelatin and TA in conjunction with hydrogen bonding [72]. When a lower concentration of TA (40 %) was used to treat the hydrogel, the crosslink effect may be predominated by TA content, resulting in the formation of a partially water insoluble crosslink network, and the hydrogel becomes rigid [72]. From the results, we may suggest that both the concentration and treating time of TA can contribute to different content of tannin presented on the surface and penetrated into GelMA-CNC hydrogel, and that different amount of water insoluble gelatin-tannin precipitated complex may be incorporated into the hydrogel. Such a precipitated complex will impact on the porous structure of the hydrogel, and consequently affect the following process of coating conductive agents and as well as influence the ions transportation rates during electrochemical performance evaluation. The optimal conditions for TA treatment on the GelMA-CNC hydrogel have been identified as 60 % TA for 24 hours, which may be probably explained by the formation of an optimum water insoluble gelatin-tannin precipitated complex (after surface peeling) that leave behind sufficient porous structure in the hydrogel to accommodate the conductive components (PANI and RGO) to be further incorporated, and that maintain the self-healing property though hydrogen bonding. Specifically, lower TA concentration (< 60 %) and/or shorter treating time (< 24hrs) were found in our study to contribute to a thin condensed layer (water insoluble gelatin-tannin precipitated complex) that adheres to the surface tenaciously and made it difficult to be peeled off completely even after freeze drying. Such a condensed layer may block the pores and hamper the ions transfer rate in the supercapacitors [31, 71]. This is because that a low amount of tannin may lead to partial interaction between gelatin and tannin [72]. Higher TA concentration (> 60 %) and/or longer treating time (> 24 hrs), on the other hand, may contribute to a large amount of water insoluble gelatin-tannin precipitated complex layered up, resulting in a plasticized texture [72], which dehydrate the hydrogel, consequently may cause shrinkage of the pore structures and affect the ions transfer rate in the supercapacitors. The quality

of PANI and RGO coating onto the hydrogel substrate using *in-situ* polymerization can be greatly influenced by the porous structure of the hydrogel especially in the condensed layer (water insoluble gelatin-tannin precipitated complex). Excellent electrochemical properties require large amounts of conductive agents evenly distributed on the surfaces of the all-in-one TA treated GelMA-CNC hydrogel as the electrode. The penetration of conductive agents into the porous structure of the TA treated GelMA-CNC hydrogel can further improve the conductivity, specific capacitance, power density and energy density of the device [47, 71].







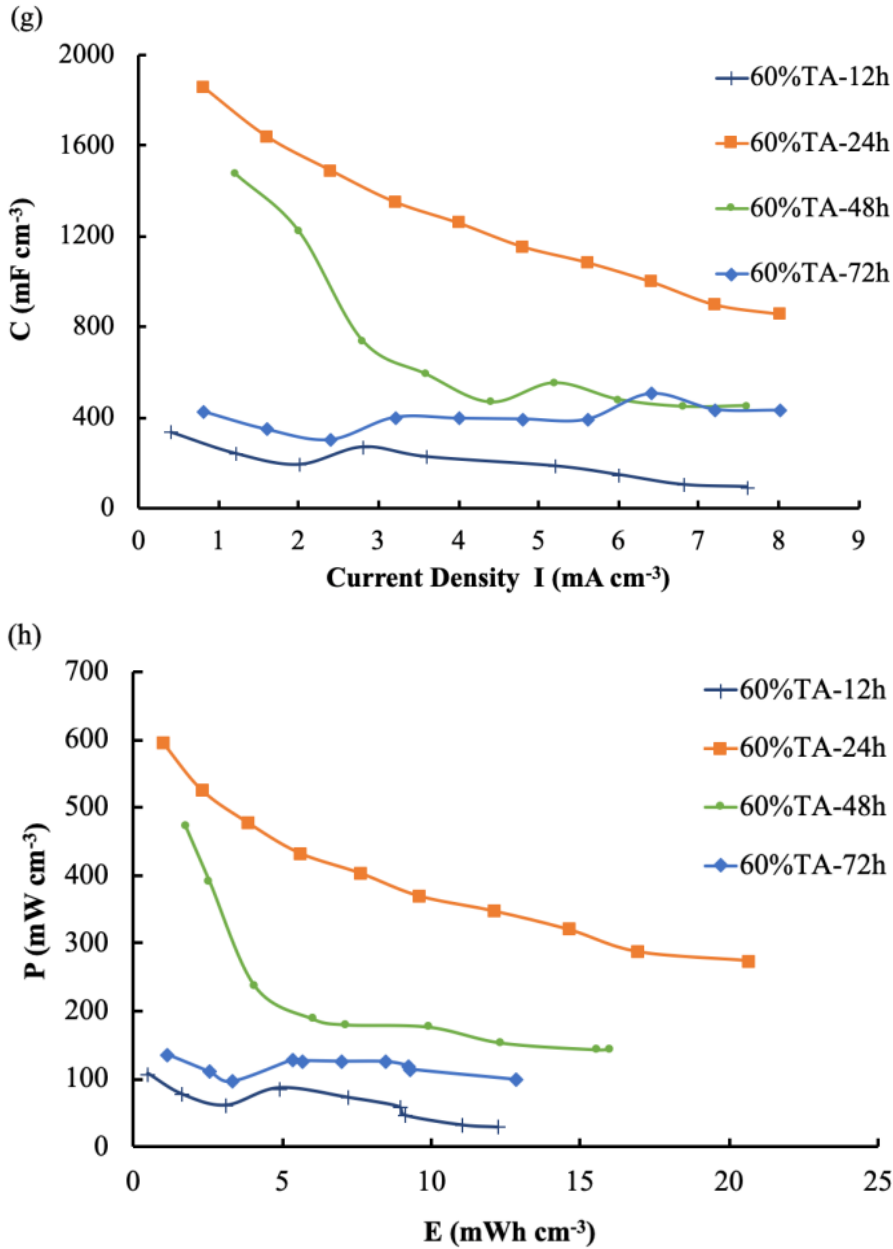
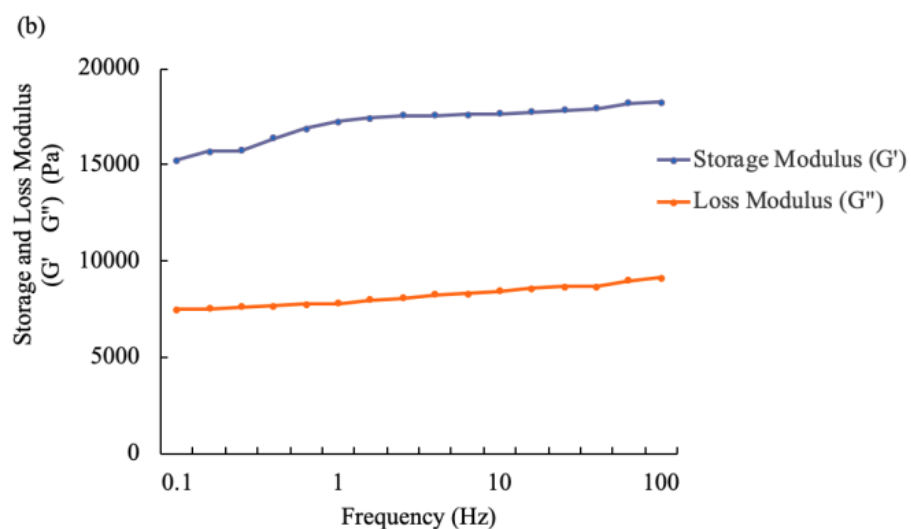
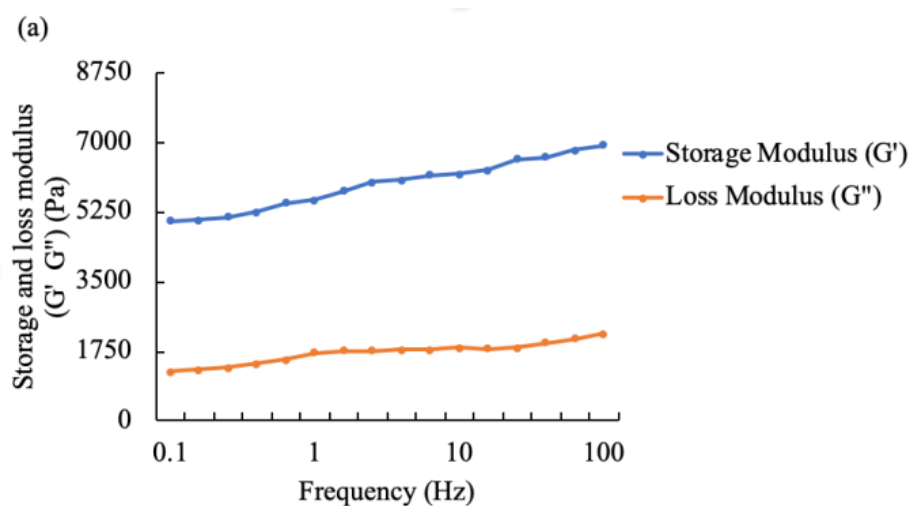


Figure 4.5 Electrochemical performance of all-in-one self-healable GelMA-CNC hydrogel SCs treated with TA for 24hrs at different concentrations. (a) Electrochemical Impedance Spectroscopy (EIS) Nyquist plots; (c) Equivalent Series Resistance (ESR); (d) Volume-specific capacitance versus current density; (e) Ragone plots. Electrochemical performance tests of all-in-one self-healable GelMA-CNC hydrogel SCs treated with 60% TA for different times. (b) Electrochemical Impedance Spectroscopy (EIS) Nyquist plots; (f) Equivalent Series Resistance (ESR); (g) Volume-specific capacitance versus current density; (h) Ragone plots.

4.3.5 Rheological tests

The dynamic mechanical properties of GelMA, GelMA-CNC, TA treated GelMA-CNC (60% for 24 hrs), and PANI/RGO coated TA-GelMA-CNC hydrogels were evaluated by rheological tests (Figure 4.6a-d). The storage modulus (G') was higher than loss modulus (G'') in all samples without any crossover traces occurred, which indicates the formation of stable hydrogels. The incorporation of CNC was found to enhance storage modulus (G') of the hydrogels, as can be observed in the GelMA-CNC and TA treated GelMA-CNC groups. The storage modulus (G') decreased in PANI/RGO coated TA-GelMA-CNC hydrogels sample because the hydrogel was immersed in sulfuric acid for *in-situ* polymerization of PANI. The results suggest that the mechanical properties can be enhanced by adding CNC, and TA treatment may further improve the mechanical strength. A trend of elevated storage modulus (G') is observed in GelMA, which may be an indication of the presence of non-covalent bonds in the hydrogel [33, 34].



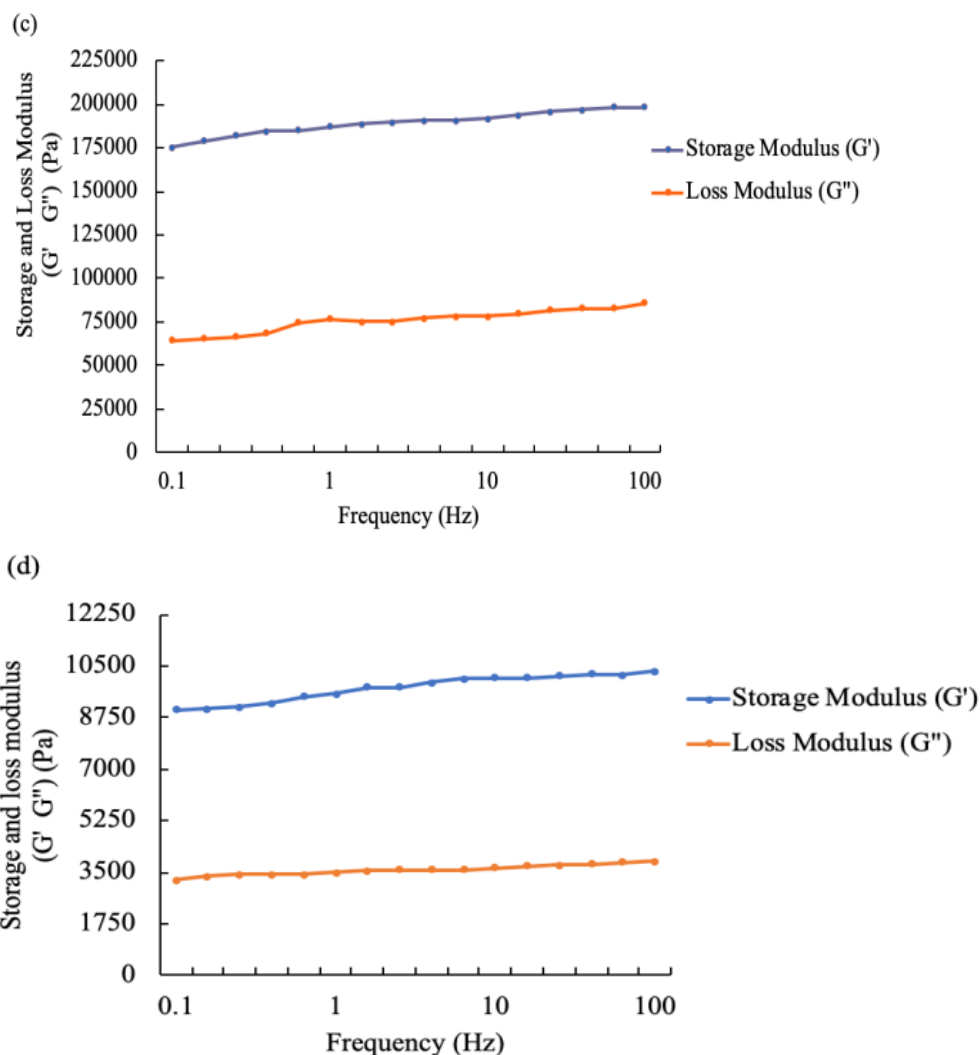


Figure 4.6 Rheological tests on (a) GelMA hydrogel; (b) GelMA-CNC hydrogel; (c) GelMA-CNC-TA; (d) GelMA-CNC-TA-PANI/RGO.

4.3.6 Mechanical Tests

The mechanical strength of supercapacitors is important for maintaining structural integrity during their applications. The mechanical strength and Young's Modulus of the all-in-one self-healable GelMA-CNC supercapacitors treated with TA under different conditions were evaluated by tensile tests (Figure 4.7a-d). GelMA and GelMA-CNC hydrogels were used as control samples. The other samples were TA treated GelMA-CNC supercapacitors coated with PANI and RGO via *in-situ* polymerization in sulfuric acid. The ultimate stress of GelMA hydrogel is 10.62 KPa at 10% strain, while the mechanical strength was improved to 13.25 KPa at 16.37% strain by incorporating CNC.

All TA treated GelMA-CNC supercapacitors show higher strain (27.61% to 85.22%) than GelMA and GelMA-CNC hydrogels, indicating that GelMA and GelMA-CNC hydrogels were more brittle than TA treated ones.

Mechanical tests were conducted on all-in-one self-healable GelMA-CNC hydrogel SCs treated for 24hrs in TA solutions with different concentrations of 40%, 60%, 80% and 100% TA (w/w) (Figure 4.7a and c). The strain of the SCs was found to increase with an increase in TA concentrations. The largest strain (71.11%) was observed in the GelMA-CNC hydrogel SC treated with 100% TA for 24 hours. The highest mechanical stress (17.42 MPa) and Young's Modulus (4.57 ± 1.14 KPa), however, were found in the SC treated with 60% TA for 24hrs.

The toughness of TA treated GelMA-CNC samples was also compared to those of GelMA and GelMA-CNC hydrogels without TA treatment (Figure 4.7c). When TA treating time was 24 hours, the highest toughness was found in 100% TA (7.35 J m^{-3}), followed by 60% (6.28 J m^{-3}), which were both significantly higher than those of GelMA (0.53 J m^{-3}) and GelMA-CNC (0.77 J m^{-3}).

Figure 4.7 (b and d) shows the mechanical properties of TA treated GelMA-CNC SCs treated in 60% TA for different times of 12hrs, 24hrs, 48hrs and 72hrs. The strain was shown to increase with longer treating time. Still the highest mechanical stress (17.42 KPa) and Yong's Modulus (4.57 KPa) were observed in the SC treated with 60% TA for 24hrs. All of the TA treated GelMA-CNC samples showed higher toughness than GelMA (0.53 J m^{-3}) and GelMA-CNC (0.77 J m^{-3}) without TA treatment. The highest toughness was found in the sample treated with 60% TA for 72 hours (8.04 J m^{-3}), followed by the sample treated with 60% TA for 24 hours (6.28 J m^{-3}).

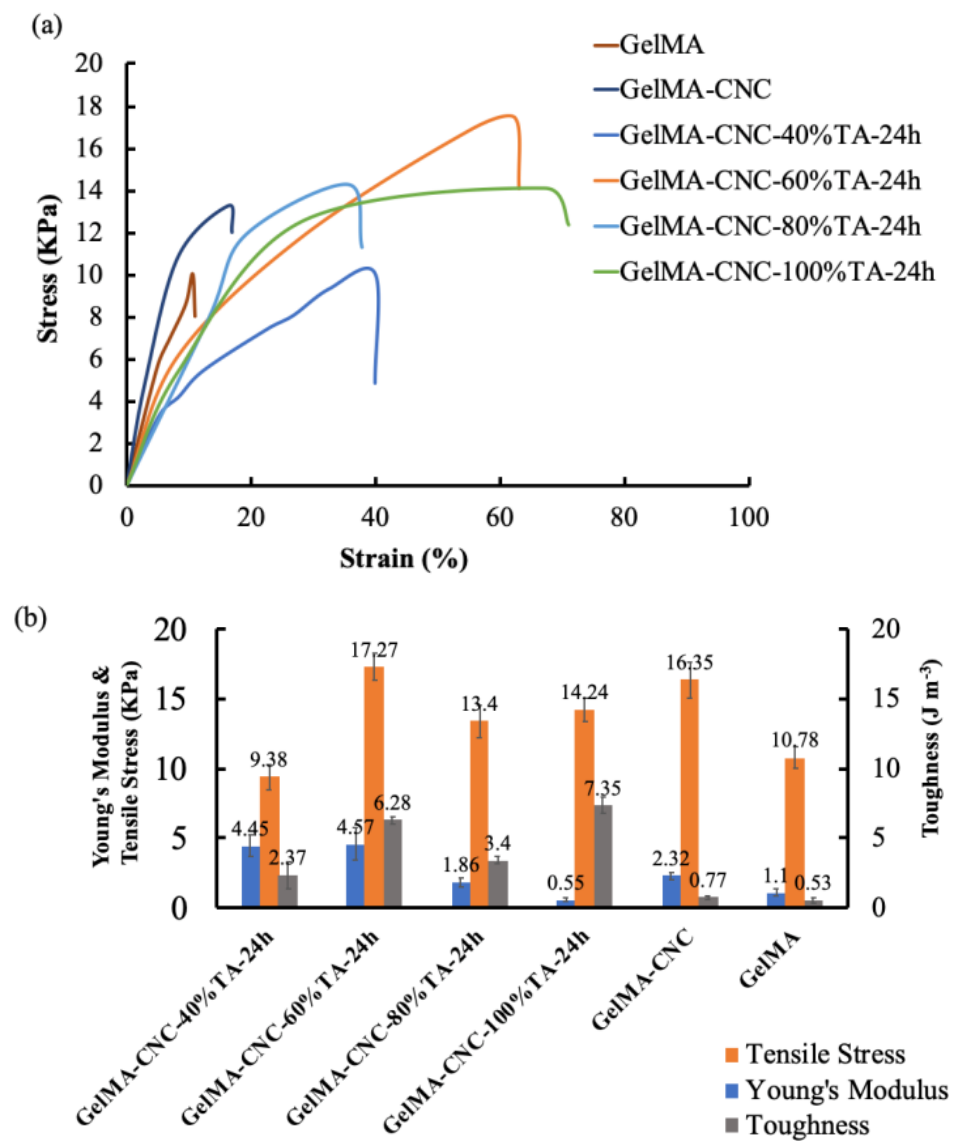
The mechanical properties of the GelMA-CNC hydrogel SCs may also depend on the amount of tannin penetrated into the porous structure after peeling off the gelatin-tannin condensed layer. The more gelatin-tannin complex left inside the hydrogel (after peeling of the surface condensed layer), the better the elongation, probably because that the colloidal protein (water insoluble complex) may enhance the elongation of gelatin hydrogel [47, 54, 72]. The gelatin-tannin complex may increase the mechanical property of the GelMA-CNC hydrogels and contribute to better mechanical properties of the hydrogel SC [72]. Overall, the all-in-one self-healable SC treated with 60% TA for 24 hours showed the best results with an ultimate stress at 17.27 ± 0.97 Kpa, a Young's Modulus at 4.57 ± 1.14 KPa, a toughness at $6.28 \pm 0.24 \text{ J m}^{-3}$, and a decent strain of 62.35%. The moderate strain of the sample may be caused by the high crosslink

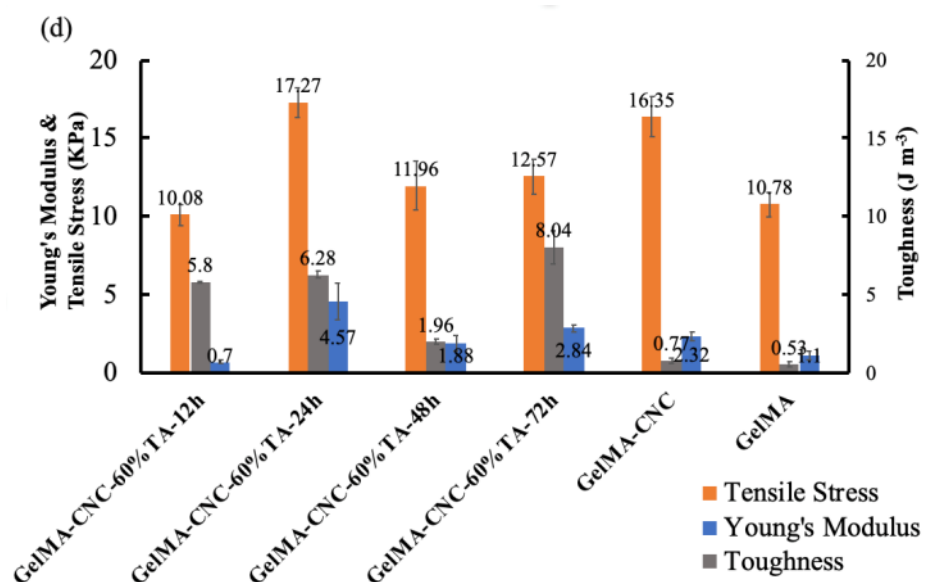
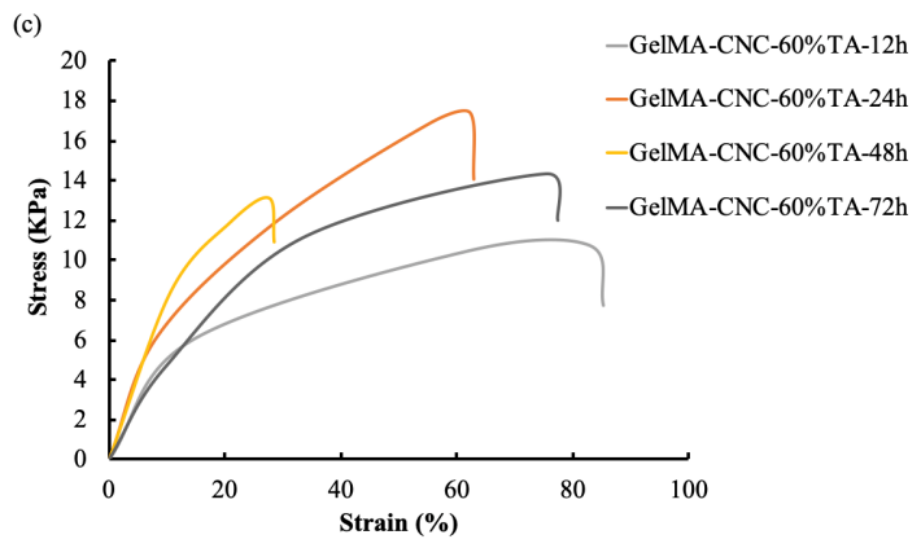
density in the GelMA-CNC hydrogel after taking off the layer of colloidal protein (tannin-gelatin water insoluble complex), which consequently led to a more brittle polymeric chain [73-75].

