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Polyaniline and Cellulose Acetate Chemomechanical Actuator and its

Selectivity for Acetone

A Thesis Presented

by

Jing Zhang

to

The Graduate School

in Partial Fulfillment of the

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in

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Abstract of the Thesis

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Polyaniline (PANI) belongs to the conducting polymers and has been studied so many years. PANI has three different states depending on different redox process. In this thesis, we used the completely reduced form leucoemeraldine base (LEB) to synthesize the Chemomechanical actuator. Cellulose Acetate (CA) was used to be the matrix because CA can provide good mechanical property for the film synthesizing. PANI and CA molecules interconnected and form the Chemomechanical actuator, which has the selectivity for acetone vapor.

We characterized the Chemomechanical actuator's bending angle and time, and its unique character for acetone selectivity. Scanning electron microscopy was conducted to observe the

actuator's morphology. EDS was also carried out to understand the element component about PANI/CA actuator. FTIR was achieved to characterize the composition. At the end, we expect the application and future work about PANI/CA actuator and lots of work will be done in the future.

Dedication Page

Dedicated to my dear Parents.

Table of contents

Chapter 1 Introduction	1
1.1 Polyaniline (PANI).....	1
1.1.1 Redox Process.....	2
1.1.2 Doping/dedoping mechanism	4
1.2 Cellulose Acetate	5
1.3 Polyaniline Composite Films	7
1.3.1 Polyaniline/Cellulose Acetate Composite Films	7
1.3.2 Polyaniline/Other Polymer Composite Films	10
1.4 Chemomechanical and Electrochemical Actuator.....	12
1.4.1 Chemomechanical Actuator.....	13
1.4.2 Electrochemical actuator.....	17
Chapter 2: Material Synthesis and Characterization	21
2.1 PANI/CA Actuator Synthesis	21
2.1.1 Chemical Used.....	21
2.1.2 PANI/CA Actuator Synthesis processing.....	22
2.2 PANI/CA Actuator Characterization and Testing	25
2.2.1 Scanning Electron Microscopy	25
2.2.2 Energy Dispersive X-Ray Spectroscopy.....	26
2.2.3 Fourier transform infrared spectroscopy.....	26
2.2.4 Bending angle and time in acetone background	26
2.2.5 Selectivity	27
Chapter 3: Result and discussion	28
3.1 Scanning Electron Microscopy	28

3.2 Energy Dispersive X-Ray Spectroscopy	30
3.3 Fourier transform infrared spectroscopy.....	30
3.4 Bending angle and time	31
3.5 Selectivity.....	33
Conclusion	35
Future work	36
Reference	37

List of Figures

Figure 1 Molecular structure of polyaniline with two units.....	2
Figure 2 Reversible redox reaction of polyaniline	3
Figure 3 Polyaniline (LEB) and (EB) Doping and dedoping process	4
Figure 4 Molecular structure of Cellulose Acetate	5
Figure 5 PANI/CA composite molecular structures	8
Figure 6 Polymer chain Sorption and desorption of organic vapor	14
Figure 7 Expansion of polymer hydrogel by guest molecules adsorption	16
Figure 8 Single layer actuator	18
Figure 9 Tri-layers actuator.....	19
Figure 10 Process of synthesizing.....	24
Figure 11 Process of making casting solution.....	24
Figure 12 Strips with dimension 3mm width and 40mm length	25
Figure 13 SEM of PANI/CA film (Mag=1.0kx, WD=8mm, EHT=20kV)	28
Figure 14 SEM of PANI/CA film (Mag=3.0kx, WD=8mm, EHT=20kV)	29
Figure 15 SEM of PANI/CA film (Mag=10.0kx, WD=8mm, EHT=20kV)	29
Figure 16 EDS of the porous PANI/CA film.....	30
Figure 17 PANI/CA thin film FTIR spectra	31
Figure 18 Bending-recovery processes	32
Figure 19 Bending angle with time changing	33
Figure 20 Selectivity under different background vapor	34