The energy dissipation of the self-healable SCs treated with 60%TA on increment strain is shown in Figure 7e, while their deformation recoverability on a controlled strain is shown in Figure 7e, in which the energy dissipation is presented during cyclic compressive loading-unloading. The hysteresis loop (Figure 4.7e) enlarges with an increase in strain, suggesting that the energy dissipation increases in the compressive procedure. Damages in the SCs can be mostly but not fully recovered when the compressive strain is less than 50%. Permanent damage may occur if maximum strain is reached during the compressive cycles.

The SC samples were run 50 compressive cyclic tests under a controlled strain (50%) to evaluate their deformation recoverability. Figure 4.7(f) shows permanent deformation/damage after each 10 cycles, which is indicated by the non-overlapped hysteresis loops due to the residual strain generated after unloading. The samples cannot sustain cyclic tensile or compressive strain higher than 50%, which matches the results from mechanical tensile test. A rubber like tough double-network hydrogels or nanocomposite hydrogels may show a similar behavior on recovery property because the energy dissipation in those types of hydrogels is attributed to the fracture of covalent bonds, thus the hysteresis loop in the first cycle can be barely recovered. Another reason may be the reversible detachment of the polymer chains [76-78].

Taken together the results from both electrochemical and mechanical evaluations, GelMA-CNC hydrogel SC treated with 60% TA for 24 hours were chosen as the optimum parameters for further fabrication of the all-in-one self-healable SCs that were tested for self-healing performance.





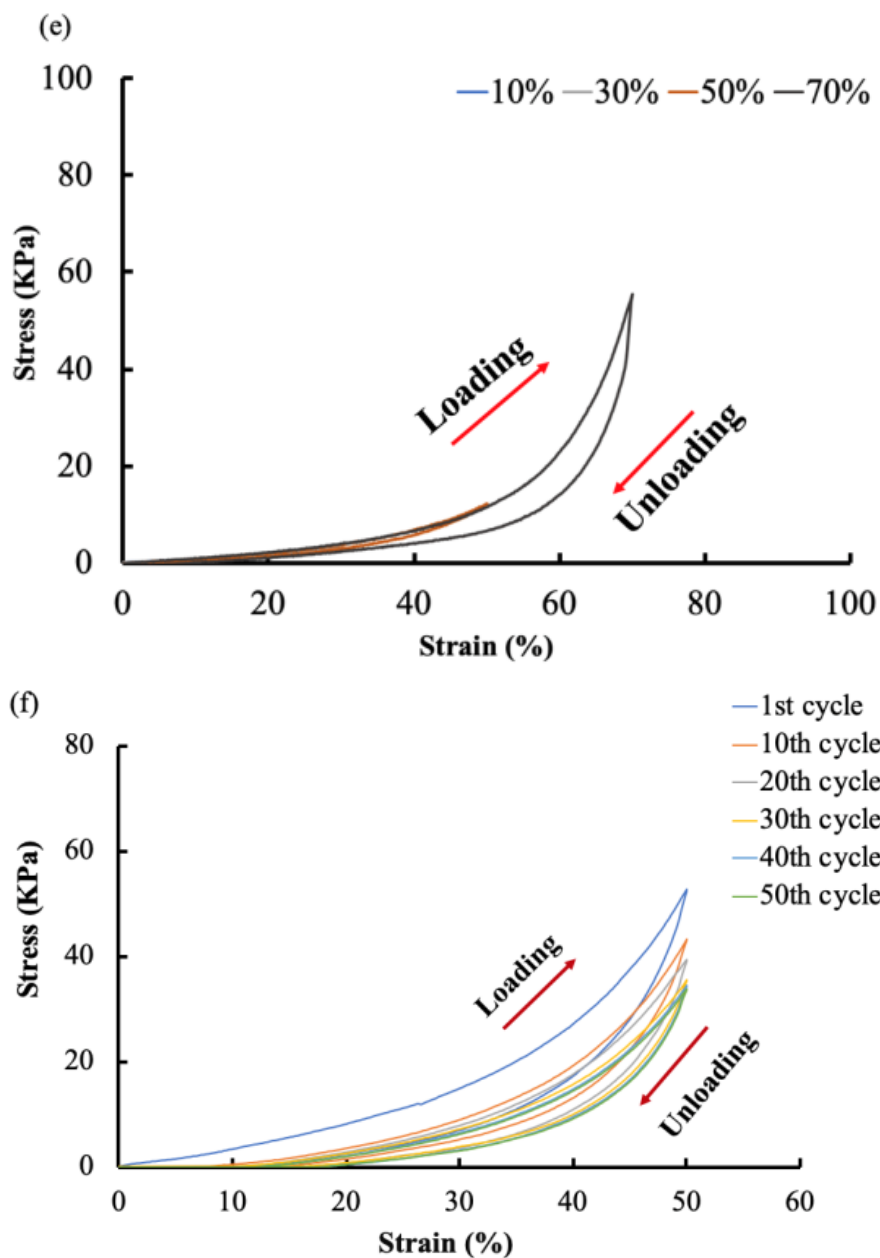


Figure 4.7 Mechanical evaluations of all-in-one self-healable GelMA-CNC hydrogel SCs (a, c) treated in TA with different concentrations of 40%, 60%, 80% and 100% TA (w/w) for 24h and (b, d) treated in 60% TA for different times of 12, 24, 48 and 72hrs. (e) Cyclic compressive loading-unloading with strain increment on all-in-one self-healable supercapacitor (60%TA-24h GelMA-CNC); (f) Cyclic compressive loading-unloading with controlled strain at 50% on all-in-one self-healable supercapacitor (60%TA-24h GelMA-CNC).

4.3.7 Self-healing evaluation

Figure 4.8 demonstrates self-healing properties of the developed all-in-one GelMA-CNC SC treated with 60% TA for 24 hours. The cut area can heal via hydrogen bonds after 6 hours at room temperature without any external stimuli. The mechanical performance of the SC after 6 hours healing was evaluated and compared with the original SC (Figure 4.8a). The healing efficiency for mechanical stress is 96%, and that for strain is 89%. After healing, the supercapacitor can be folded and twisted moderately, without any visible difference from a pristine SC (Figure 4.8b-d). The all-in-one configured self-healing SC maintained its conductivity after healed (Figure 4.8e-f).

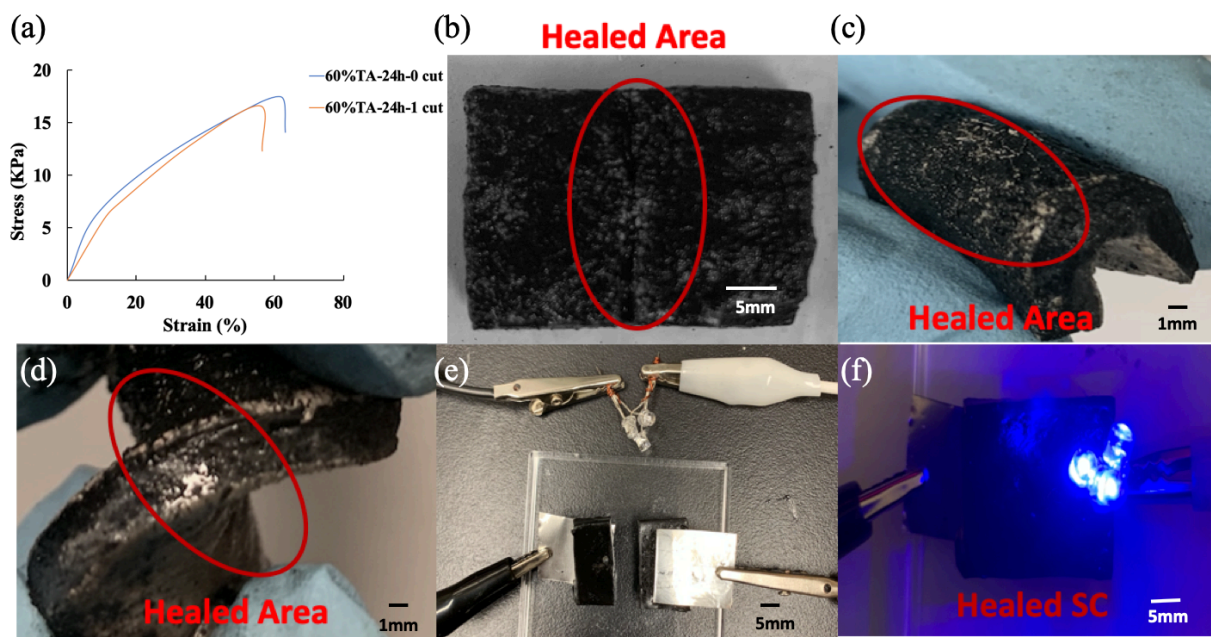


Figure 4.8 Self-healing property of TA treated GelMA-CNC SC. (a) Strain-stress curves after 6 hours healing; (b) The two cut surfaces were allowed to touch and heal for 6 hours at room temperature; (c) The self-healed SC can be folded and (d) twisted; (e-f) The SC maintained its conductivity after healing.

Electrochemical Impedance Spectroscopy (EIS) (Nyquist plots) (Figure 4.9a), specific capacitance (Figure 4.9b), equivalent series resistance (ESR) (Figure 4.9c) and powder density vs. energy density (Ragone plots) (Figure 4.9d) were evaluated after each cut-healing process and compared with the performance of the original sample.

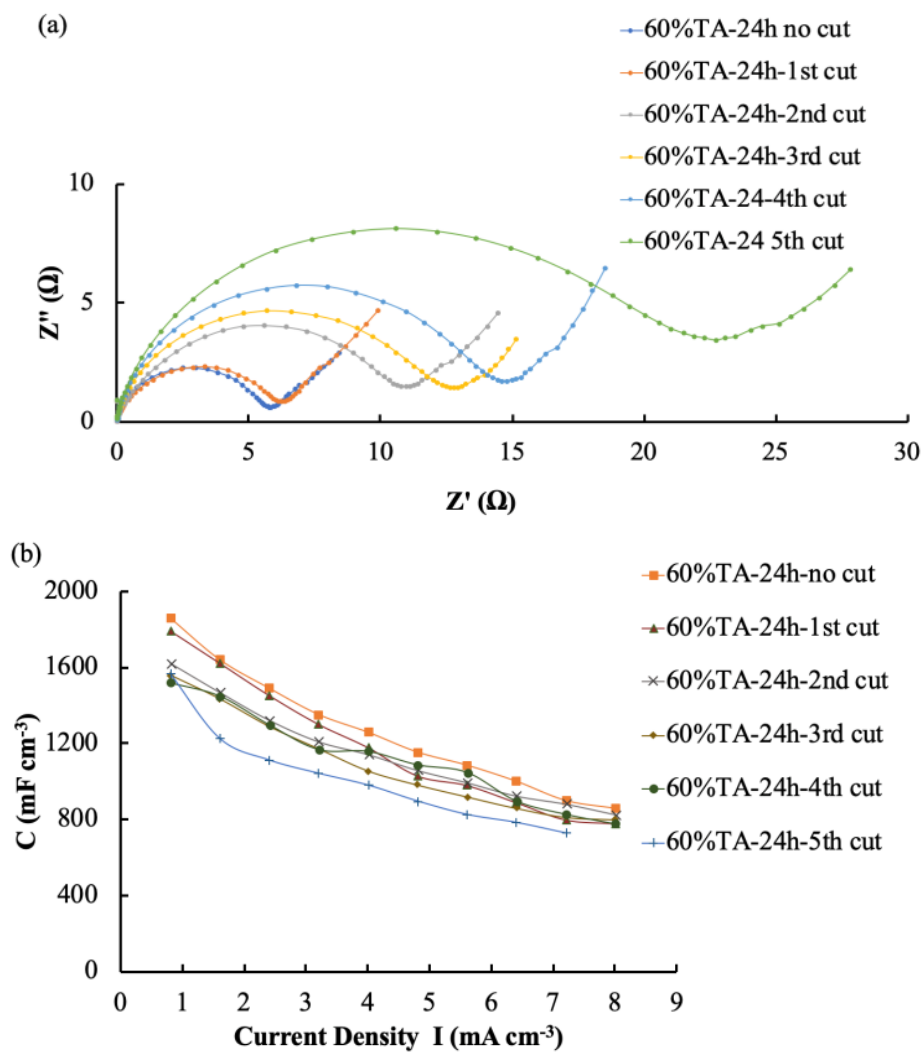
The EIS value (Figure 4.9a) shows $6.30 \, \Omega$ after the 1st cut-heal process, which is not significantly increased as compared to $5.86 \, \Omega$ for the pristine SC. However, EIS value reached

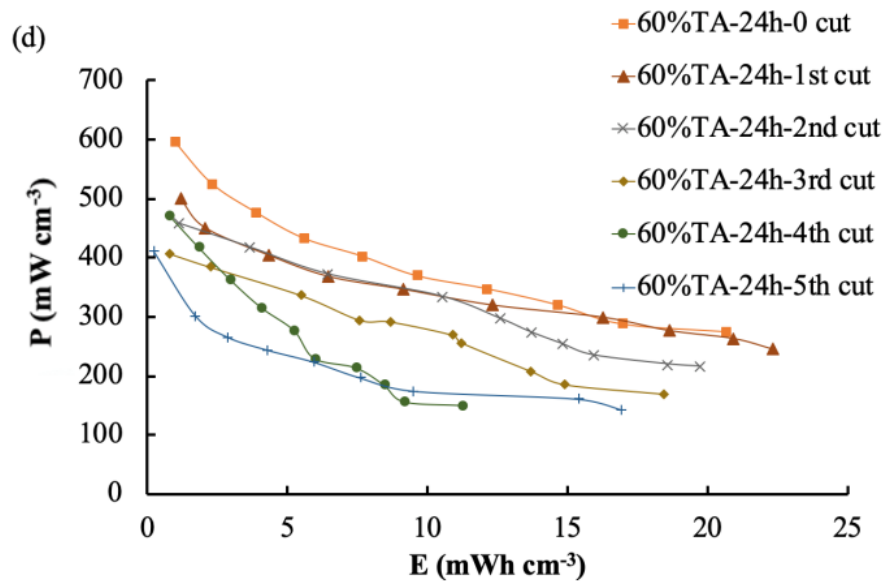
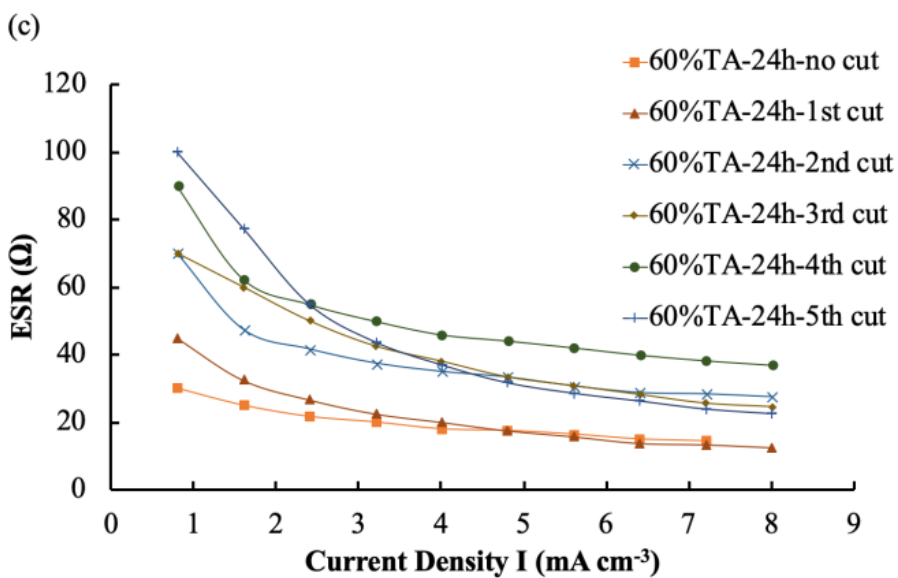
10.95 Ω after the 2nd cut-heal process. The EIS further increased with more cut-heal processes and reached 22.7 Ω after the 5th cut-heal process.

The result for specific capacitance matched that of EIS (Figure 4.9b). There is no significant difference between the pristine SC sample and the sample after the 1st cut-heal process. However, the specific capacitance dropped from 1861.21 mF cm⁻³ to 1566 mF cm⁻³ after 2nd cut-heal process at 0.8 mA cm⁻³ current density. There're no significant drops between the 3rd and 4th cut-heal processes. Notably, the specific capacitance shows significant decrease after the 5th cut-heal process, especially when the applied current density is larger than 1.6 mA cm⁻³. After five cut-heal processes, the specific capacitance remains 84% of the value for the pristine sample.

Similar results were found from ESR calculations (Figure 4.9c). ESR increased from 30 Ω to 45 Ω after the 1st cut-heal process at the current density of 0.8 mA cm⁻³. ESR value after the 1st cut-heal process almost overlapped with the pristine SC sample when the current density is over 3.2 mA cm⁻³. A significant increase in ESR values has been observed after more than two cut-heal processes. After 5 cut-heal processes, the ESR reached 100 Ω at an applied current density of 0.8 mA cm⁻³, and ESR decreased to 22.50 Ω when 8.0 mA cm⁻³ was applied.

The power density and energy density (Figure 4.9d) gradually decreased after cut-heal processes. The maximum power density dropped from 595.59 to 500.09 mW cm⁻³ after 1st cut-heal process, but the largest energy density almost remained the same as the pristine value at 20.90 mWh cm⁻³. After the 2nd cut-heal process, the power density did not show significantly decrease while the energy density increased. A significant drop of both power density and energy density can be found after the 4th cut-heal process as compared to the previous value. Overall, the maximum power density dropped from 595.59 mW cm⁻³ to 406 mW cm⁻³, and the largest energy density dropped from 22.30 mWh cm⁻³ to 15.37 mWh cm⁻³. The power density remains 82% after one cut-heal process, and 69% after five times cut-heal processes as compared to the pristine data. The energy density remains about 100% after one time cut-heal process, and 74% after five times cut-heal processes as compared to the pristine data.





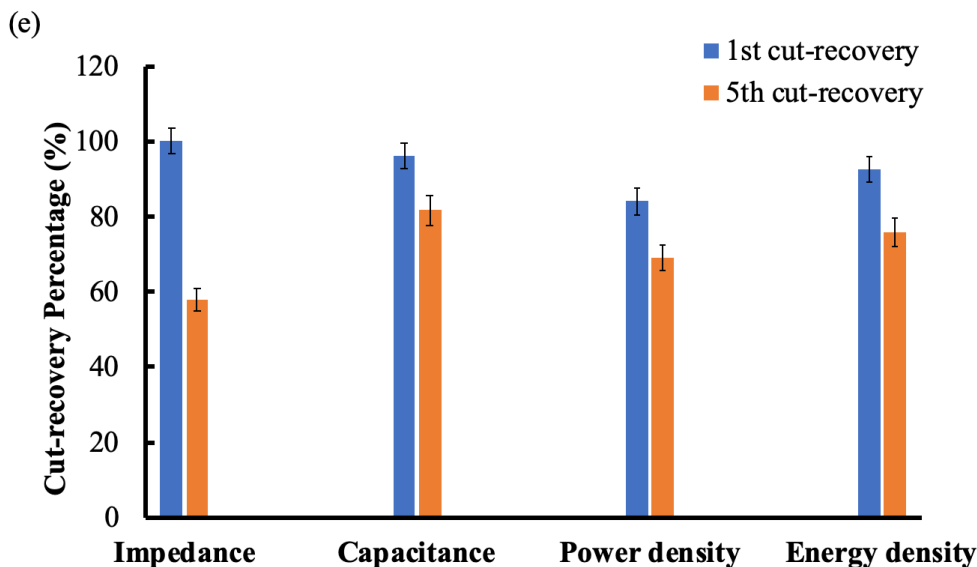


Figure 4.9 Performance of the all-in-one self-healable GelMA-CNC SC before & after five cut-heal processes. (a) Recovery on Electrochemical Impedance Spectroscopy (EIS) Nyquist plots; (b) Recovery on volume-specific capacitance versus current density; (c) Recovery on Equivalent Series Resistance (ESR); (d) Recovery on Power density and Energy density Ragone plots; (e) Recovery percentages on the electrochemical performance (impedance, capacitance, power density and energy density).

The SCs showed excellent electrochemical performance after up to five cut-healing cycles. This maybe because the two phenolic hydroxyls of gallols in tannic acid can chelate metal ions to form oxygen anions to give stable pentacyclic complexes. The gallols from tannic acid can be oxidized to quinones, which will further undergo nucleophilic reactions through Schiff base reaction (Figure 4.10). The hydroxyl group from tannic acid can form non-covalent hydrogen bonding to achieve self-healing property. Tannic acid is therefore an excellent natural compound to fabricate functional materials including self-healing and adhesive hydrogels [32, 47].

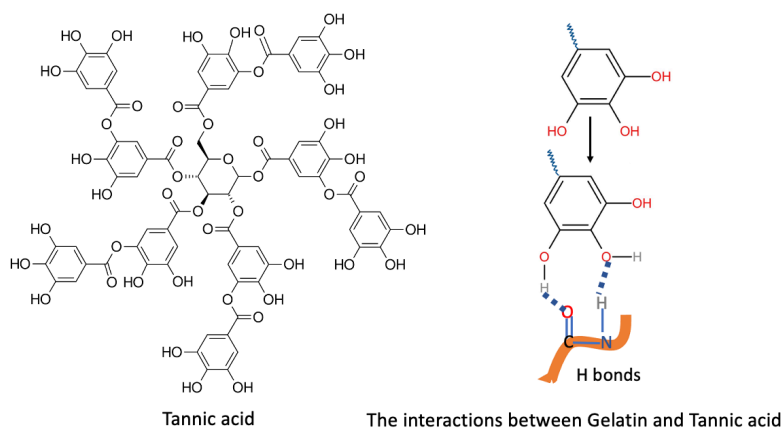


Figure 4. 10 The interactions between gelatin and tannic acid.

To wrap up all results from electrochemical performance evaluations, this current study successfully fabricated an all-in-one self-healable SC that maintains excellent specific capacitance, power density and energy density after cut-heal processes. The electrochemical performance decreases after more than one cut-heal processes. Healing efficiency on specific capacitance in this current study is 96% after one cut-heal cycle, and still can maintain 84% after five cut-heal cycles (Figure 9e), which is comparable with some recent studies [40, 42-44]. A self-healable SC by vinylimidazole, can be healed at room temperature, which can recovery most of electrical properties after healing [44]. In another study, an all-in-one SC was developed with single wall nanotube and polyvinyl alcohol (PVA) that contains self-healing property through hydrogen bonding [43], which showed 80% healing efficiency on specific capacitance. The self-healable SC in our current study is made by natural polymers without chemical crosslinking that shows similar healing efficiency on specific capacitance, which is comparable with the former studies that SC was made by synthetic polymers. The resistance of the device in our current study is 5.67Ω (before cut), which is a fold lower than the former study [43] and our SC device shows only 0.71Ω increase after one cut-healing process.

4.4 Conclusion

A first-of-its-kind all-in one configured flexible and autonomously self-healable SC based on inexpensive and biodegradable natural polymers of gelatin and cellulose nanocrystals was successfully developed in this chapter. Self-healing capacity of the GelMA-CNC hydrogel was endowed by tannic acid treatment, which also makes its feasible to coat conductive agents (PANI and RGO) onto the surface via *in-situ* polymerization. This autonomously self-healable SC can heal within 6 hours without any external stimuli under room temperature. It shows excellent original conductivity and low resistance. The specific capacitance, energy density and power density reach $1861.21 \text{ mF cm}^{-3}$, $20.65 \text{ mWh cm}^{-3}$, and $595.59 \text{ mW cm}^{-3}$ respectively, which is comparable to other similar studies. The specific capacitance, energy density and power density remain 96%, 100% and 82% of their original data respectively after one cut and healing cycle, and retain 84%, 69% and 82% of their pristine value after five cut and healing cycles. Overall, the all-in-one configuration of this self-healable SC may contribute to its excellent electrochemical

performance. This self-healable supercapacitor also showed excellent mechanical properties, suggesting a great potential in such advanced applications as energy storage devices, E-skin and sensors for medical care.

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CHAPTER V

Self-powered and plant-wearable hydrogel as LED power supply and sensor for promoting and monitoring plant growth in smart farming

Abstract

Multifunctional smart devices are highly demanded within developing of “Internet of Things”. It attracts to develop an advanced material to meet the requirements of smart devices. Synthetic polymers such as polyacrylic acid showed great potential to be the candidate on developing multifunctional smart devices due to its proper mechanical performance that could further expend more applications in different uses. This study developed a versatile double-network hydrogel from polyacrylic acid, reduced graphene oxide and polyaniline that can serve as: 1) a clean energy harvesting device for self-powered light fertilizer for plants, 2) a supercapacitor for energy storage, 3) plant growth sensor, and 4) an ammonia sensor. Polyacrylic acid double-networked with the conductive nanofiller reduced graphene oxide and then coated with polyaniline are incorporated with double networking (PAA-RGO-PANI, PRP) that significant improved mechanical stress from 300 KPa to 1050 Kpa. The excellent stretchability (650 %) and strength makes it suitable for agriculture-purposed sensor that satisfies the plant growth. The electrical performance of the triboelectric energy harvester (PRP-TENG) provides high power density at 424 mW /m² from sound wave, wind, and mechanic pressure. The PAA-RGO-PANI supercapacitor can maintain a stable capacitance at 2330 mF cm⁻² after 5000 cycles. The self-powered system combined with PRP-TENG and supercapacitor shows great potential in modern agriculture system and even in plant-machine interaction.

Key words: Double network hydrogel, tough, stretchable hydrogel, plant writable hydrogel, self-powered system, light fertilizer, plant sensor, smart farming

5.1 Introduction

Global climate change and food insecurity are the emerging threats to mankind. A growing population and increasing global food demand call for higher productivity and efficiency in farming [1-3]. Applying large amount of synthetic fertilizers may push the crops' productivity to the limit but exert environment problems [4-6]. For example, nitrous oxide is one of the main gases emitted by agriculture activities and accounts for about half of the warming effect [7, 8]. Phosphorus from the fertilizer stimulates the growth of algae, which causes oxygen depletion in water [4-6]. There is a need to reduce agriculture greenhouse gas emissions to reduce their impact on climate change. To date, smart farming which can improve the quantity and quality of farm products in an eco-friendly manner has been developed [9]. Sensing technologies and light fertilizers are the two techniques that relied on by smart farming.

In smart farming, light emitting diode (LED) has been applied in the modern greenhouse to replace the conventional soil fertilizer due to chemical free with fast crop harvest cycles [10-14]. The peak emission wavelengths of light emitting diode (LED) lights range from UV-C (~250 nm) to infrared (~1000 nm) [10-14]. By tuning the LED lights to the wavelengths that match the photoreceptor of specific plants, the plants can reach higher productivity [12-14]. For example, red and blue LED lights greatly promote the growth of leafy vegetables, tomatoes, cucumbers and peppers [10-14]. Despite of their excellent performance in agriculture, large energy consumptions of the LED booster systems restricts their practical application [10-14]. Thus, a self-powered light fertilizer system is demanded to fulfill the large energy consumption.

Our environment is full of clean energy such as air flow, sound and rain. They could be harvested and converted into electricity via the newly developed triboelectric nanogenerators (TENGs) [15-19]. Triboelectric materials can convert mechanical energy into electricity storage to drive light fertilizer, sensors or actuators [20, 21]. Recent studies developed triboelectric energy generator using different triboelectric polymers including polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET) to harvest clean energy (Table 5.1) [15, 19, 22, 23]. However, in order to achieve high energy harvest efficiency, such triboelectric materials (PVDF, PTFE, PET) need surface modification strategies to increase effective contact area [24, 25]. Special patterns such as nanowire and nanoparticles were commonly used for surface modification of the triboelectric materials [26]. To fabricate these

special patterns, high-cost and intricate techniques like inductively coupled plasma dry etching were used [27, 28].

Sensor technology is one of the most important building blocks in smart farming. It entails the deployment of a variety of sensors that are integrated via networks. Plant wearable sensors that facilitate site-specific monitoring on ambient conditions such as temperature, moisture level and soil nutrients as well as monitoring on the plant growth rate [29]. A precise management can be achieved during farming processes; thus, efficiency and productivity are improved. Real-time plant wearable sensors developed by polymer tapes and/or PDMS as their substrates (Table 5.2), but they have limitation on the sensing ranges. For example, a tape wearable sensor showed only 7% strain corresponded with resistance change [30]; while a PDMS based plant sensor had a linear correlation within 25% strain [31]. On other hand, film sensors made of carbon material offers a way to monitor ammonia gas, which is one component that needs to be monitored in farm system as well. Although film sensors have short response time with high sensitivity, they still limit on stretchability [32-34]. All the aforementioned materials that were used to make plant real-time wearable sensors & ammonia sensors have limited stretchability, thus, are not feasible materials for fast-growing plants [31, 35, 36] (Table 5.2). Moreover, the electrodes of the sensors were made by noble metals (Au, Ti) are costly. To install these electrodes on the sensors, advanced techniques such as E-beam, high pressure vapor are required [37, 38]. There has been a call for researches that accelerate the development of stretchable, cost-effective, fast-response, easily-accessible, and highly sensitive plant wearable sensors for smart farming. Hydrogel based sensors have attracted great interests nowadays because of its superior mechanical properties, ease of fabrication, high electrochemical activity, and multiple functions. The polyacrylic acid (PAA) hydrogel shows remarkable stretchability and strength due to the dual-crosslinked network. The reversible ionic bonding formed between Ca^{2+} and PAA and the nonreversible chemical bonding between PAA and chemical crosslinker constitutes the dual-crosslinked. The remarkable mechanical performance of the PAA hydrogel makes it a promising material to develop plant wearable sensors. PAA based TENG device has been showed great energy harvest performance, but it still need in-depth investigation for more applications [39]. This type of PAA hydrogel TENG in smart farming system is never explored.

Herein, we synthesized a versatile polyacrylic acid hydrogel integrated with reduced graphene oxide and polyaniline (PAA-RGO-PANI) coating for smart farm system development (Figure 5.1).

RGO has higher C/O ratio in aromatic graphene structure [40] and thus has better conductivity than GO. In addition, the mechanical property of RGO is comparable with GO, it could increase the mechanical stress of PAA hydrogel. Moreover, RGO has been proven to enhance the performance of nano energy harvest device since it could increase the polarization of triboelectric materials [39, 41-44]. Thus, in our current study RGO instead of GO is introduced to porous PAA nanocomposite as the conductive nanofiller. Currently, reduction of graphene derivatives such as GO has emerged as the primary strategy that can yield considerable amount of highly processable RGO [45, 46]. To achieve the reduction of GO, thermal reduction such as thermal annealing [47], microwave [48], and photo reduction [49] has been developed based on the fact that the rapid increase temperature decomposes the oxygen containing groups on GO carbon lattice into gases and creates pressure high enough to separate two stacked GO platelet [48]. The superior aqueous dispersibility of GO makes chemical reduction another favored option to reduce GO. Several chemical reduction methods have been developed recently, including electrochemical reduction [50], solvothermal reduction [51], and reduction by chemical reagent such as hydrazine [52], sodium borohydride (NaBH_4) [53], ascorbic acid [45, 46], and hydroiodic acid [54]. Here, an eco-friendly hydrothermal reduction was chosen to reduce GO as it requires neither extreme condition nor harmful chemical reagent. Polyaniline (PANI) is one of the most promising conductive polymer that widely used for developing energy storage device due to its controllable conductivity, low cost, easy synthesis procedure and exhibits robust behavior in a normal ambient environment [55]. In the previous study, a self-powered PANI-coated worn-out cotton textile showed an enhanced electrical output voltage than the pristine worn-out cotton textile [55], indicating that PANI coating can improve the output performance of TENG. PANI can be easily doped by various chemical molecules, thus, can show high electrochemical reactivity to ambient conditions [56, 57]. In addition, PANI coated hydrogel has been proven to exhibit excellent electrochemical performance when it incorporated with RGO [58, 59]. Thus, PANI is coated on the surface of the PAA-RGO hydrogel enhance the sensitivity of PAA-RGO hydrogel. Here, a “standard” procedure to prepare PANI coating was used, but at higher acidity and reduced temperature to increase the conductivity of the resulting PANI [60]. In detail, the aniline was oxidized by ammonium peroxydisulfate in acidic aqueous medium at 0 °C. Owing to the incorporation of PANI and RGO, our plant wearable PAA-RGO-PANI achieves versatility: dual functional sensor that can monitor both growth rate and ambient condition, clean energy harvesting (PRP-TENG) from dynamic

sources, an energy storage (supercapacitor). Thus, using our PAA-RGO hydrogel solely is sufficient to build a multifunctional smart farming system.

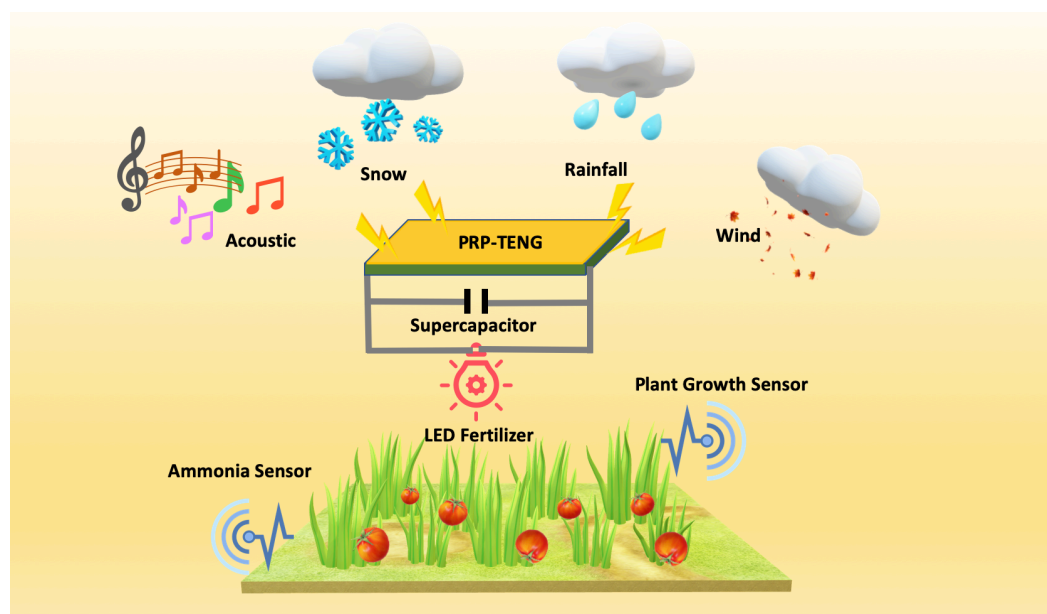


Figure 5.1 Smart farming system is built by a versatile conductive hydrogel (PAA-RGO-PANI).

Table 5.1 Recent studies on harvesting clean energy by piezoelectrical and triboelectrically energy generators

Materials	Method	Mechanism	Application	Energy harvest source	Frequency	Voltage (V)	Current (μ A)	Power	Mechanical Stress (KPa)	Strain (%)	Ref
PVDF ¹ /nanofiber	Coating	Triboelectric	TENG/Sensor	Acoustic	170 Hz	200	175	7 W/m ²	N/A	N/A	[20]
PVDF/Vitamin B ₂	Coating	Piezoelectric	PENG/Sensor	Mechanical	6 Hz	61.5	12.2	9.3 mW/m ²	N/A	N/A	[16]
FEP ² /PVA ³	Liquid film	Triboelectric	TENG	Water droplet	20 Hz	24	50 nA	137.4 nW	N/A	N/A	[24]
PTFE ⁴ /PET ⁵	Hybrid device	Triboelectric	TENG	Rainfall	0.35 ml/s	30	200	16.31 mW/m ²	N/A	N/A	[23]
PAA/RGO/PANI	Crosslinked Hydrogel	Triboelectric	TENG Supercapacitor Plant sensor Ammonia sensor	Acoustic/wind/rainfall mechanical	4Hz-1KHz	21.77	48.69	424 mW /m ²	1050	650	Current Study

1. Polyvinylidene fluoride
2. Fluorinated ethylene propylene
3. Polyvinyl alcohol
4. Polytetrafluoroethylene
5. Polyethylene terephthalate

Table 5.2 Recent similar studies on plant growth sensor

Sensor Composition	Functions	Method	Signalling Model	Thickness (μm)	Resistance ($\text{K}\Omega$)	$\Delta R/R_0$ (%)	Strain Sensing Range	Mechanical Stress (KPa)	Strain (%)	Ref
Ti/Au/PDMS ¹	Growth sensor Strain sensor	Coating/E-beam	Leaf surface moisture Elongation/temperature	110	0.5	0-550	25%	N/A	35	[32]
CNT ² /Graphite	Growth sensor Strain sensor	Brush-tape	Elongation	30	N/A	0-600	7%	N/A	150	[37]
Chitosan/Graphite	Growth sensor	Brush coating	Elongation Leaf surface moisture	30	3-6	0-200	150%	N/A	N/A	[36]
PAA/RGO/PANI/PDMS	Growth sensor Supercapacitor Ammonia sensor Energy harvest	Crosslinking	Elongation	350	0.5-1	0-1000	200%	1050	650	Current study

1. Polydimethylsiloxane
2. Carbon nanotube
3. p-doped poly(3,4-propylenedioxythiophene)

Table 5.3 Summary of recent studies on ammonia sensor

Sensor Composition	Functions	Method	Signalling Model	Thickness (mm)	Resistance (K Ω)	Time to reach balance (s)	Range of [NH ₃] (ppm)	Mechanical Stress (KPa)	Strain (%)	Ref
V-RGOH ¹	NH ₃ and NO ₂ Sensor	Sputtering coating	Electron transfer	300 nm	2.3	300	10 -100	N/A	N/A	[33]
PVA ² / carrageenan	NH ₃ and NO ₂ Sensor	Crosslink/ polymerization	Electron transfer	1	N/A	300	5 – 40	830	330.44	[35]
AAc/ DMAEMA ³	NH ₃ sensor	Crosslink	Change of swelling	5	N/A	4 h	18 - 40	N/A	N/A	[34]
PAA/RGO/PANI	Ammonia sensor Plant sensor Energy Generator	Crosslink polymerization	Electron transfer	2	0.5-1	60	8.62 -5636.5	1050	650	Current study

1. Vitamin C reduced graphene oxide
2. Polyvinyl alcohol
3. acrylic acid (AAc) and 2-(dimethylamino)ethyl methacrylate (DMAEMA)

5.2 Materials & Methods

Materials

A double network polyacrylic acid hydrogel was made by acrylic Acid (AA), Calcium Chloride (CaCl_2), *N-N'* methylenebisacrylamide (MBA), and Ammonium Persulfate (APS) that were purchased from Sigma-Aldrich (Canada). Aniline (Sigma-Aldrich, Canada) was used for synthesis of conductive polymer polyaniline. Reduced graphene oxide was made from Graphene Oxide (GO) powder that was purchased from Wuxi Chemical Company, China. All materials were received as ACS level unless otherwise stated. All of the detail procedure was described below.

Method

5.2.1 Reduced Graphene Oxide

Reduce graphene oxide was made by the hydrothermal conversion method, a greener approach to the reduction of GO. GO (5mg/ml) was added in deionized water with an ultrasonic homogenizer for one hour until it got well dispersed. The solutions were then placed in a Teflon coated autoclave and placed in an oven at 180°C for approximately 8 hours. GO got reduced in 8 hours. RGO was taken out after heating 8 hours and followed by freeze drying. Freeze dried RGO power will be obtained and dispersed it into DI water as 5 mg/mL, 10 mg/mL and 15 mg/mL and ultrasonication until they got well dispersed for further use.

5.2.2 Conductive Polyacrylic acid hydrogel

The conductive PAA hydrogels were synthesized in a modified method according to a previous study [85]. RGO in three different concentrations (5, 10, or 15 mg/mL) were well dispersed in deionized water by an ultrasonic homogenizer for one to two hours. The AA monomer was diluted by RGO solution (5, 10, or 15 mg/mL) to 20% concentration. 30 μL calcium chloride (30 mg/mL) was added to serve as physical crosslinker, along with 30 μL chemical crosslinker MBA (30 mg/mL) and 30 μL of initiator APS (300 mg/mL). This mixture was allowed to cure in a warm water bath at 40-50°C for 20 minutes to yield the PAA-RGO hydrogel.

The PAA-RGO hydrogels were coated with polyaniline to further increase their conductivity. The polyaniline was prepared as follows: 300 μL of aniline monomer was added into 50 mL of 1M HCl with constant stirring in an ice-water bath for 10 minutes. 375 mg of APS was dissolved in 10 mL of 1M HCL cooled to 0 °C. The hydrogels were immersed in the solution for polymerization at 0°C for 8 hours, then washed with deionized water several times to

remove residual aniline monomers and APS. This yields a PAA-RGO with both surfaces coated with polyaniline nanocomposite electrodes.

5.2.3 SEM characterization

The lyophilized hydrogels samples were placed on a wafer for gold coating. The morphologies of samples were characterized by a JEOL JSM-5900LV scanning electron microscope.

5.2.4 FTIR characterization

Fourier transformed infrared (FTIR) spectra (Thermo Nicolet iS10 FTIR Spectrometer) was used to investigate the intermolecular interactions among PAA, RGO, PANI. The spectra were obtained from lyophilized samples of PAA, PAA-RGO, PAA-RGO-PANI at room temperature.

5.2.5 Rheology characterization

All rheology experiments were conducted on a TA Discovery Hybrid Rheometer. The hydrogels (8mm in diameter and 1mm in thickness) were loaded onto the parallel plate, the diameter of the parallel plate is 20 mm. During oscillation frequency experiments, the samples were measured in the frequency ranging from 0.1 to 100 rad s⁻¹ with a constant strain of 0.5% at 21°C.

5.2.6 Mechanical Testing

The mechanical properties of samples were measured using an Instron 5965 mechanical analyzer. The tensile tests were performed on the hydrogel samples at a speed of 10 mm min⁻¹ until breaking. The narrow section size of all samples is 25 mm (length) × 20 mm (width) × 2.5 mm (thickness). All samples were tested with three replications, the total number of 30 samples were tested. The Young's modulus was calculated as the slope in the initial linear region on the stress-strain curves, and the toughness was calculated with the areas under strain-stress curve [86].

5.2.7 PRP-TENG clean energy harvesting

The PRP-TENG clean energy harvesting device was assembled in a three-layer sandwich-like composed by a polyimide film (top layer), a freeze dried PAA-RGO- PANI nanocomposite (50 mm × 50 mm × 5 mm), and an aluminum film as an electrode. An open circuit was connected with this PRP-TENG device for harvesting clean energy. Acoustic energy source was set up

by a speaker at 85 dB and 1k Hz. A 500 g weigh was placed on and slide across the top of the device to simulate special weather conditions like heavy rainfall. Wind source was set up by a fan running at 1600 rpm.

5.2.8 Electrochemical Test

An PAA-RGO-PANI hydrogel supercapacitor was assembled by sandwiching the hydrogel between two pieces of aluminum foil as the current collectors and sealed by parafilm to prevent moisture evaporation. The electrochemical properties of the assembled SCs were investigated using an electrochemical workstation. The electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency ranging from 10^5 to 10^{-2} Hz, 10 mV AC amplitude and zero DC amplitude. The Galvanostatic Charge-Discharge (GCD) measurements were performed from 0 to 0.8 V at a constant current 5mA. The cyclic voltammetry (CV) curves were recorded from 0 to 0.8 V at scan rates ranging from 0.002 to 1 V s⁻¹. The capacitance of a single electrode that was assembled for SC can be calculated from GCD curves as a function of the discharging slope after the IR drop:[63]

$$C = 2I\Delta t/(\Delta V - V_{IR})$$

where I is the discharge current; Δt represents the time span of a full discharge; ΔV is the potential change after a full discharge; V_{IR} indicates the potential drops at the initial discharge stage, which is mainly attributed to the intrinsic resistance.

5.2.9 Fabricating ultra-thin plant growth sensor

An ultra-thin plant growth sensor for aloe leaves was fabricated in several steps. An ultra-thin layer of polyvinyl alcohol (PVA) (10 %) was coated on an aluminum film by spin coating. The PVA layer can serve as a hydrophilic media to allow the PAA-RGO hydrogel thin layer got evenly crosslinked afterwards. PAA-RGO mixture was prepared before crosslinking, a mask was covered onto the dried PVA layer and the PAA-RGO mixture was filled into the interspace of the mask for crosslinking under a warm condition (40 – 50 °C). The PVA layer was washed off by DI water after PAA-RGO got crosslinked. PANI was then coated onto the crosslinked PAA-RGO. PDMS was spin-coated onto the hydrogel to stabilize the sensors, then the sensors were attached onto the aloe leaves. The final size of an ultra-thin growth sensor is 35 mm in length, 5 mm in width, and 350 μ m in thickness. The aloe leaves growth rate was calculated by:

$$\text{Aloe leaves growth rate (\%)} = \frac{\Delta \text{ length of growth (cm)}}{\text{Initial length of the leaf (cm)}}$$

5.2.10 Fabricating elastic band pepper fruit growth sensor

To fabricating the elastic band, a mold was used when crosslinking PAA-RGO hydrogel. The mold size is 2 mm in thickness, the circumferences are depended on the pepper fruits sizes. PANI was coated after crosslinking of PAA-RGO hydrogel. A Pokit meter (Pokit Innovation Pty Ltd, Sydney) was connected in series to achieve wireless function. Vaseline was applied on the surface of the elastic band sensors to minimize the moisture evaporations and stabilize the sensors during the data collection. The pepper fruits growth rate was calculated by:

$$\text{Pepper fruits growth rate (\%)} = \frac{\Delta \text{length of circumference of pepper fruit (cm)}}{\text{Initial length of the circumference (cm)}}$$

5.2.11 Ammonia Sensor Test Set up & Data Collection

In preparation for testing, hydrogel sensors were cut into specific size (10 mm × 10 mm × 5 mm) and allowed to air dry to remove the excessive surface liquid before being placed in a sealed plastic chamber with 2 ml ammonia gas of various concentrations. Copper wires were used to connect a hydrogel sample to a wireless multimeter before the chamber was sealed (Figure 15b). Processor was used to record data in the form of resistance changes once every 2 seconds. A test was done when the resistance reading reached equilibrium.

5.3 Results & Discussion

5.3.1 PAA-RGO-PANI hydrogel

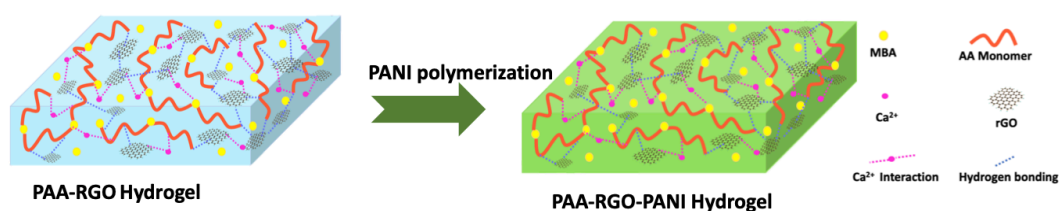
The multifunctional PAA-RGO-PANI hydrogel (Figure 5.2a) showed several significances in this current study to contribute to agriculture: high efficiency to harvest clean energy even in a low stimulation rate; stable and high sensitivity to monitor plant growth in a long-term use; quick response to detect trace amount of ammonia gas. One of the networks was from an acrylic acid and ionic crosslinkers (Ca^{2+}), which served as dynamic and reversible crosslinking. The other network in this hydrogel was constructed by a chemical crosslinker (methylenebisacrylamide), which caused the *in situ* polymerizations among acrylic acid monomers. The Ca^{2+} crosslinked poly acrylic acid network was referred as PAA. RGO was incorporated with the hydrogel to fabricate the PAA-RGO hydrogel which had increased conductivity and mechanical property. Different RGO concentration, 5 mg/mL, 10 mg/mL, and 15 mg/mL were used and the corresponding hydrogels were referred as PAA-RGO (5 mg/mL),

PAA-RGO (10 mg/mL), and PAA-RGO (15 mg/mL). The hydrogel was then coated with polyaniline for electrical capacitance and overall electrical performance, giving rise to the PAA-RGO-PANI hydrogel. This hydrogel can be custom-shaped for different applications, and the detail of working performance will be discussed in applications section.

5.3.2 Characterizations

SEM micrographs (Figure 5.2b-f) showed the hydrogels' morphology changed with different compositions. Figure 5.2b showed evenly distributed porous structure of the PAA hydrogels with pore sizes in micrometers. Figure 5.2c-e showed different concentrations of RGO (5 mg/mL – 15 mg/mL) incorporated PAA hydrogels, in which RGO nanofiller evenly distributed into the polymer matrix. Figure 5.2f-g showed that PANI was evenly coated onto the PAA-RGO (15 mg/mL) substrate, which contributed to the great electrochemical performance of the PAA-RGO-PANI nanocomposite. As the RGO concentration increased from 5 mg/mL to 15 mg/mL, RGO fillers that can be observed in the PAA hydrogel increased. FTIR characterizations (Figure 5.2h) were conducted to verify the existence of the physical interactions. FTIR spectrum of 1697 cm^{-1} can be assigned to the carboxylic groups in the PAA side chains [61]. It can be seen that in the FTIR spectrum of PAA-RGO hydrogel, the spectrum peak at 1541 cm^{-1} can be assigned to RGO nanofiller in PAA [62]. PANI gives typical peaks at 1402 cm^{-1} (benzenoid ring C=C stretching) and at 1566 cm^{-1} (quinoid ring C=C stretching) that indicating PANI in the emeraldine salt state [63-65]. PAA-RGO-PANI had higher nitrogen content, indicating the existence of PANI in PAA-RGO-PANI.

(a)



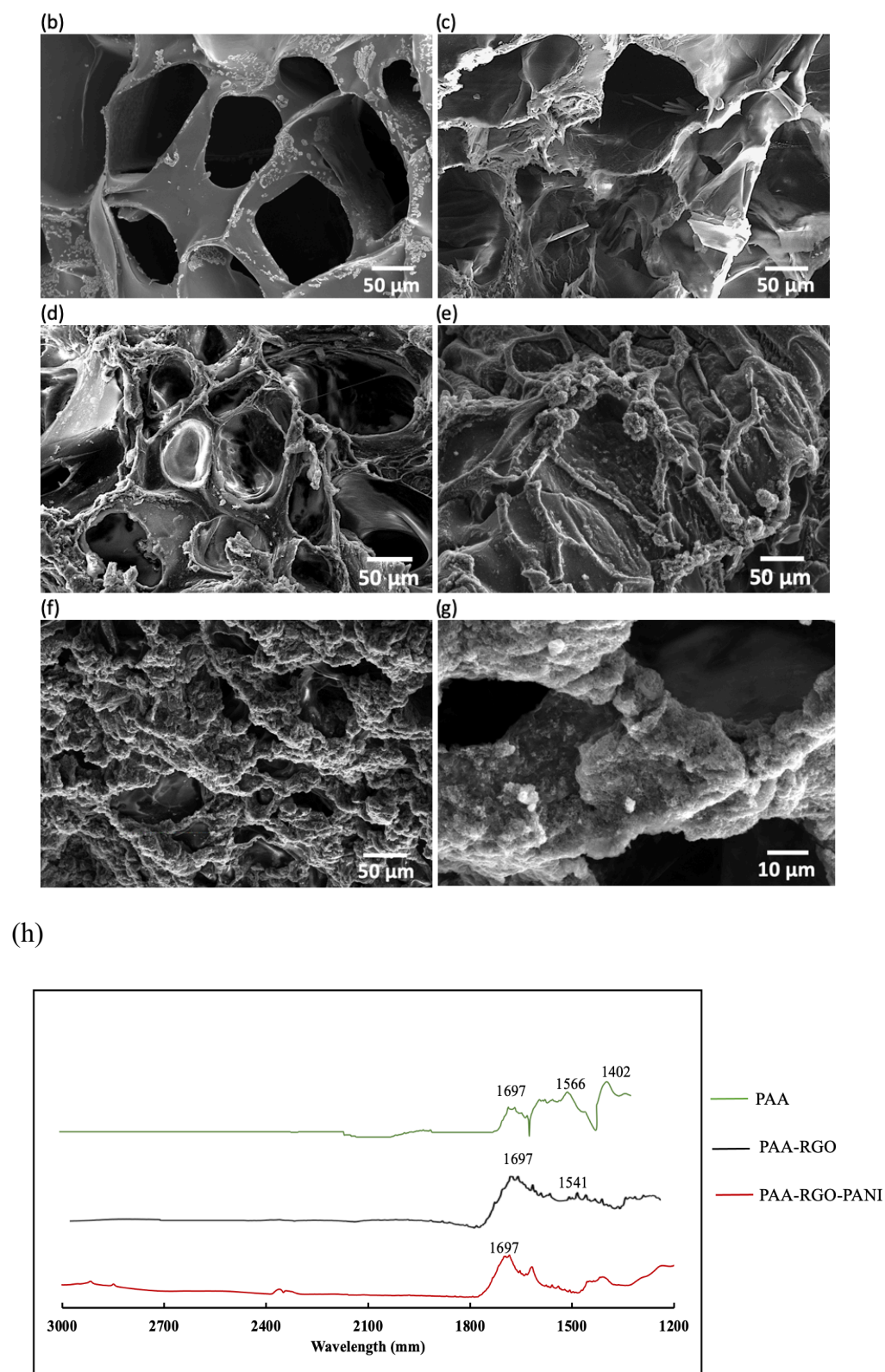
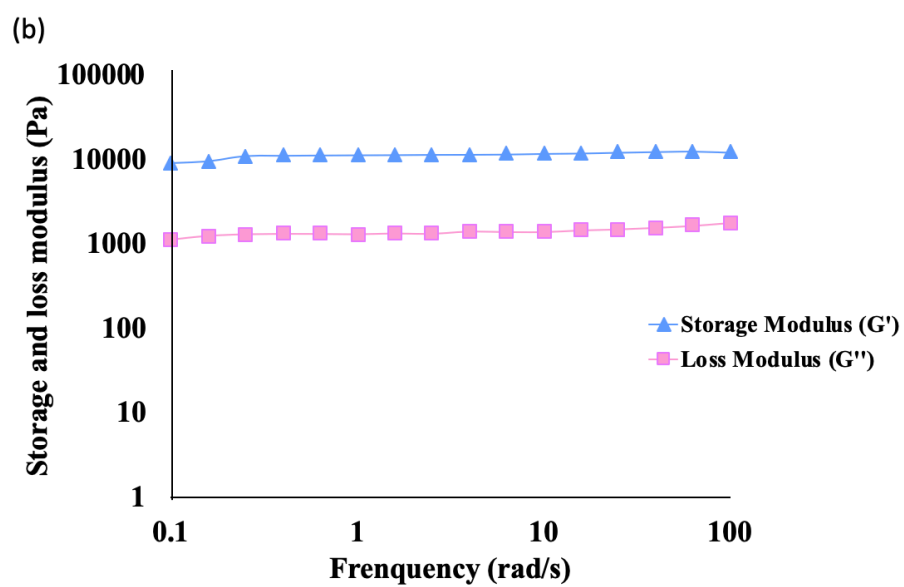
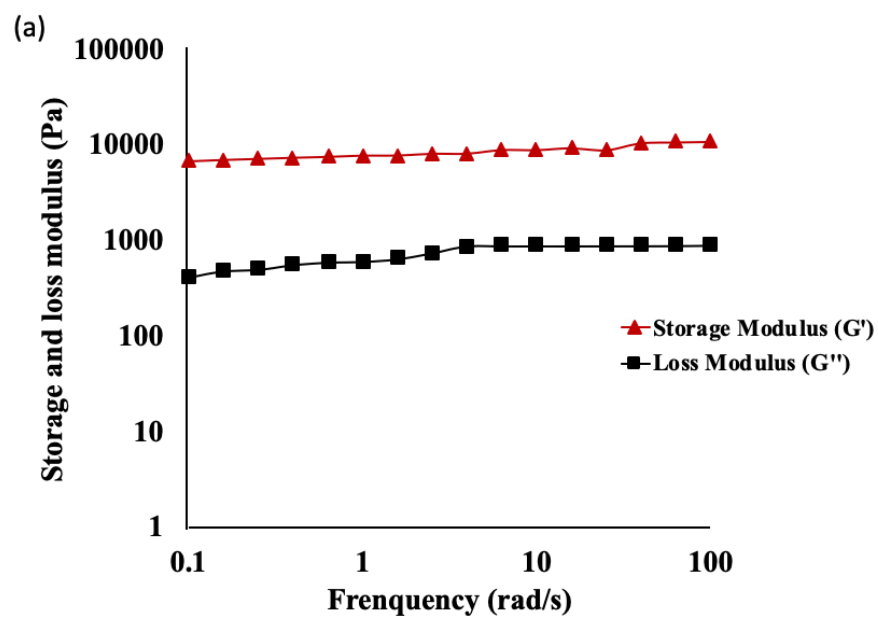


Figure 5.2. Fabrication and characterization of PAA-RGO-PANI. (a) Double network crosslink of acrylic acid monomers and incorporated with RGO nanofiller to fabricate PAA-RGO hydrogel and coated with PANI. (b) SEM image of PAA hydrogel; (c) SEM image of PAA-RGO (5 mg/mL) hydrogel; (d) SEM micrographs of PAA-RGO (10 mg/mL) hydrogel; (e) SEM micrographs of PAA-RGO (15 mg/mL) hydrogel; (f-g) SEM micrographs of the surface on

PAA-RGO (15 mg/mL)-PANI hydrogel; (h) FTIR spectrum of PAA, PAA-RGO and PAA-RGO-PANI hydrogel samples.

5.3.3 Evaluation of Rheological test

The dynamic mechanical properties of PAA and PAA-RGO-PANI hydrogels were evaluated by frequency sweep tests (Figure 5.3a-d). The result for PAA hydrogel was shown in Figure 3a; and the results for PAA-RGO (5 mg/mL)-PANI, PAA-RGO (10 mg/mL)-PANI and PAA-RGO (15mg/mL)-PANI hydrogels were shown in Figure 5.3b,c and d, respectively. The storage modulus (G') was flat and higher than loss modulus (G'') in all samples, indicating the stable solid-like behavior of these hydrogels [66]. The incorporation of amount of RGO (5 mg/ml to 15 mg/mL) was found to enhance storage modulus (G') from about 10 KPa to 63 KPa of the hydrogels, as can be observed in the Figure 3. A trend of elevated storage modulus (G') was observed in the samples, which was because of the RGO nanofiller. The storage modulus (G') increased when more RGO (15 mg/mL) presents in the PAA hydrogels. The PANI coated samples showed higher storage modulus (G') when compared to the samples without PANI, because that PANI reinforced the strength of the hydrogel. The results suggest that the mechanical strength can be enhanced by adding RGO nanofiller and PANI coating.



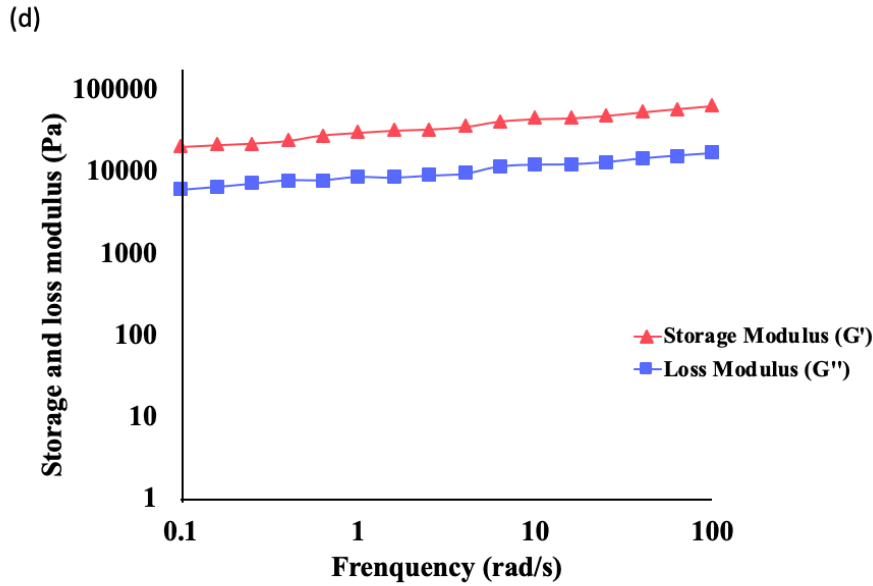
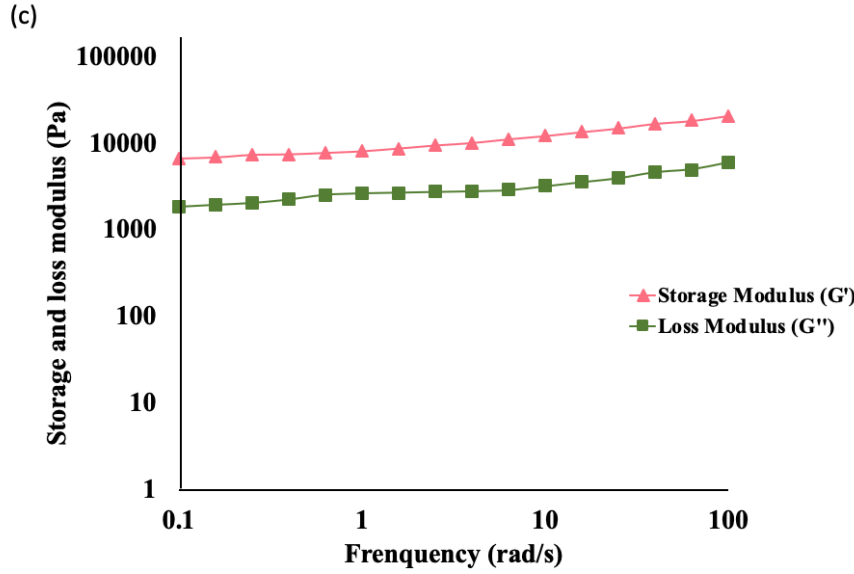


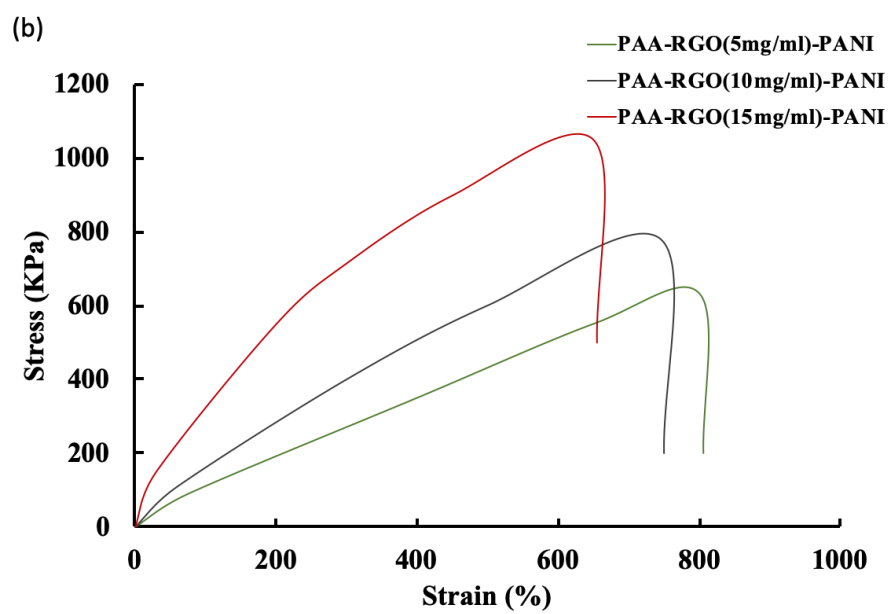
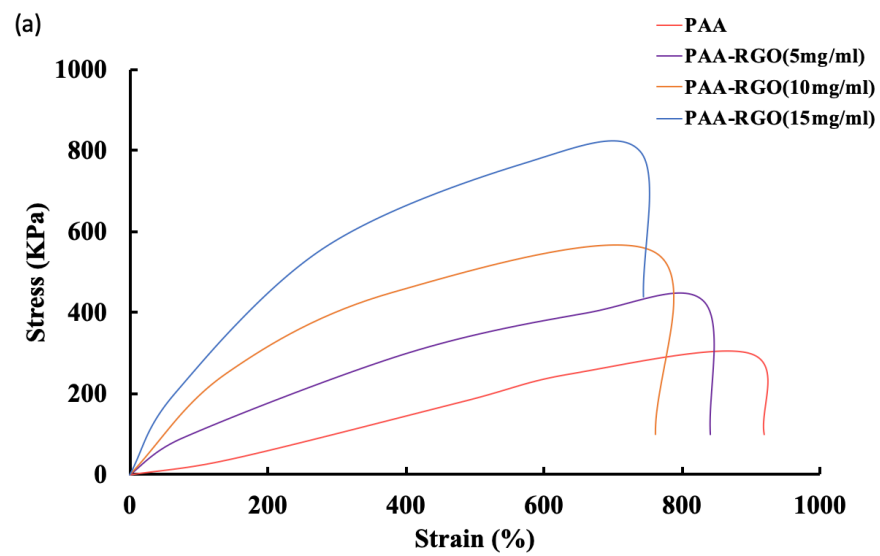
Figure 5.3 Rheology tests for (a) PAA hydrogel; (b) PAA-RGO (5 mg/mL)-PANI hydrogel; (c) PAA-RGO (10mg/mL)-PANI hydrogels; (d) PAA-RGO (15mg/mL)-PANI hydrogels.

5.3.4 Mechanical Properties

Strain-stress curves of PAA, PAA-RGO and PAA-RGO-PANI hydrogels were shown in Figure 5.4a-b. PAA hydrogels reached a ultimate tensile strength of 300 ± 5.86 KPa with a strain to failiure of 900 ± 5.67 %. It can be observed that the strength of the hydrogel was significantly increased from 300 ± 5.86 KPa to 430 ± 7.64 KPa when 5 mg/mL RGO was added. As increasing amount of RGO into the PAA hydrogel, the mechanical strength was further increased. The mechanical stress of the hydrogel shows a tensile strength of 550 ± 9.41 KPa when RGO concentration doubled. The PAA-RGO hydrogel reached 800 ± 10.36 KPa in

tensile strength when 15mg/mL RGO presented in the hydrogel. A decrease from $900 \pm 5.67\%$ to $800 \pm 6.89\%$ in strain was showed when the concentration of RGO rose from 5 mg/mL to 15 mg/mL. The mechanical strength, however, was dramatically increased almost three times when 15 mg/mL RGO was added. Young's modulus and toughness of PAA and PAA-RGO hydrogels were shown in Figure 5.4c. Young's Modulus of PAA hydrogel sample was 26.98 ± 1.61 MPa, and the toughness was 1.15 ± 0.15 MJ m⁻³. As the amount of RGO increased from 5 mg/mL to 15 mg/mL in the PAA hydrogels, Young's modulus raised from 105.63 ± 4.84 MPa to 306.27 ± 5.26 MPa. Toughness showed a similar increasing trend from 1.59 ± 0.05 MJ m⁻³ to 3.85 ± 0.34 MJ m⁻³. The results indicated that RGO as a nanofiller incorporated in the hydrogel could effective reinforce the mechanical stress of PAA-RGO hydrogel [67].

The tensile strength showed also an increase after polyaniline was coated on the PAA-RGO hydrogels. The PAA-RGO (5 mg/mL)-PANI hydrogel had a tensile strength of 630 ± 8.75 KPa and a strain to failure of $803 \pm 7.89\%$; The PAA-RGO (10 mg/mL)-PANI hydrogel had a tensile strength of 780 ± 9.34 KPa and a strain to failiure of $745 \pm 5.56\%$; The PAA-RGO (15 mg/mL)-PANI hydrogel had a tensile strength of 1050 ± 8.34 KPa and a strain to failure of $659 \pm 5.78\%$. Young's modulus and toughness of PAA-RGO-PANI hydrogels were shown in Figure 5.4d. Young's Modulus increased from 149.17 ± 7.71 MPa to 464.33 ± 5.69 MPa and toughness increased from 1.82 ± 0.15 MJ m⁻³ to 4.53 ± 0.27 MJ m⁻³. The results of Young's Moldulus and toughness in our current study agreed with similar studies [68, 69]. PANI could increase the mechanical stress and Young's modulus of the hydrogels, but decreases in strain. The intrinsic brittleness of PANI derives from rigid polymer backbone [70, 71]. Moreover, the strong physical interactions such as π - π interactions between RGO and PANI could further strengthen the combination of PANI and RGO nanofillers [69]. Overall, our conductive hydrogel samples exhibit excellent mechanical properties in stress, strain and toughness and can be used to fabricate electrical devices that could apply in agriculture system.



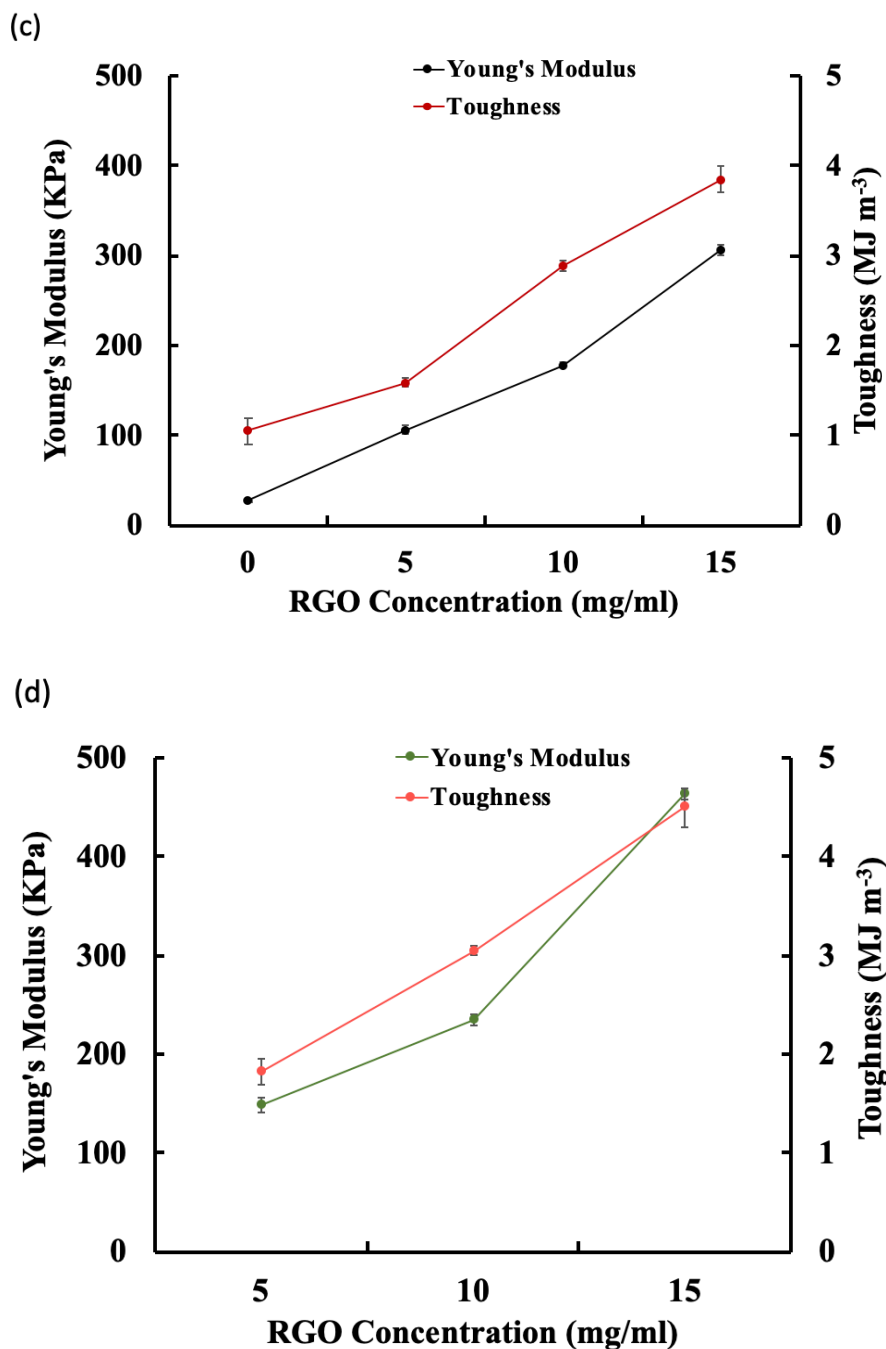


Figure 5.4. Strain-stress curves of (a) PAA and PAA-RGO hydrogels; (b) PAA and PAA-RGO-PANI hydrogels; Young's Modulus and toughness of (c) PAA and PAA-RGO hydrogels; (d) PAA-RGO-PANI hydrogels.

5.4 Applications on Agriculture

5.4.1 PRP-TENG clean energy harvesting devices

A PRP-TENG clean energy harvesting device was assembled by a polyimide film (PI), a freeze-dried PAA-RGO-PANI hydrogel, a piece of aluminum film was used as current collector, and the whole device was three-layer sandwich like assembled (Figure 5.5a) and connected to PAA-RGO-PANI supercapacitors with a bridge rectifier into an open-circuit to

power the LED lights (Figure 5.5c). The electrical performance of different sample compositions was evaluated in several key factors (Table 5.4) including the performance on nano energy generator: open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and the electrochemical performance on supercapacitor: power, electrochemical impedance spectroscopy (EIS), voltage drop (V_{IR}) and capacitance. The samples contain RGO nanofiller showed better electrical performance than the sample without RGO nanofiller. As with amount of RGO nanofiller increased from 5 mg/ml to 15 mg/mL, the electrical performance got significant improved. In addition, there's remarkable increase of electrical performance when the PAA-RGO samples coated with PANI (Table 5.4). This is because the conductive agents such as RGO nanofiller and PANI were evenly distributed in the porous structure in PAA-RGO-PANI nanocomposite (Figure 5.5a). The porous structure results in extremely high specific surface and ultralow density, which makes it possible to support a large loading of nano-size conductive fillers (RGO). Furthermore, the porous structure enables large contacting areas when triboelectrification happens, offering large number of electrons on the surface of the PAA-RGO-PANI nanocomposite during the triboelectrification process. Therefore, the sample with best electrical performance (PAA-RGO (15mg/mL)-PANI) has been chosen for further tests on the performance of PRP-TENG, supercapacitors and wireless sensors.

The PRP-TENG device achieves energy conversion based on the coupling effect of triboelectrification and electrostatic induction, the energy conversion process in an open circuit is briefly described in Figure 5b. There're no charges on the PI surface or the PAA-RGO-PANI nanocomposite surface at the initial stage. Triboelectrification happens when PI is in contact to PAA-RGO-PANI nanocomposite as a result of external force (mechanical pressing or air vibrations): PI is a triboelectric material that has strong potential to gain electrons on its surface (negative charged), while PAA-RGO-PANI nanocomposite has strong potential to loss electrons on the surface (positive charged). Thus, the contact between the PI surface and the PAA-RGO-PANI surface resulted in negative charges on the PI surface and positive charges on the PAA-RGO-PANI surface. Meanwhile, negative charges were induced in the aluminum foil, and the generated charges in the three layers end up with an equilibrium status. When the two material surfaces started to separate (pressure released stage), the electrostatic potential between PI and PAA-RGO-PANI nanocomposite decreased. The generated charges cannot be held by the system any longer. Consequently, the electrons on the aluminum foil flow to the ground. During the contacting stage, the electrostatic potential increased and more charges could be held in the system, driving the electrons flow from the ground to the aluminum foil. Thus, the open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) can be generated by cyclic

“contact-release” processes. Our PRP-TENG was highly durable, which was indicated by the unimpaired internal microstructure after multiple cyclic “contact-release” process. The electrical power could be stored in five PAA-RGO-PANI hydrogel supercapacitors in series to power 20 LED lights (Figure 5.5c).

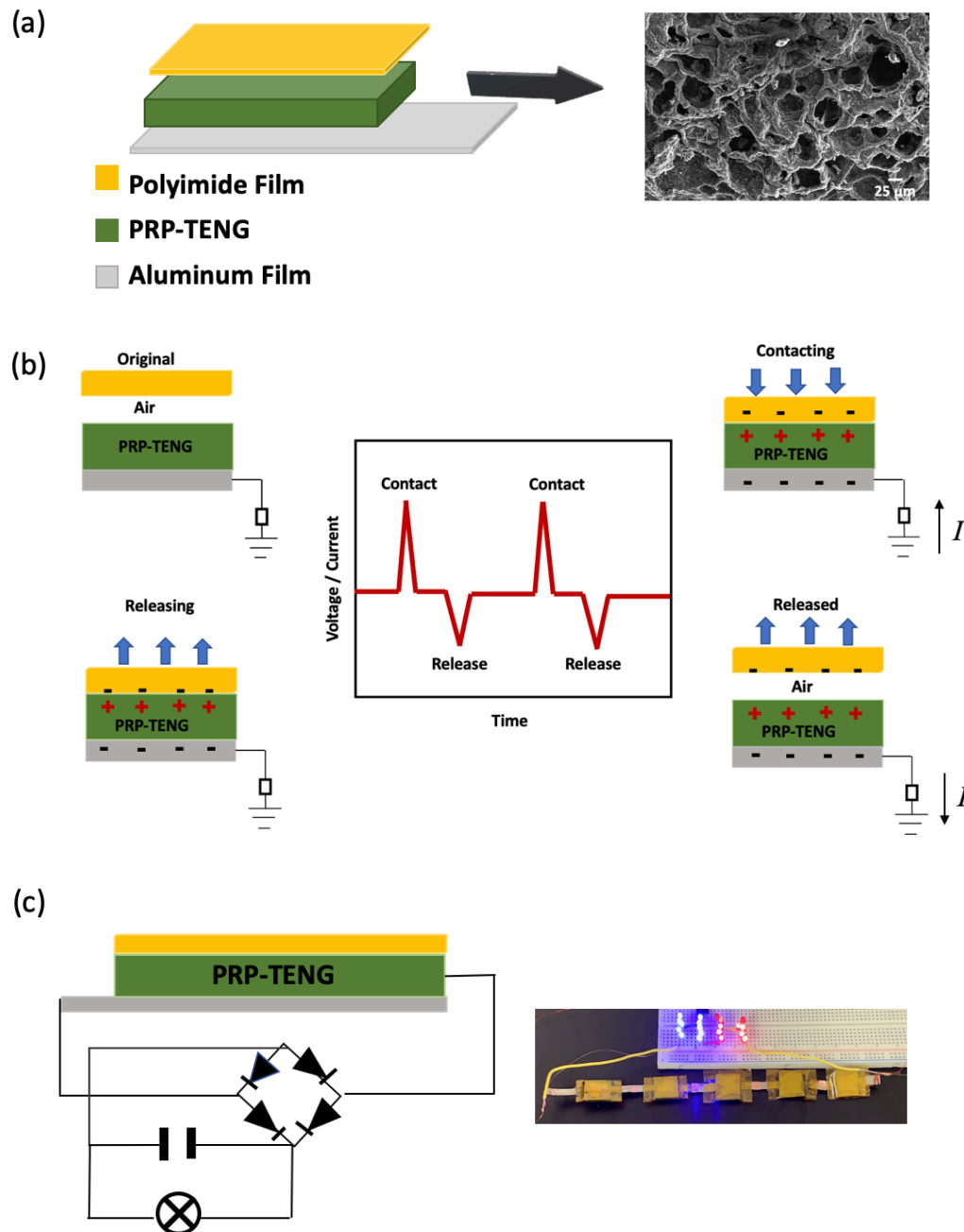
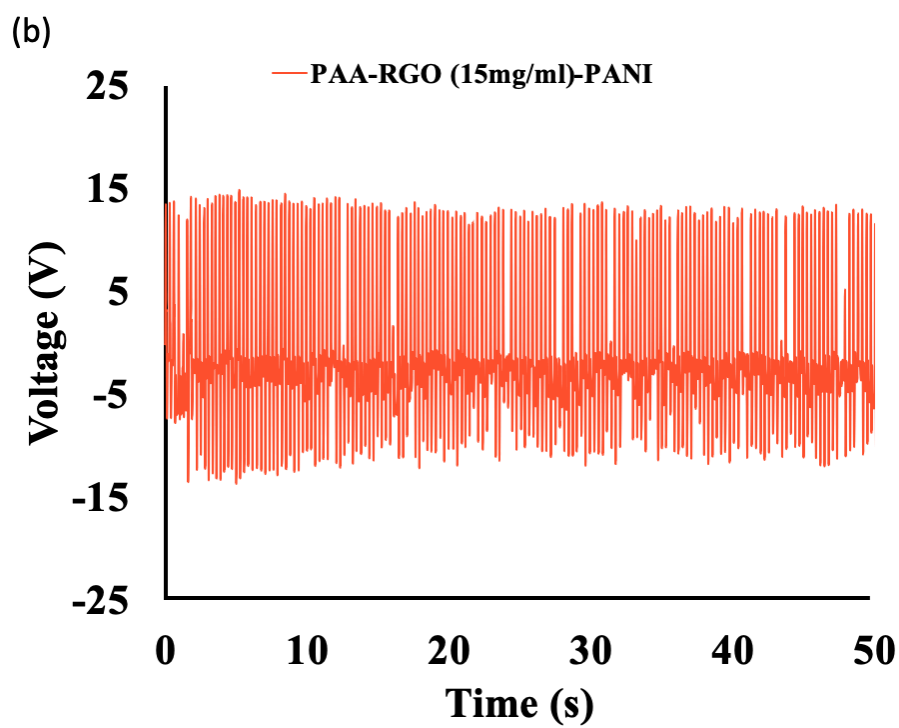
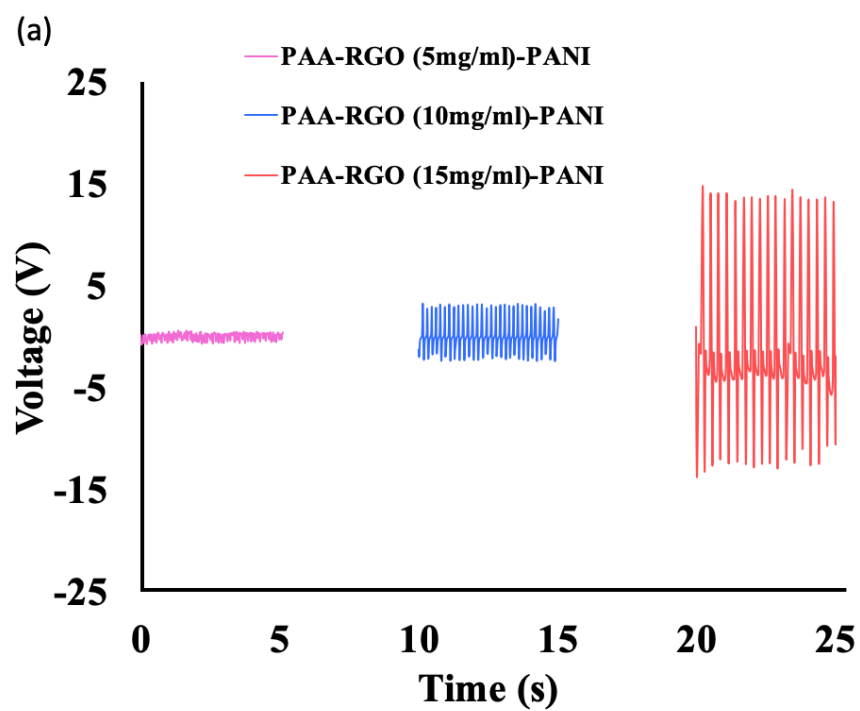


Figure 5.5 PAA-RGO-PANI nanogenerator (PRP-TENG). (a) The composition of PRP-TENG and SEM image of PRP-TENG; (b) The mechanism of PRP-TENG contact-release processes; (c) PRP-TENG linked a bridge rectifier in the circuit with PAA-RGO-PANI supercapacitors to power 20 LED lights.

5.4.2 Acoustic energy harvest by PRP-TENG

To evaluate the electric output of the PRP-TENG in capturing acoustic energy, a speaker was set as an acoustic source to trigger the PRP-TENG. Previous studies indicated that plants growth rate and crop yield can be significantly promoted upon exposure to only a short period of music at 1k Hz for 3 hours daily [72-77]. Thus, the acoustic source at 85 dB and 1k Hz to test the acoustic energy harvesting performance of the PRP-TENG in this study (Figure 5.6a & c). The results showed higher output voltage and current could be captured by PRP-TENG when higher amount of RGO was presented in PAA-RGO-PANI nanocomposite. The maximum V_{oc} provided by PRP-TENG that contains 15 mg/mL RGO was 14.23 V and the maximum I_{sc} of this PRP-TENG reached to 48.69 μ A. While, the PRP-TENG that contains 5 mg/mL RGO showed a maximum V_{oc} of 0.55 V and a maximum I_{sc} of 2.54 μ A. PRP-TENG sample that contains 10 mg/mL RGO shows a maximum V_{oc} of 3.25V and a maximum I_{sc} of 8.77 μ A respectively. Figure 5.6b & d shows a stable energy harvesting from acoustic source of the PRP-TENG that contains 15 mg/mL RGO. When applied a stable acoustic energy source at 85 dB and 1k Hz for in continuously for 50 seconds, the PRP-TENG that contains 15 mg/mL RGO could maintain a stable V_{oc} of 12.67 ± 1.13 V, and a stable I_{sc} of 15.67 ± 6.89 μ A.



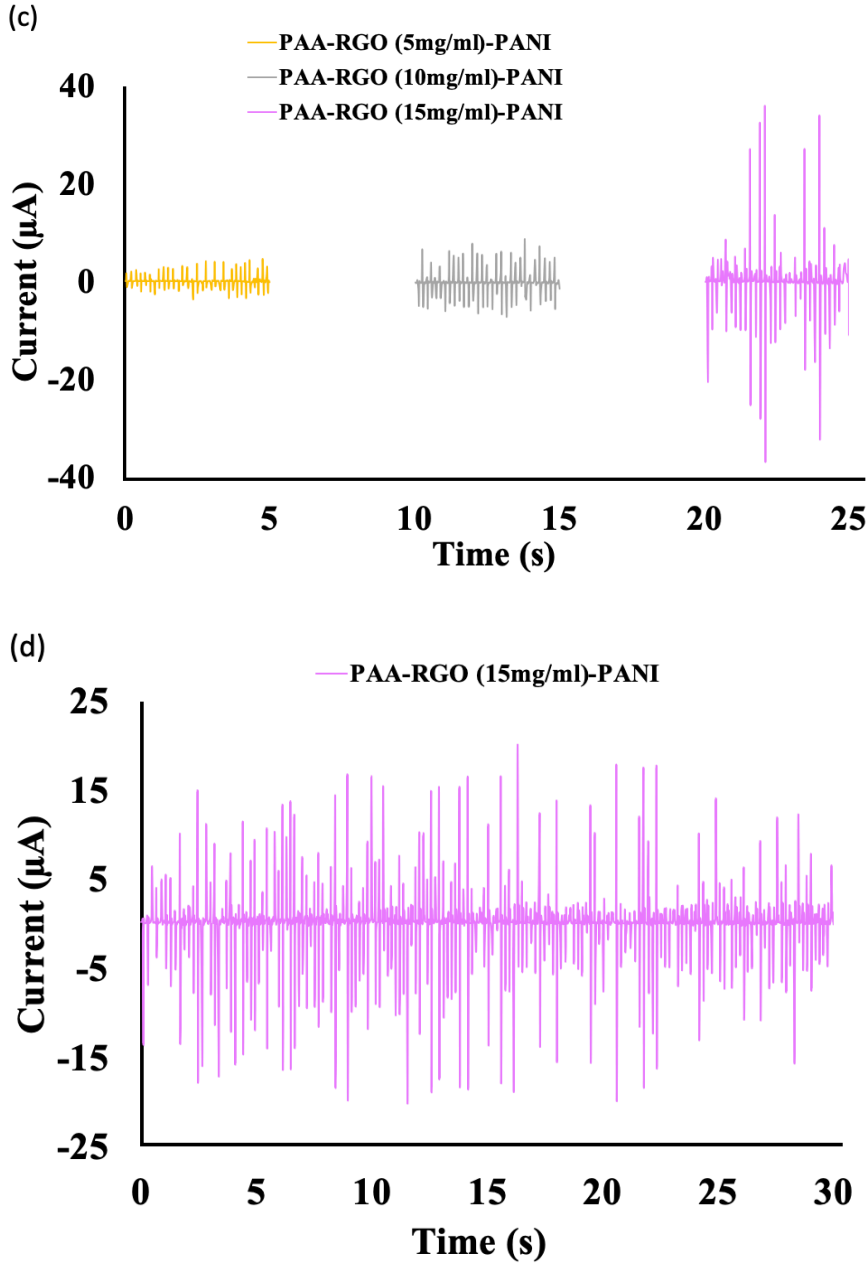
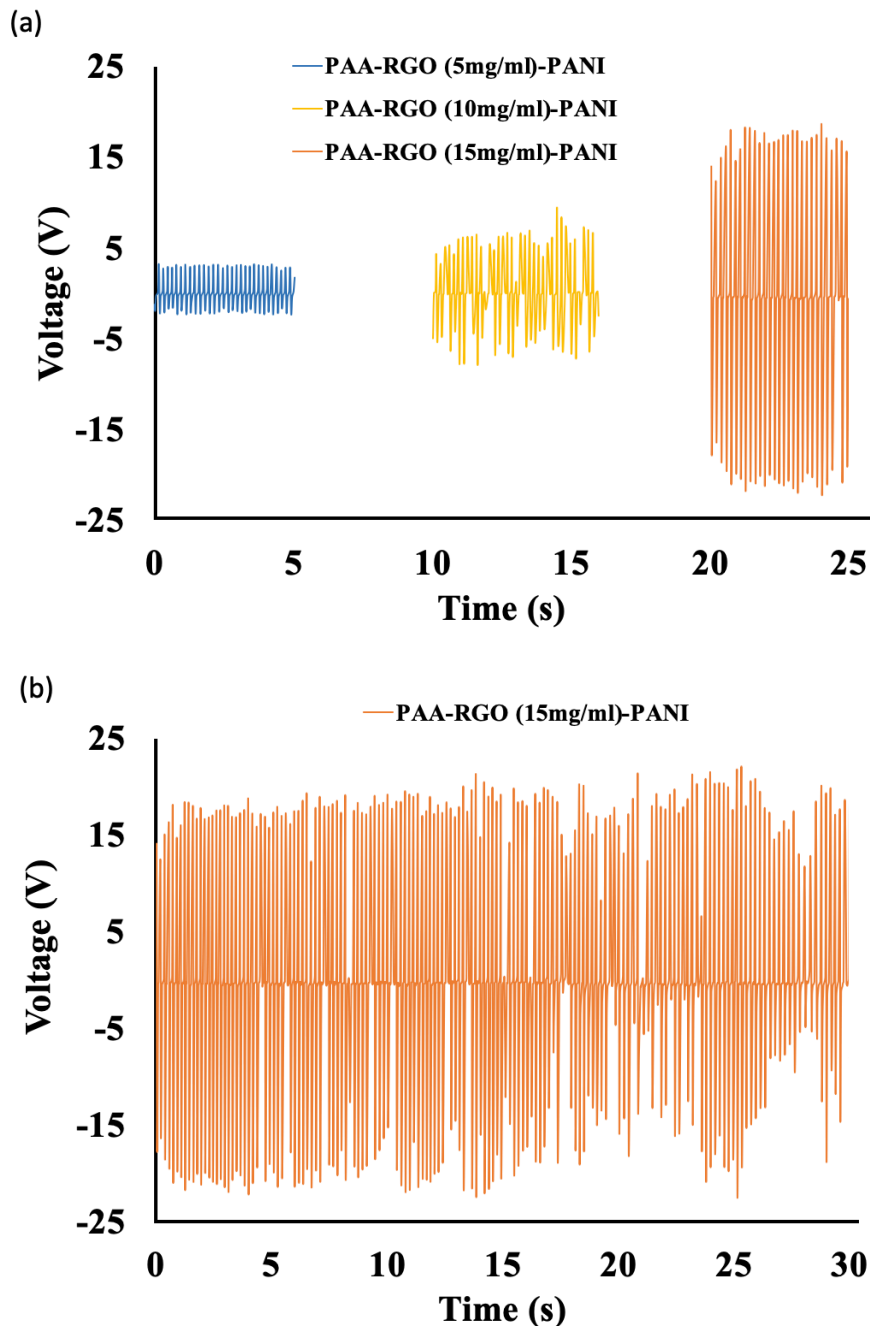


Figure 5.6 Acoustic energy (85 dB at 1k Hz) capture by PRP-TENG. (a) Output voltages generated by PRP-TENG containing different concentrations of RGO; (b) A continuous output voltage generated by PAA-RGO (15mg/ml)-PANI; (c) Output current generated by PRP-TENG containing different concentrations of RGO; (d) A continuous output current generated by PAA-RGO (15mg/ml)-PANI.

5.4.3 Mechanical energy harvest by PRP-TENG

To evaluate the mechanical energy harvesting performance of the PRP-TENG from rainfall, a 500 g weigh was put on the PRP-TENG and moved across on top to simulate special weather conditions like heavy rainfall (Figure 5.7). The V_{oc} and I_{sc} of the PRP-TENGs are demonstrated in Figure 5.7a-d. It can be seen that the V_{oc} and I_{sc} increased with the increase in the amount of

RGO nanofiller in the triboelectric composites, which can be attributed to the increased triboelectric active sites in the PRP-TENG. The highest peaks of V_{oc} and I_{sc} of the PRP-TENG that contains 15 mg/mL RGO reached 21.77 V and 48.68 μ A, respectively. While, the PRP-TENG that contains 5 mg/mL RGO produced a maximum V_{oc} of 3.02 V and a I_{sc} of 10.43 μ A; PRP-TENG that contains 10 mg/mL RGO showed a maximum V_{oc} of 8.35V and a I_{sc} of 17.48 μ A. Figure 8b & d shows a stable V_{oc} (21.77 ± 2.25 V) and a I_{sc} (48.69 ± 6.78 μ A) that were harvested by the PRP-TENG contains 15 mg/mL RGO.



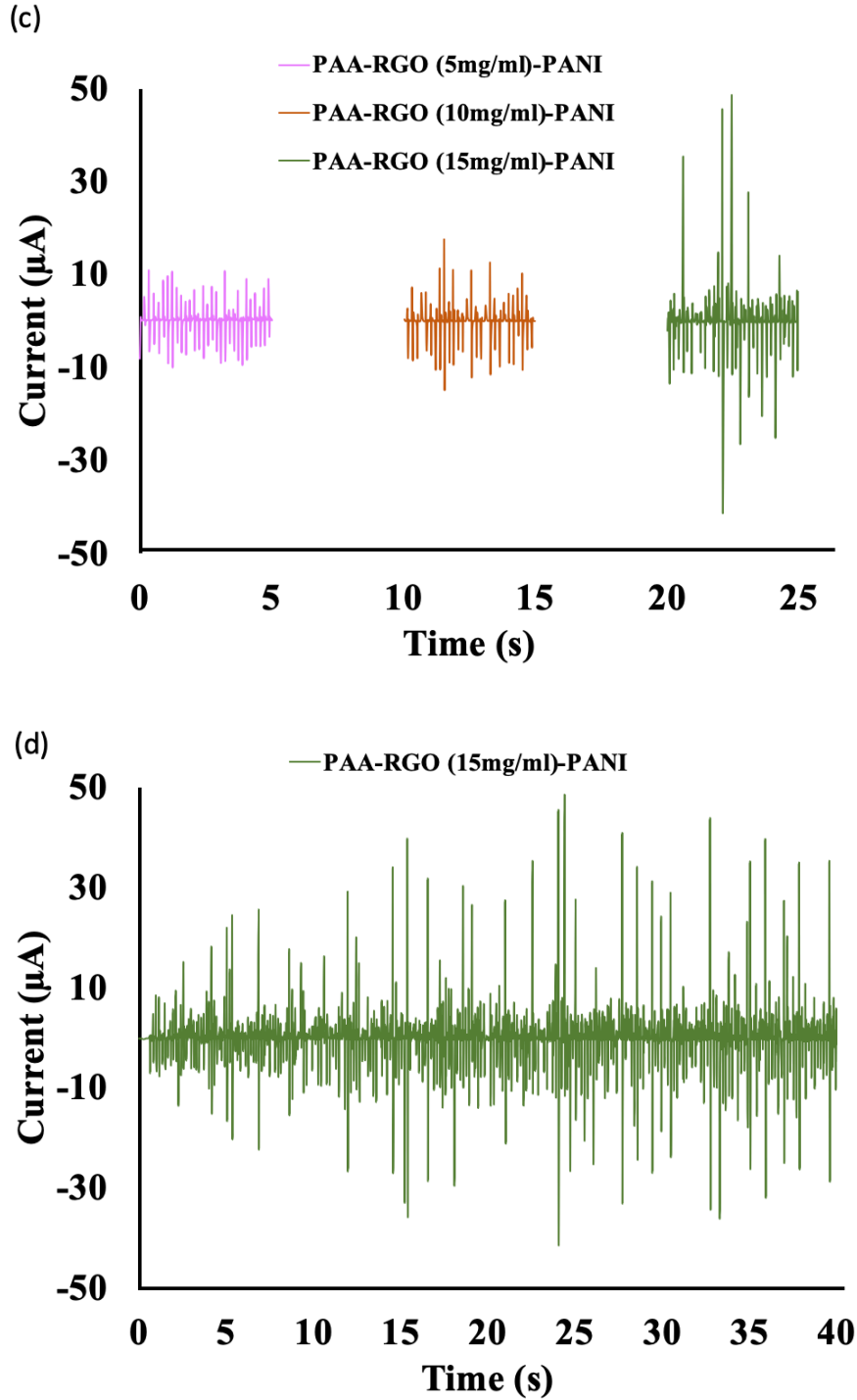
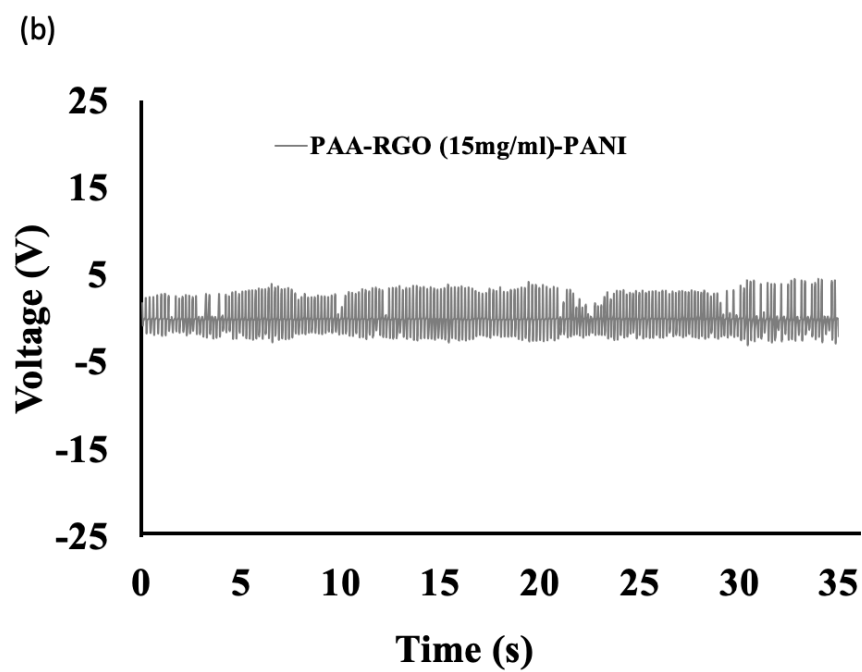
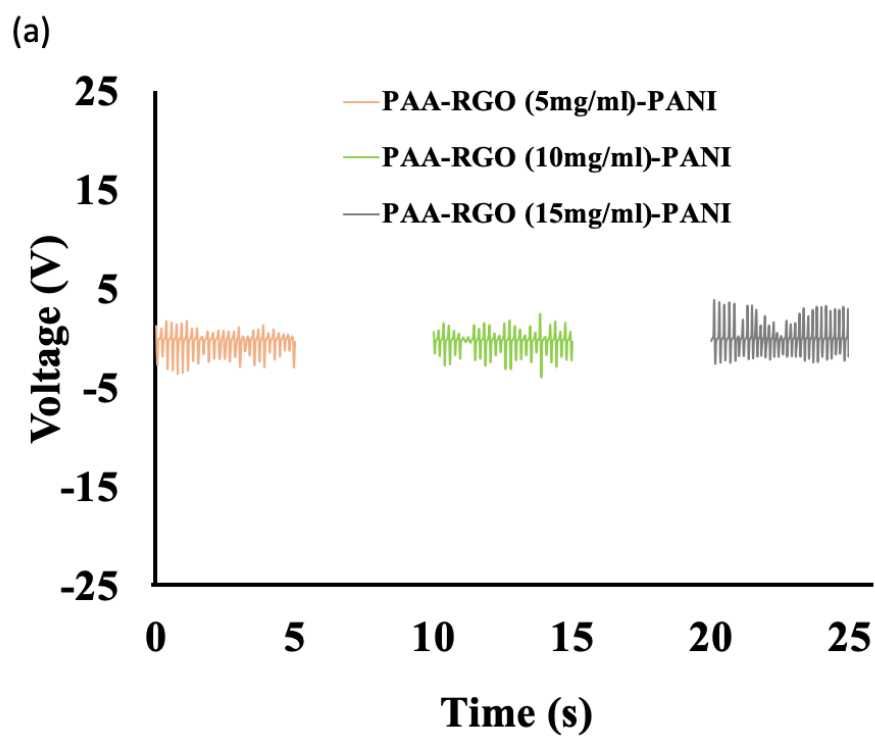


Figure 5.7 Pressing energy (85Kpa) at 4Hz capture by PRP-TENG. (a) Output voltage generated by PRP-TENG containing different concentrations of RGO; (b) A continuous output voltage generated by PAA-RGO (15mg/mL)-PANI; (c) Output current generated by PRP-TENG containing different concentrations of RGO; (d) A continuous output current generated by PAA-RGO (15mg/mL)-PANI.

5.4.4 Wind energy harvest by PRP-TENG

Wind energy harvesting is evaluated on a PRP-TENG that stimulated by a fan speed of 108 cfm. The V_{oc} and I_{sc} are evaluated in Figure 5.8a-d. Figure 5.8a & c show the peaks of V_{oc}

and I_{sc} that are generated by the PRP-TENG contains 15 mg/mL RGO from wind energy reached to 8.63 V and 7.32 μ A respectively. While, the maximum V_{oc} and the maximum I_{sc} were observed in the PRP-TENG that contains 5 mg/mL RGO and 10 mg/mL to be 0.96 V-2.47 V and 2.44 μ A - 2.83 μ A, respectively. Figure 5.8b & d show that the PRP-TENG contains 15 mg/ml RGO could maintain 3.4 ± 0.92 V on output voltage, while the I_{sc} could maintain on 7.96 ± 2.48 μ A in continuously wind stimulations (fan speed at 1600 rpm). The resistance of a PRP-TENG sample was 65.97 k Ω and the corresponding resistivity was 0.97 k Ω ·m.



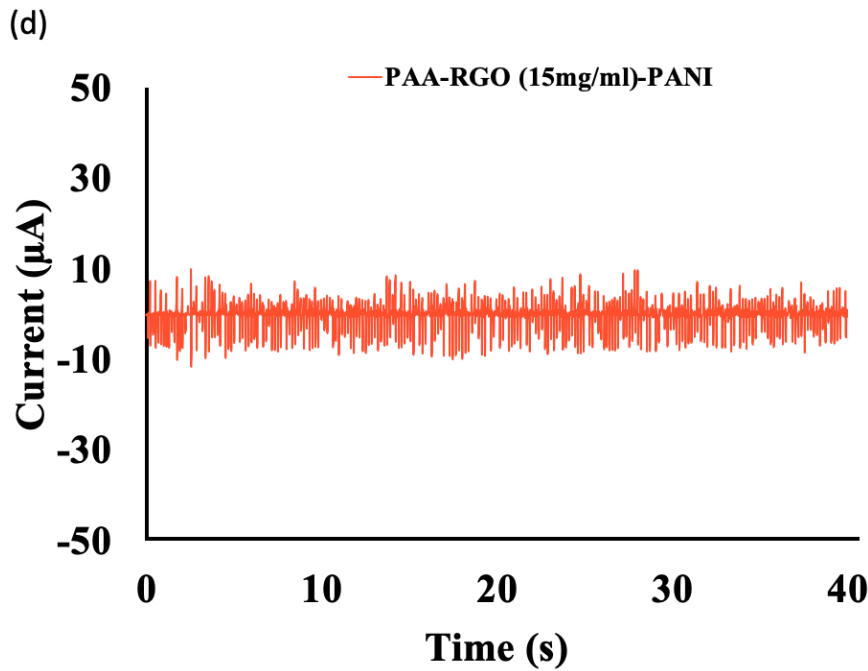
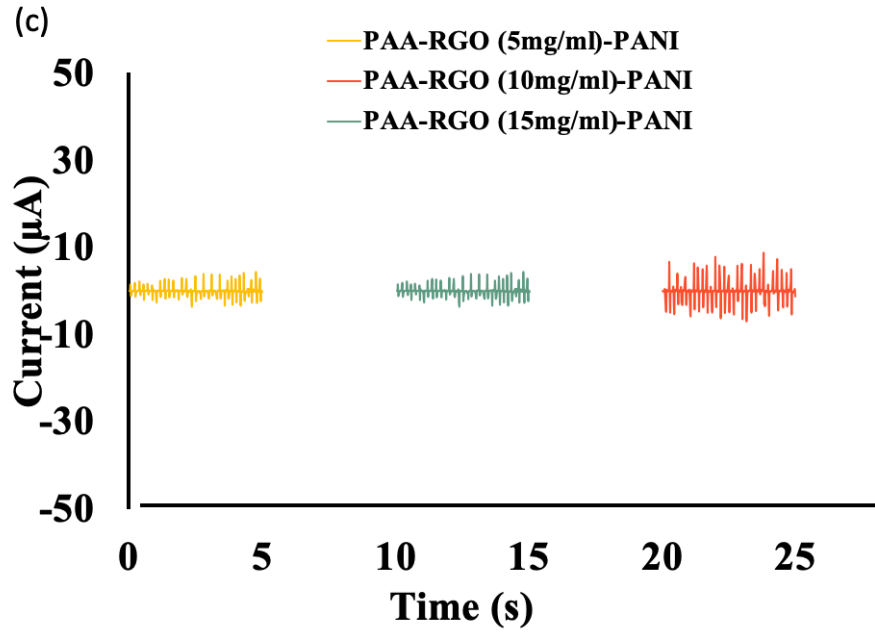


Figure 5.8 Wind energy captured by PRP-TENG. (a) Output voltage generated by PRP-TENG containing different concentrations of RGO; (b) A continuous output voltage generated by PAA-RGO (15mg/mL)-PANI; (c) Output current generated by PRP-TENG containing different concentrations of RGO; (d) A continuous output current generated by PAA-RGO (15mg/mL)-PANI.

To sum up, the PRP-TENG can harvest energy from three clean energy sources: acoustic, mechanical pressing, and wind. There's difference in the magnitude of the generated electricity which may originate from the different contacting areas of the device during the cyclic contact-

release processes. The asymmetry in the positive and the negative peak values in the open-circuit voltage and short-circuit current can be explained by the triboelectrification effect between PRP-TENG and polyimide in the cyclic contacting-releasing processes. The magnitude of triboelectrification effect can be increased by several factors such as increasing the external pressure, frequency of stimulation, contacting surface areas between the two triboelectric materials [78-80].

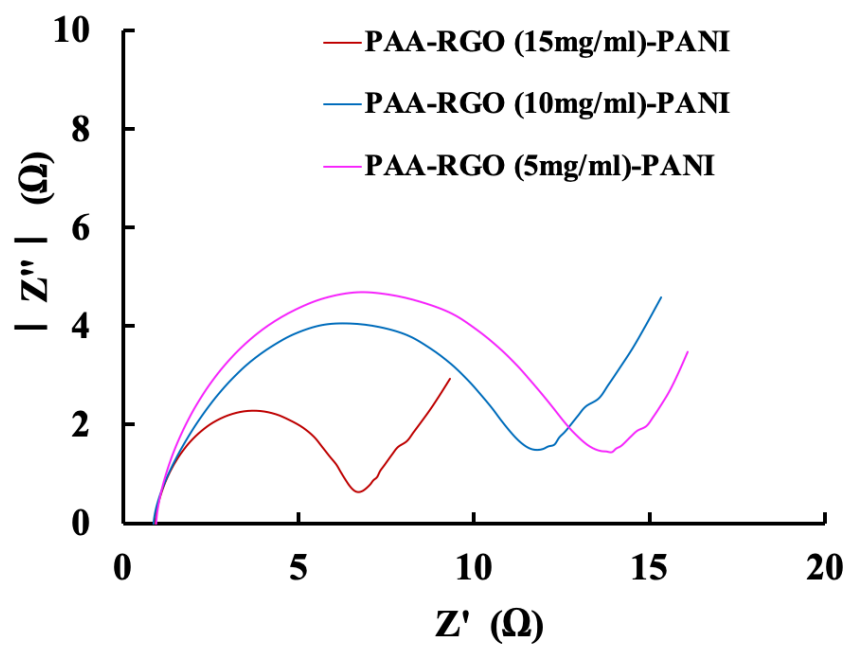
In this study, the highest open-circuit voltage and short-circuit current were found when a 500 g weigh was pressed on the PRP-TENG device. The 500 g weigh imposed higher pressure on the device compared to the pressure imposed by acoustic and wind, suggesting that the higher the pressure applied on the PRP-TENG device, the higher the energy collecting efficiency of this device. In addition, V_{oc} and I_{sc} get significantly increased when the RGO concentration in PRP-TENG increase from 5 mg/mL to 15 mg/mL, the PRP-TENG that contains 15 mg/mL could provide a power up to 424 mW m^{-2} . It is indicated that the energy harvesting performance of PRP-TENG can be improved by enhancing the conductive fillers. Nano energy generators that are made of PVDF, PET or PTFE were developed in previous studies to collect acoustic energy or rainfall energy, however, the maximum power density of these devices ranged from 9.3 mW m^{-2} to 16.31 mW m^{-2} which is much smaller than our PRP-TENG' power density (424 mW m^{-2}) [19, 22, 23]. Moreover, the porous structure of the PRP-TENG increased the contacting area between PRP-TENG and polyimide, which may enable the device to capture low-pressure mechanical energy, thus may increase the efficiency of energy collection.

5.4.5 Electrochemical performance of the PAA-RGO-PANI supercapacitor

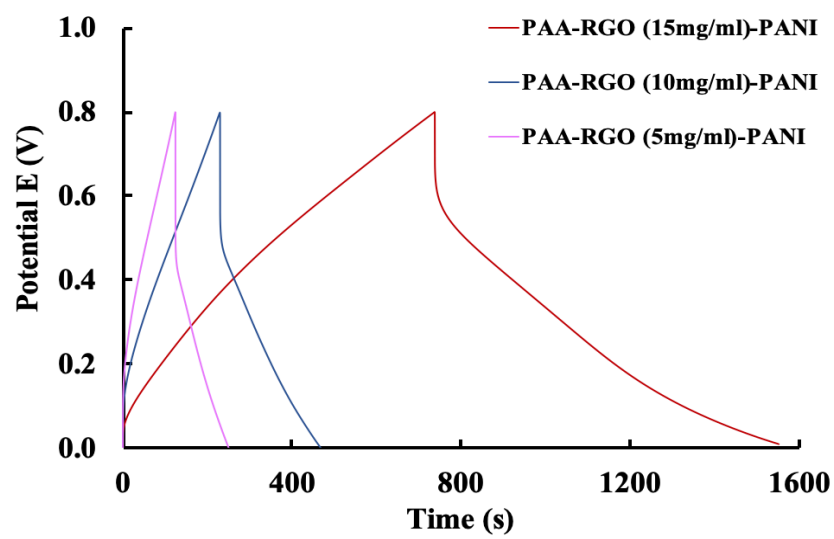
Fiber-based supercapacitors have emerged as energy storage systems for wearable devices recently due to their remarkable stretchability [81-84]. However, energy density of fiber-based supercapacitor is usually unsatisfying. The superior stretchability of our PAA-RGO-PANI has been discussed and yet our PAA-RGO-PANI hydrogel holds greater promise as energy storage system for plant-wearable device. The electrochemical performance of the PAA-RGO-PANI supercapacitor was evaluated and the results shown in Figure 9a-d. The Nyquist plots of the PAA-RGO-PANI supercapacitor obtained from Electrochemical Impedance Spectroscopy (EIS) are shown in Figure 5.9a. The Nyquist showed significant decreases in the charge transfer resistance with the increase in the RGO concentration from 5 mg/mL to 15 mg/mL. The lowest charge transfer resistance (6.3Ω) is found in PAA-RGO (15mg/mL)-PANI, while the highest

charge transfer resistance is found in PAA-RGO (5mg/mL)-PANI at 12.97 Ω . Charge-discharge curves are shown in Figure 5.9b. All samples were tested in charge-discharged cycles by 5 mA. The V_{IR} drop is getting smaller (0.36 - 0.21V) with the increased amount in RGO concentration from 5 mg/mL to 15 mg/mL in PAA-RGO-PANI hydrogel, which may impact on the energy consumptions when switches from charging to discharging status. It means during the charge-discharge cycles, the supercapacitor that assembled with PAA-RGO (15 mg/mL)-PANI could have less energy waste than the one who was assembled with PAA-RGO (5mg/mL)-PANI. Cyclic voltammetry (CV) tests (Figure 5.9c) agreed with the results of the charge-discharge test. The supercapacitor that made by PAA-RGO (15 mg/mL)-PANI showed larger CV area than the supercapacitor that made by PAA-RGO (10 mg/ml)-PANI and PAA-RGO (5mg/mL)-PANI. The cyclic tests were conducted with 5000 charge-discharge cycles with 5mA in each sample. The supercapacitor that contains 15 mg/mL RGO show the highest capacitance at 2500 mF cm⁻², and it is stable at 2330 mF cm⁻² after 5000 cycles. However, the supercapacitor that contains 5 mg/ml RGO and 10 mg/ml showed significant lower capacitance at 1850 mF cm⁻² and 890 mF cm⁻² respectively. Especially, the supercapacitor that made by PAA-RGO (5mg/mL)-PANI showed the lowest capacitance at 280 mF cm⁻² after 5000 charge-discharge cycles.

(a)



(b)



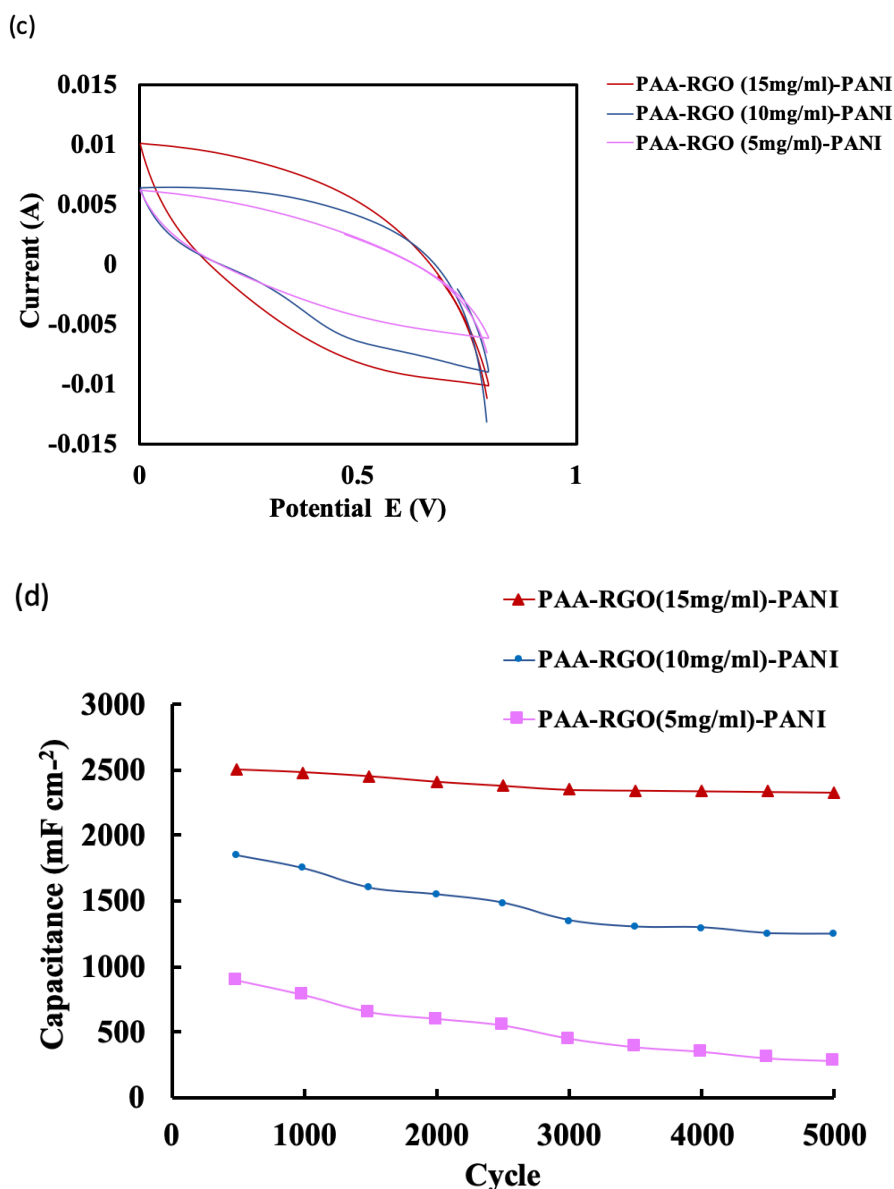


Figure 5.9 Electrochemical performance of the PAA-RGO-PANI supercapacitor. (a) Electrochemical Impedance Spectroscopy (EIS) Nyquist plots; (b) Charge-discharge tests; (c) Cyclic voltammetry tests; (d) Capacitance over 5000 charging-discharging cycles.

In sum, the supercapacitor was made by PAA-RGO (15mg/mL)-PANI showed the best electrochemical performance when compared to other hydrogel samples. In order to make clear comparisons among all the conductive hydrogel samples, the PAA sample and other conductive hydrogels PAA-RGO (5mg/mL – 15 mg/mL) without coating PANI have been evaluated as well, and the data has been summarized in Table 5.4. In conclusion of the evaluation results on mechanical tests and electrical performance, the conductive hydrogel sample PAA-RGO (15mg/mL)-PANI showed the outstanding results in all tests. Therefore, we chose this hydrogel

sample (PAA-RGO (15mg/mL)-PANI to develop wireless wearable sensors and ammonia gas sensors to monitor plants growth rate, and the evaluations will be discussed in next sections.

Table 5.4 Summary of comparison on electrical performance of hydrogel samples

Sample compositions	V_{oc} (V)	I_{sc} (μ A)	Power ($mW\ m^{-2}$)	EIS (Ω)	V_{IR} (V)	Capacitance ($mF\ cm^{-2}$)
PAA	0.075	0.003	N/A	2.5K Ω	0.8	N/A
PAA-RGO(5mg/ml)	0.67	0.45	0.12	805	0.73	89
PAA-RGO(10mg/ml)	1.32	0.76	0.4	468	0.68	146
PAA-RGO(15mg/ml)	2.63	5.89	6.20	205	0.54	321
PAA-RGO(5mg/ml)-PANI	3.02	12.43	15.02	12.97	0.36	890
PAA-RGO(10mg/ml)-PANI	8.35	17.48	58.38	10.96	0.32	1850
PAA-RGO(15mg/ml)-PANI	21.77	48.68	424.0	6.30	0.21	2500

5.4.6 The performance of plant growth sensor

In this study, two types of wireless sensors were developed from PAA-RGO (15 mg/mL)-PANI: an ultra-thin wearable sensor for aloe leaves and an elastic band sensor for pepper plants (Figure 5.10). The growth rate of aloe leaves and pepper fruits showed in Figure 5.11a & 5.13a respectively. The resistance records of the plant wearable sensors showed in Figure 5.11c & 5.13c respectively. To demonstrate the long-term use of the sensors, they were tested for 18 day to monitor plants' growth. PDMS was used to seal the hydrogel to minimize the confounding resistance changes due to moisture evaporation.

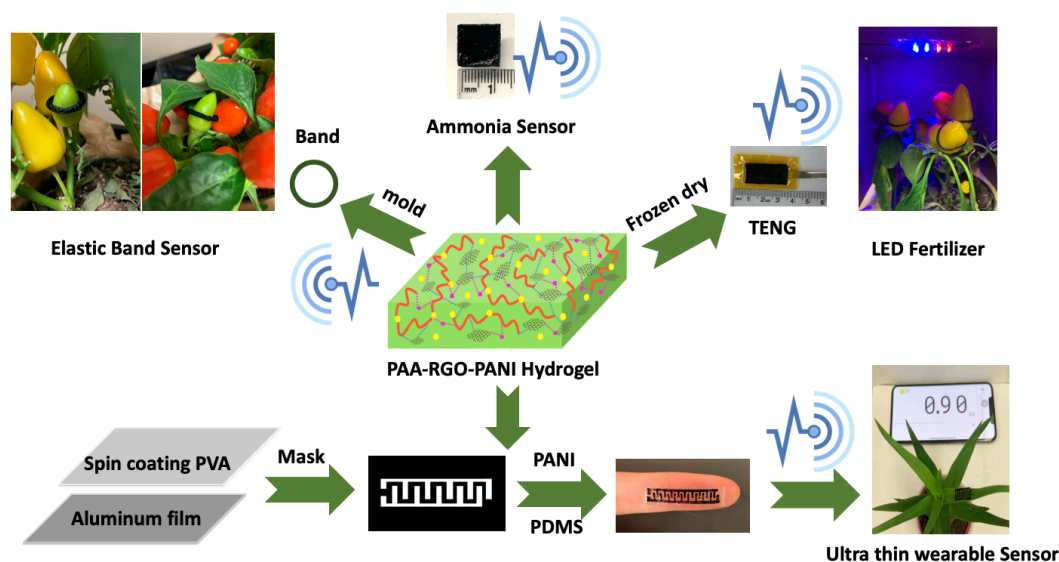


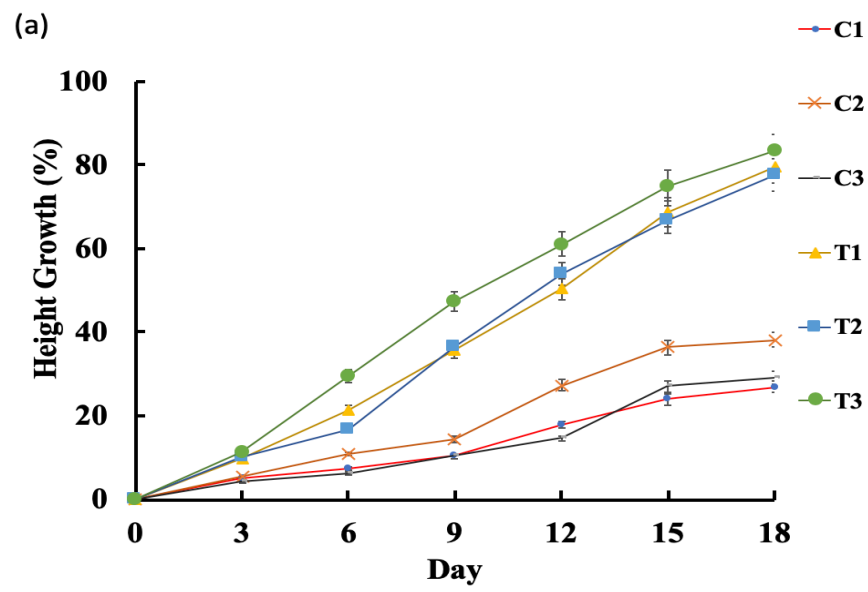
Figure 5.10 The schema diagram of wireless plant-wearable sensor.

To test the effect of the self-powered (PRP-TENG) LED fertilizer in promoting plant growth, the plants (aloe and pepper fruit) were put under LED three hours per day, and total number of 18 days. The untreated plants worked as control groups and were marked as “C”, and LED lights treated groups were marked as “T”. Three aloe leaves were randomly chosen from the

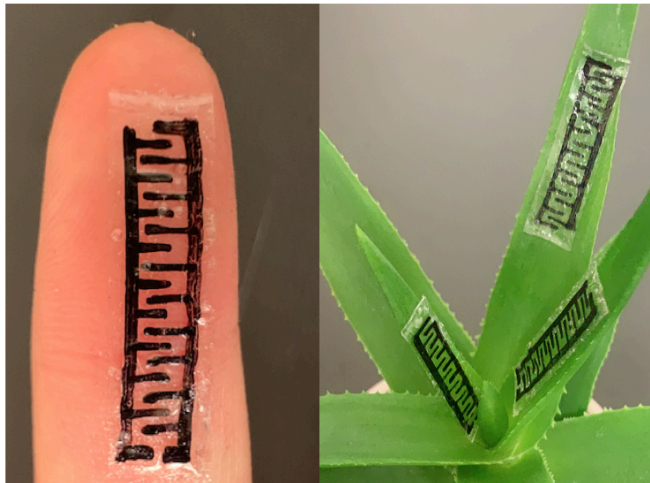
control group (C1, C2, C3) and LED treated group (T1, T2, T3); and the same method were applied to the pepper fruits. Both of control group and LED treated group were watered daily with same amount of water, there's no soil fertilizer applied to them during the 18 days growth monitoring.

The percentages of growth in aloe leaves and peppers are shown in Figure 5.11a and Figure 5.13a. It can be seen that the aloe leaves and pepper fruits exposed to LED lights showed significant higher growth rate than the control groups. All the aloe leaves and pepper fruits in control groups showed a stable growth from day 1 to day 9, while the LED treated groups show sharp growth rate increase after day 3 day. After day 18, the length of aloe leaves in the control group showed an average growth rate of $35 \pm 9.6 \%$. While the LED treated groups had a significant higher leaves growth of $80 \pm 5.8 \%$ on average (Figure 5.11a). There's similar result found in pepper fruits growth, which is measured in the widest part of the circumference on the fruit (Figure 5.13a). After 18 days, the pepper fruit's circumference increased about $78 \pm 8.6 \%$ on average in the control group, while the LED treated pepper fruit's circumference increased $160 \pm 24.8\%$ on average.

A linear relationship between the resistance changes of the plant growth sensors and the strain is shown in Figure 5.12a and Figure 5.14a. The gauge factor of the wireless ultra-thin wearable sensor for aloe plants is 4.50 in an elongation up to 200%. On the other hand, the gauge factor of the elastic band sensor for pepper fruits is 4.58 with an increasing the elongation from 0 to 200 %. This working range is totally fit for both aloe leaves and pepper fruits in this 18-day experiment. The growth rate of both type of plants (Figure 5.11a & 5.13a) are in this sensing working range (0-200%). The resistance changes in bar charts of the ultra-thin sensor in response to aloe leaves' growth and the elastic band sensor in response to pepper fruits' growth during the 18-day monitoring are shown in Figure 5.12c-d and Figure 5.14c-d. Our results in the current study demonstrated superior performance compared to existing reports. The plant sensors that are based on PDMS and latex substrates showed a linear relationship (gauge factor: 3.9) between resistance and strain when the strain is less than 25% [31, 36], suggesting that the working range of this strain sensor should below 25%. In this study, our plant sensors had not only a larger linear detection scale (up to 200 %) but also a higher sensitivity which is indicated by the larger gauge factors.



(b)



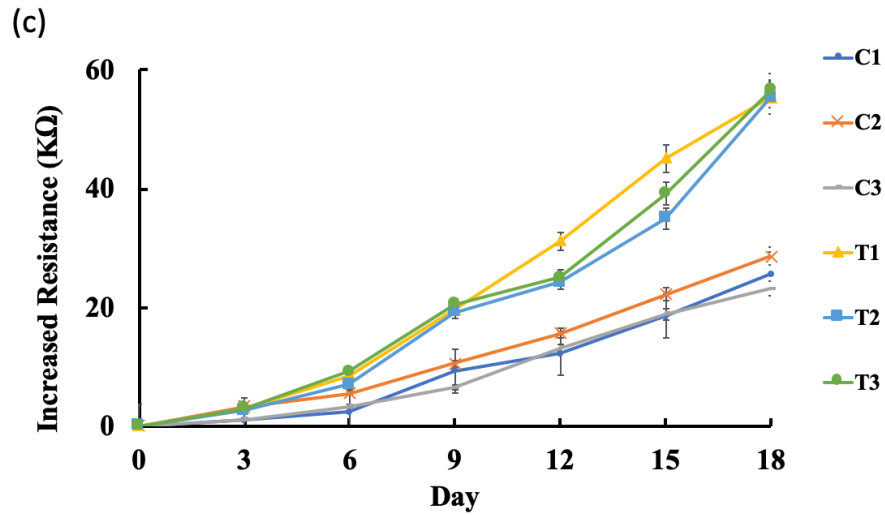
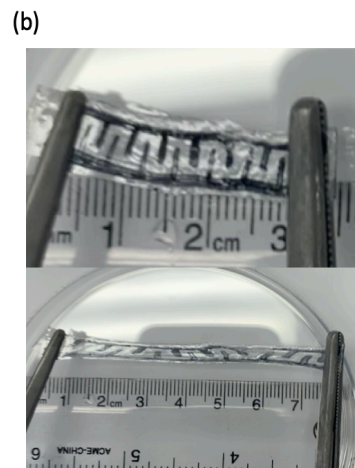
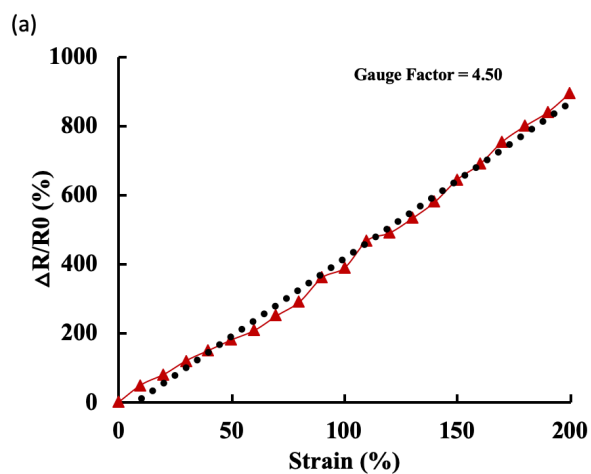


Figure 5.11 The ultra-thin plant growth sensor. (a) The aloe leaves growth rate in 18 days; (b) Photo images of the ultra-thin wearable sensor; (c) The resistance of ultra-thin plant wearable sensor during aloe leaves growth in 18 days; (d) Photos of ultra-thin wireless sensor on aloe leaves (control group) and aloe plant with LED light treatment group.



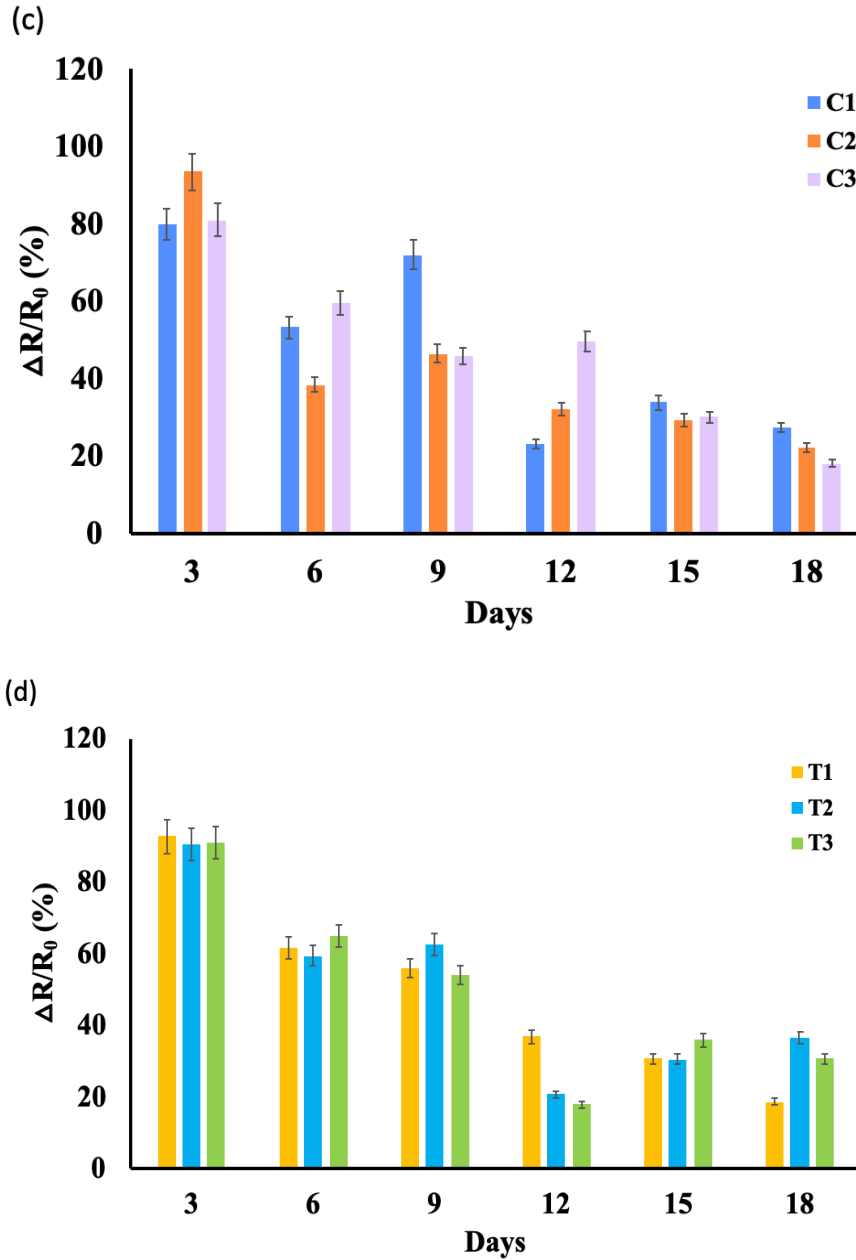
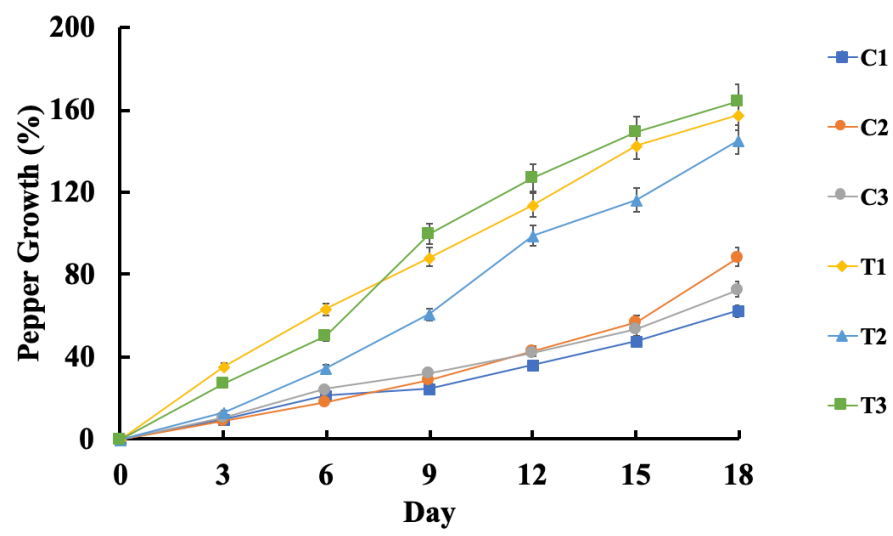


Figure 5.12 The performance of ultra-thin plant growth sensor for leaves. (a) The resistance changes vs. strain for the ultra-thin wearable sensor; (b) Photo images of ultra-thin wearable sensor during stretching; (c-d) The percentage of resistance changes of aloe leaves growth in 18 days.

(a)



(b)



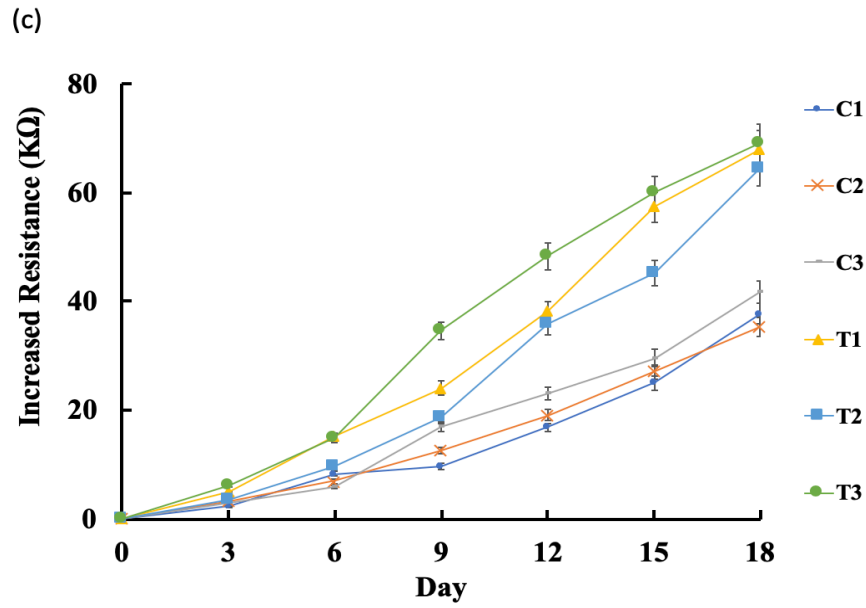
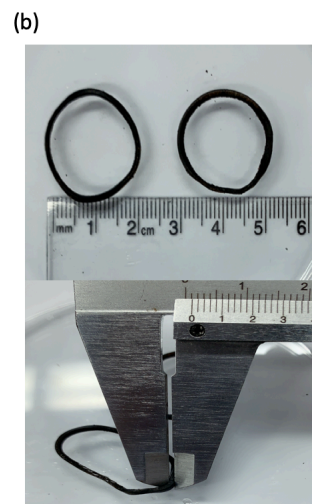
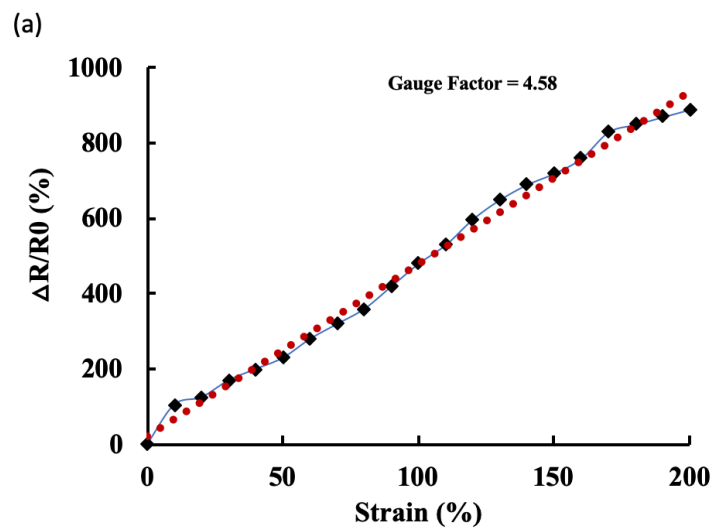


Figure 5.13 The elastic band growth sensor for pepper plants. (a) The percentage of pepper growth; (b) Pictures of elastic band growth sensor on control group; (c) The resistance of elastic band pepper plant growth sensors; (d) Photo images of elastic pepper fruits growth sensors on LED light treatment group.



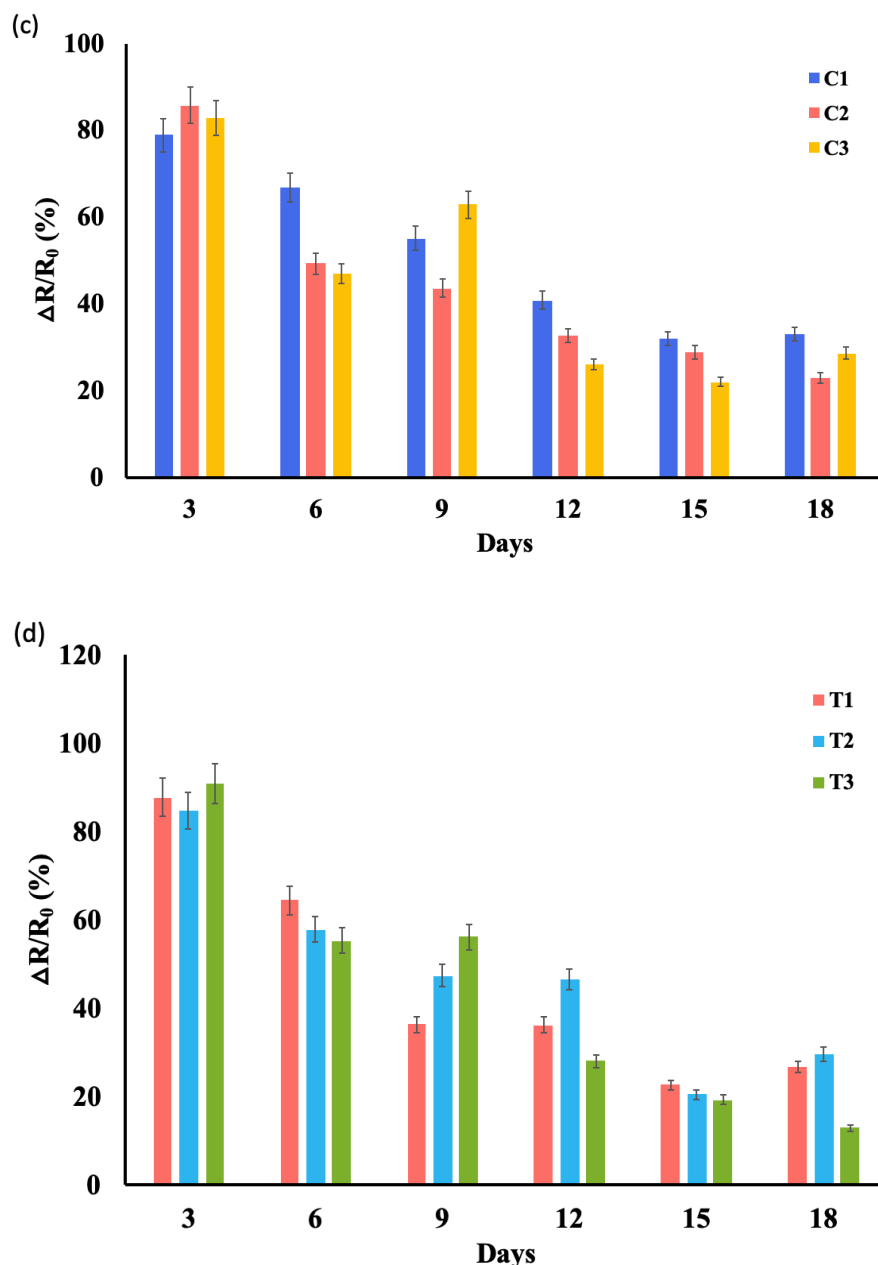


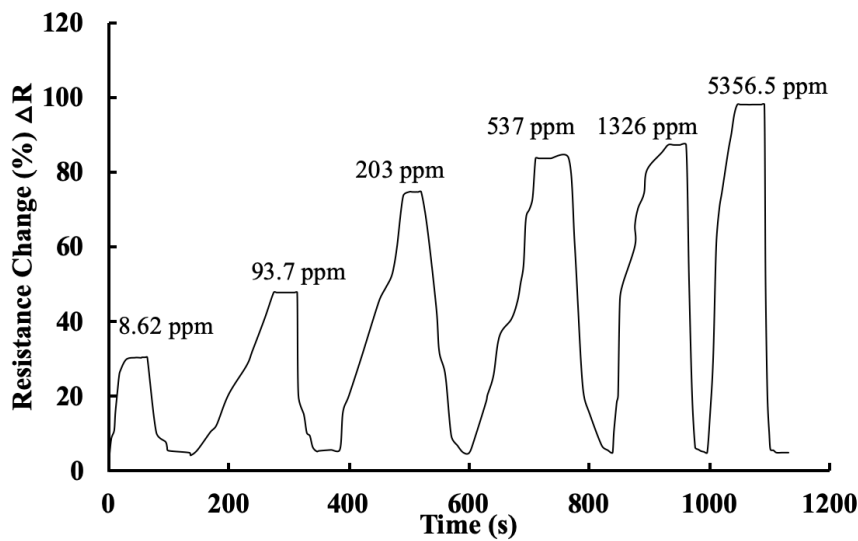
Figure 5.14 The performance of elastic band sensors. (a) The resistance changes vs. strain for the elastic band sensor; (b) The pictures of elastic band sensor; (c-d) The percentage of resistance changes with peppers growths.

5.4.7 Performance of the ammonia sensor

Ammonia solutions of different concentrations were used to evaluate the sensitivity of PAA-RGO (15mg/mL)-PANI hydrogel in a sealed container (Figure 5.15). It has been shown that the multiple usages of the same sample PAA-RGO (15mg/mL)-PANI. The conductive hydrogel sample PAA-RGO (15mg/mL)-PANI worked as ammonia sensor and detected different concentrations of ammonia gas ranging from 8.62 ppm to 5356.5 ppm (Figure 5.15a). The more concentrated the ammonia gas was, the more the resistance changed, and the less the time was

taken to reach the equilibrium resistance. It took 60 seconds to reach equilibrium upon exposure to 8.62 ppm ammonia gas. Figure 16 shows the results of PAA-RGO-PANI hydrogel ammonia sensors containing different amounts of RGO (5 mg/mL, 10 mg/mL, 15 mg/mL) detecting ammonia gas of various concentrations. It is shown that the better the conductivity of the PAA-RGO-PANI hydrogel, the higher the sensitivity, and the less the time needed to reach stable readings.

(a)

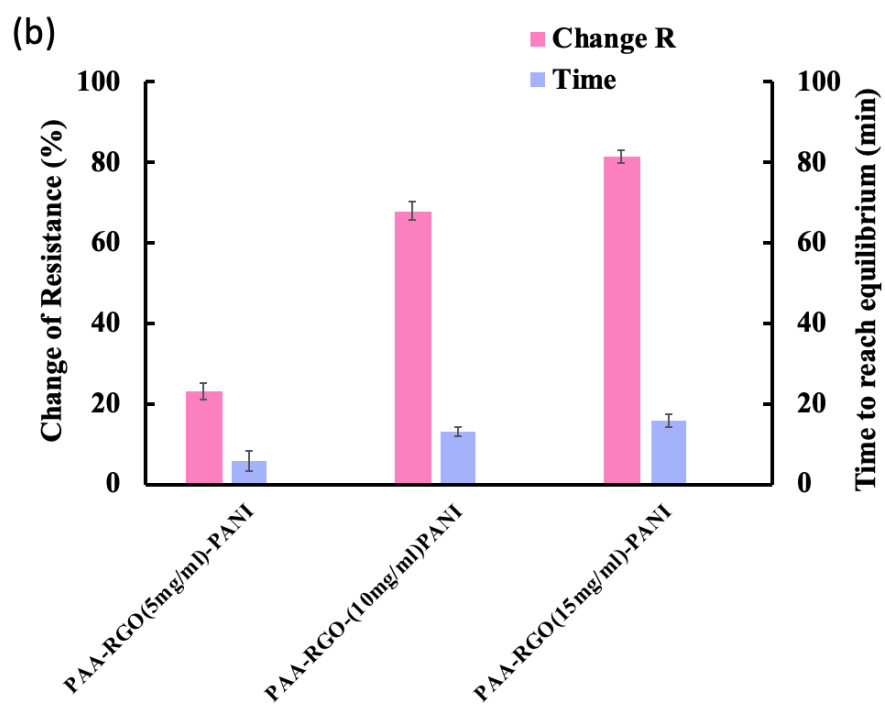
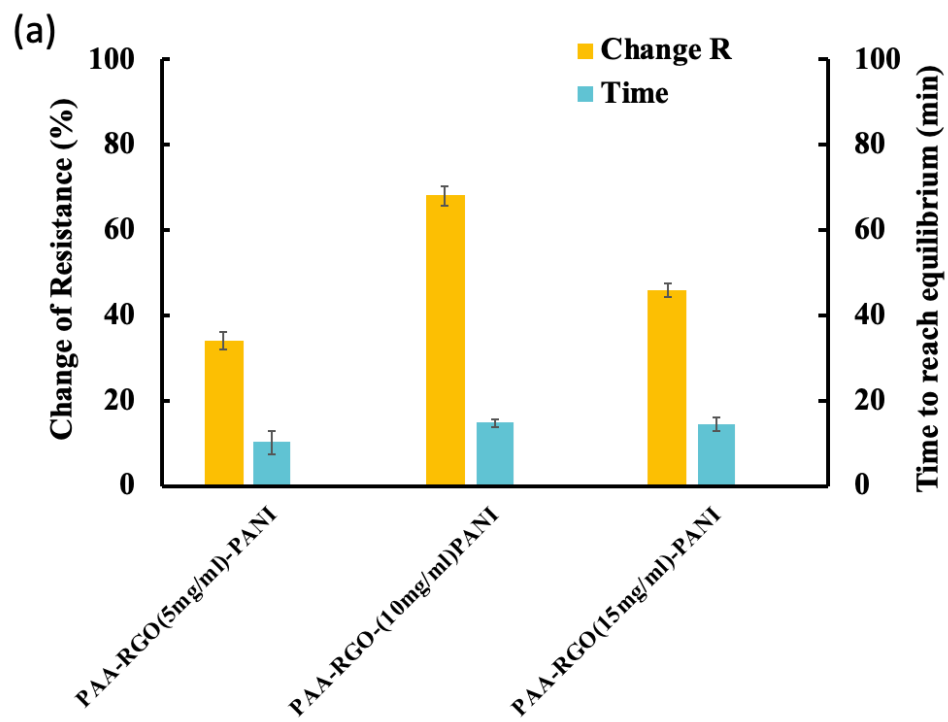


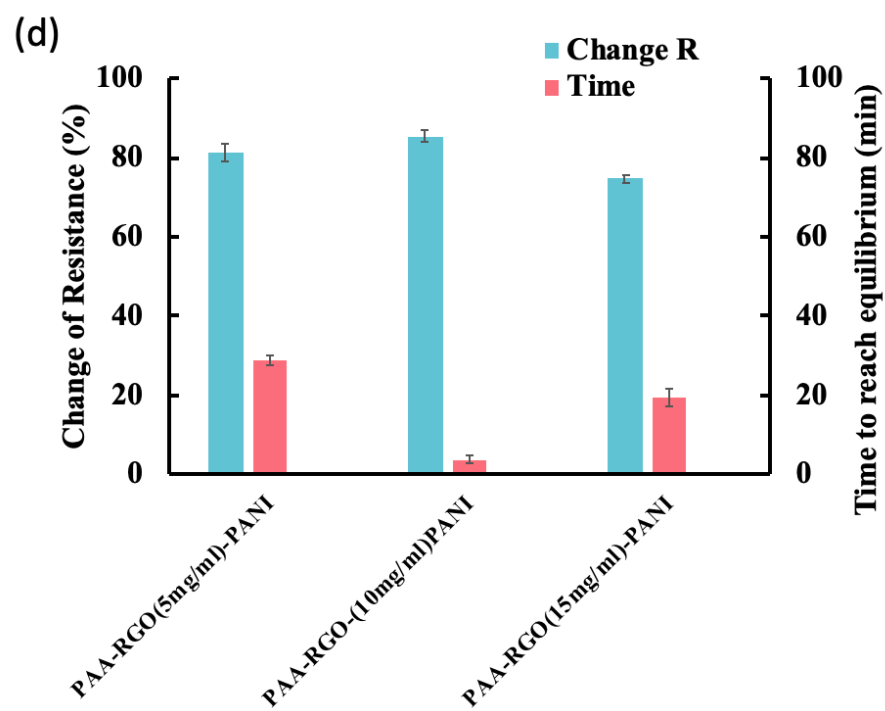
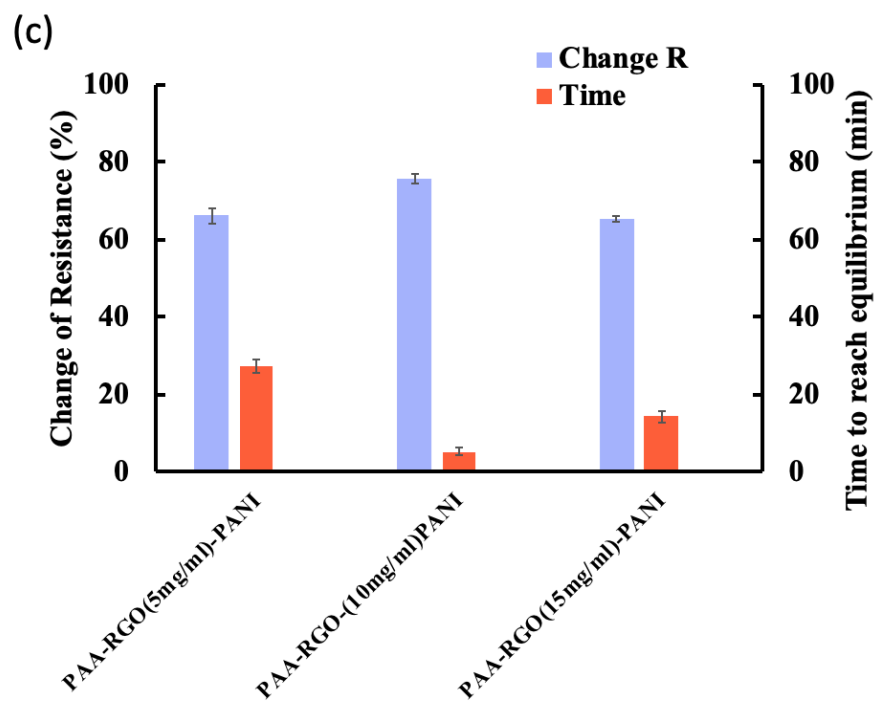
(b)



Figure 5.15 PAA-RGO-PANI hydrogel as the ammonia sensor. (a) PAA-RGO (15mg/ml)-PANI detects the ammonia gas in different concentrations; (b) The photos of the ammonia detector wireless device.

The PAA-RGO-PANI shows high sensitivity to ammonia gas because the absorbed NH_3 molecules take protons away from PANI backbone to form NH_4 , in addition to (electron donor) having *n*-doping effect on the *p*-type PANI backbone [56, 57]. Specifically, upon exposure to the ammonia gas, the PAA-RGO-PANI hydrogel adsorbed ammonia gas to form protonated ammonium cations on PANI (emeraldine salt) via acid–base interactions, which remove polarons and consequently to form the insulator emeraldine base. As a result, the resistance of PAA-RGO-PANI hydrogel increased until an equilibrium is reached [56, 57]. In addition, carbon materials like RGO which is rich in $\text{C}=\text{C}$ sp^2 carbon atoms that is a *p*-type behavior acting as a hole-transporting matrix. When ammonia molecules tached RGO, they donate long pair electrons to RGO results in filling up the holes and decrease the electron transfer mobility. Thus, the resistance is increased. Both of PANI and RGO provide synergisms for achieving superior ammonia sensing performance. A previous study reported an ammonia sensor made of nitrogen-doped RGO and PANI nanocomposite which can detect 100 ppm ammonia gas within 10 mins, while the ammonia sensor that made without RGO did not show significant sensing response. Moreover, as the amount of RGO presented in the sensor, the higher sensing response ($> 500\%$) they got [57]. Another study developed a hydrogel sensor for detecting ammonia gas at a lower concentration of 5-40 ppm in 300 seconds [34]. The PAA-RGO-PANI sensor developed in this study is comparable to those previous studies. It can detect ammonia gas with a wide range of concentrations, from 8.68 ppm to more than 5000 ppm. With the increase of RGO concentration from 5mg/mL to 15mg/mL, the sensitivity increased. The sensor that has the RGO concentration of 15 mg/mL can detect ammonia gas at a lower concentration of 8.62 ppm in 60 seconds.





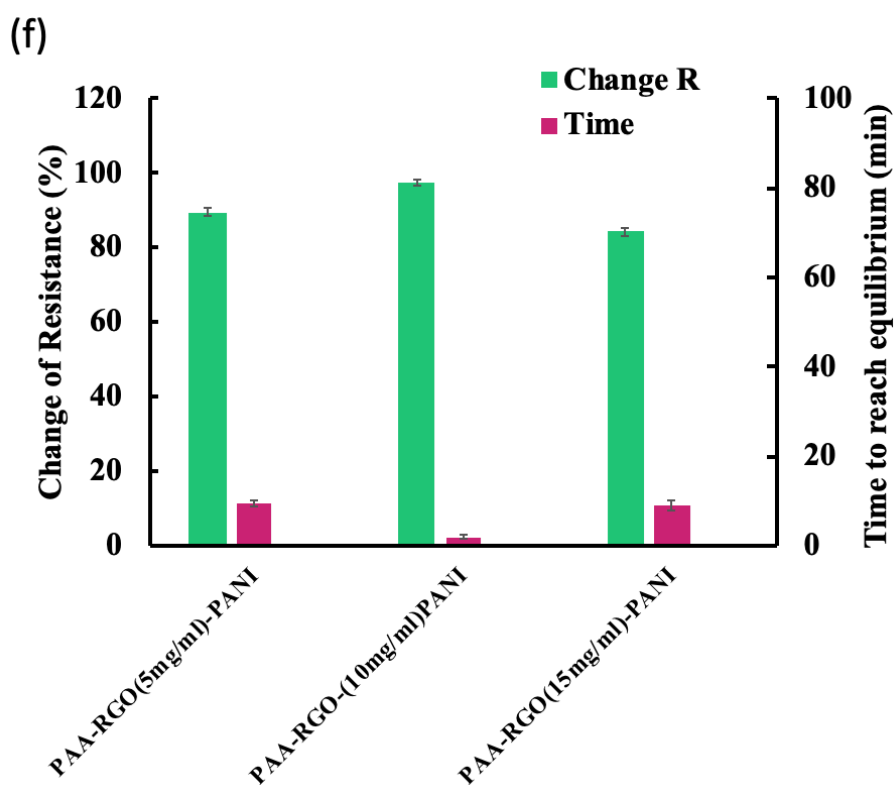
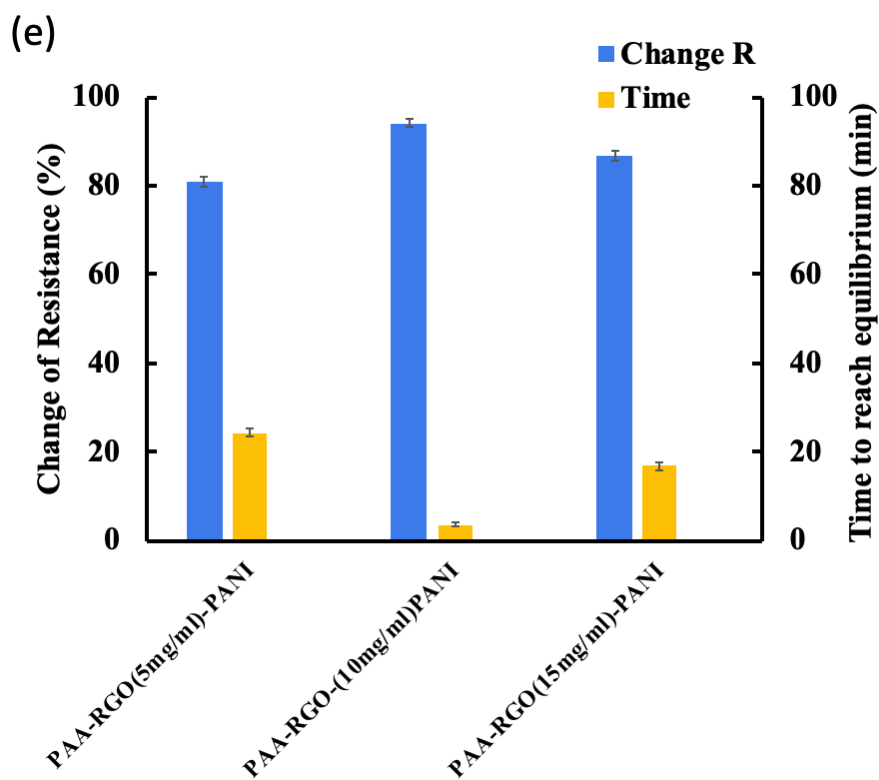


Figure 5.16 PAA-RGO-PANI hydrogel sensors containing different amounts of RGO (5mg/ml, 10mg/ml, 15mg/ml) in detecting ammonia gas at (a) 8.62 ppm (0.15%); (b) 93.7 ppm (1.5%); (c) 203 ppm (3%); (d) 537 ppm (7.5%); (e) 1325.7 ppm (15%); and (f) 5356.5 ppm (30%).

5.5 Conclusion

A versatile double-networking PAA-RGO-PANI hydrogel was successfully developed for multiple applications in agriculture and smart farming systems: A PRP-TENG that harvested clean energy such as acoustic energy, rainfall, and wind energy and convert them to electrical power with a power density of 424 mW/m^2 an open-circuit voltage up to 21.77 V , and a current up to $48.69 \text{ }\mu\text{A}$; A PAA-RGO-PANI supercapacitor that served as an energy storage device offering power to support LED lights continuously for promoting plant growth. The capacitance of the PAA-RGO-PANI supercapacitor can be maintained at 2330 mF cm^{-2} after 5000 cycles. The excellent mechanical performance (1050 KPa in stress and 650% in strain) and facile fabrication process of the PAA-RGO-PANI hydrogel allows its application in customized shaped sensors for plant growth monitoring or ammonia detection. The sensors maintained excellent sensitivity to plant growth up to 18 days, suggesting its great potential for long-termly uses. This conductive hydrogel exhibits low charge transfer resistance at $6.30 \text{ }\Omega$ and can detect ammonia gas at a low concentration of 8.62 ppm within 60 seconds. This multifunctional hydrogel shows excellent performances and great potential in the development of agriculture and smart farming.

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CHAPTER VI

Conclusion and Future Perspective

6.1 Summary of The Thesis

The arrival of the era of Internet of Things (IOT) calls for the research and development of multifunctional flexible conductive materials for the fabrications of smart devices like flexible energy storage device (supercapacitors) and biosensors. This thesis work is composed of three related projects under such a theme:

In the first project, a flexible and lightweight supercapacitor was developed from a nanocellulose substrate loaded with a high mass loading ratio of conductive agents (PANI and RGO). The loading ratio of the conductive agents were optimized to balance between mechanical and electrochemical performance of the developed supercapacitor.

To explore the advanced functions for flexible conductive materials, specifically, to endow self-healing capacity so as to extend their service life, an all-in-one configured flexible and autonomously self-healable supercapacitor based on gelatin and cellulose nanocrystals was developed in the second project. The self-healing capacity of the hydrogel supercapacitor was achieved by tannic acid treatment, which also makes its feasible to coat conductive agents (PANI and RGO) onto the surface via in situ polymerization.

To enhance the mechanical performance of conductive hydrogel, a multifunctional double networking flexible and stretchable tough conductive hydrogel (PAA-PANI-RGO) was developed in the third project for smart farming systems. This versatile conductive hydrogel can be used to fabricate several components for the smart farming system, including a clean energy harvester, a supercapacitor that served as an energy storage device offering power to support LED lights continuously for promoting plant growth. The excellent mechanical performance the conductive hydrogel allows its application in custom shaped sensors for plant growth monitoring and ammonia detection.

6.2 Comparisons and Reflections

During the three projects, both natural polymers (Nanocellulose, cellulose nanocrystals, modified gelatin) and synthetic polymers (polyacrylic acid) were used as the substrates for developing flexible conductive materials. Generally, natural polymers have abundant resources in nature; they are biodegradable, eco-friendly, and more biocompatible than synthetic polymers. However, synthetic polymers provide more versatility for materials design and development to achieve certain properties (like high mechanical performance) or multiple functions in the development of smart electronics. Also both fibrous membranes and hydrogels

have been used as the two different formats for the substrates. Some specific comparisons and reflections on the three projects are list below:

When nanocellulose was used to develop an ultra-light weight flexible supercapacitor, the fabricated supercapacitor showed high electrochemical performance in the repeatable charge discharge cycles. The excellent working performance was achieved due to the high surface-to-volume ratio of nanocellulose that allows large amount of conductive agents to be incorporated without causing material fracture. Although there are lots of advantages to use nanocellulose as the substrate, among which sustainability is one of the most important, there are also limitations for nanocellulose membranes to be used for developing flexible conductive materials. Nanocellulose based conductive membranes are difficult to twist and stretch. It is also hard to impart self-healing property to a membrane material, although self-healing is a valuable feature for smart electronics to extend their service life: The electrochemical performance may get significantly decreased when physical damages occur on the membrane electrodes.

To improve the design on flexible supercapacitors based on natural polymers, in the second project, a self-healing hydrogel-based supercapacitor was developed from GelMA-CNC treated with tannic acid. This supercapacitor can maintain its electrochemical performance after several cut and healing cycles. Still, this design needs further enhancement on mechanical toughness, since weak mechanical performance will limit the applications of flexible conductive materials.

Since synthetic polymers generally show significant advantage over natural polymers in terms of mechanical performance such as toughness, high stretchability and flexibility, synthetic polymer substrate (PAA) was used for the third project. The flexible conductive hydrogel made from PAA not only showed excellent mechanical properties, but also showed remarkable electrochemical performance. Those versatility of the developed conductive hydrogel also allows the possible development of multiple electronic devices in a smart farming systems, which include an energy storage device (supercapacitor), two types of biosensor (a strain sensor and a gas sensor), and a nano energy generator. This multifunctional hydrogel is promising for smart farming and biomedical applications.

6.3 Future Perspectives

In the future research and development, we believe that the following aspects are worth further efforts:

Firstly, the methods for loading conductive agents onto the substrates need to be further improved to ensure even dispersion of conductive agents in the substrate, which can play an essential role in the electrochemical and mechanical performances of the hydrogels.

Secondly, it is still a challenge to balance between different performances of the conductive hydrogels, for example, the efforts to enhance healing efficiency of conductivity may lead to certain loss of healing efficiency of mechanical properties. This is especially tricky for multifunctional materials that are expected to meet demands from different applications.

Thirdly, most attention has been focused on the sensor performance rather than the packaging, integration, and practical processing of hydrogel sensors. However, water loss from hydrogel sensors may influence the stability of the signals for data analysis. As a result, the long-term stability of flexible sensors is crucial and needs more efforts in research. Stability of flexible sensors in extreme environments such as temperatures below 0 °C or above 100 °C are difficult to maintain.

Finally, 3D printing is an effective technology to fabricate three-dimensional materials with intricate structures that meet custom demands. Development of appropriate hydrogel systems for 3D printing is still challenging yet rewarding.

In briefly, future investigations related to flexible conductive materials may be devoted to explore efficient and facile procedures to fabricate multifunctional materials with both outstanding electrochemical and mechanical performance, and other adds-on features including but not limited to biocompatibility, sustainability, 3D printability. The future of flexible conductive electronic devices may be largely dependent on how effectively we can balance their functionality, stability as well as the costs.