List of Tables

Table 1 PANI/CA films produced by chemical polymerization method	9
Table 2 PANI/CA films produced by electrospinning method	10
Table 3 PANI/Other polymer composites films.....	12
Table 4 Chemomechanical actuators	17
Table 5 Electrochemical actuators by different layers	20
Table 6 Chemical Properties used in synthesis	22

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Chapter 1 Introduction

1.1 Polyaniline (PANI)

Polymers have dramatic advantages such as low weight, ease of fabrication and can be combined with other materials to form composites when comparing with metals and inorganic materials. But most of the previous polymers are insulated because of carbons in the polymer chain are combined in covalent bonds; therefor there are no free electrons. Conducting polymers (CP) such as polyaniline (PANI), polythiophene (PTs) and polypyrrole (PPy) is an important branch of polymers and have been considered to reach the metallic field by doping with oxidizing or reducing agents [1]. The processing of doped polyaniline in m-cresol was reported in 1992 for enhancing the conductivity. Since polyaniline (PANI) as one of the electrically conducting polymers won the 2000 Nobel Prize in chemistry, it has attracted enormous attention as a promising material for a wide of applications.

Polyaniline can be synthesized by electrochemical or chemical oxidation of aniline [2]. Polyaniline has the abilities of easy preparation, low cost, excellent chemical stability, and good conductivity [3-4]. As one of the most studied materials, a number of applications of polyaniline have been reported such as semiconducting materials for electric and optical devices [5-6], electrodes of batteries [7], conducting polymer actuators for potential applications in advanced robotics, microactuators and artificial muscles [8]. In advance, polyaniline can be fabricated at nanoscale and be synthesized to polyaniline-based chemical sensors [9].

1.1.1 Redox Process

Polyaniline has base form and salt form depending on different preparation. And for polyaniline base, there exists three kinds of forms depending on three different oxidation states. They are completely oxidized form pernigraniline base (PB), completely reduced form leucoemeraldine base (LEB) and half oxidized form emeraldine base (EB) [4]. The colors of pernigraniline base, leucoemeraldine base and emeraldine base are violet, light grey or blue and dark blue respectively. There is two types of monomer structural unite in the main polymer chain: the benzenoid diamine and the quinoid diimine. Figure 1 shows the chemical structure of the units. To illustrate the chemical structure of each form, we can use the value x on the two units. Different oxidation is depending on the different x values. With the values of $x=0$, it is called pernigraniline which is the completely oxidized form. With the values of $x=1$, it is called leucoemeraldine which is the completely reduced form. Besides, when $x=0.5$, it is called the emeraldine which is half oxidized form.

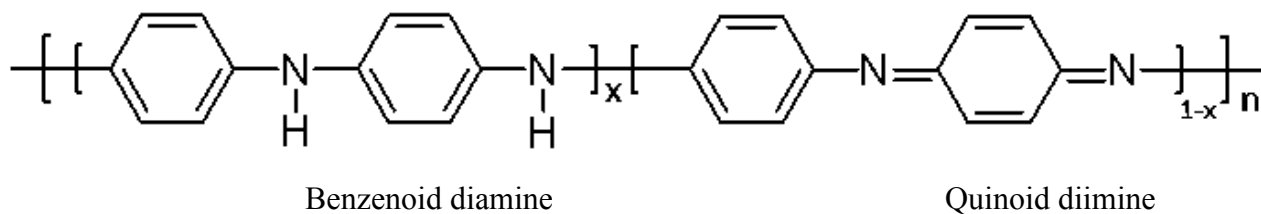


Figure 1 Molecular structure of polyaniline with two units

These three oxidation states can be transferred on the degree of protonation by different reversible reducing or oxidizing mechanism [10]. Figure 2 shows the reversible redox process of three states. From leucoemeraldine base, pernigraniline can be reached by oxidizing emeraldine. During this oxidation process, the unbound electron of amine nitrogen in leucoemeraldine is

removed by the oxidant and a proton is released. An imine is formed by the unbound electron after resonance to the neutral position. Pernigraniline will be eventually formed by oxidizing all amine nitrogen to imine in the polymer chain. On the contrary, reducing pernigraniline to emeraldine and then will form leucoemeraldine.

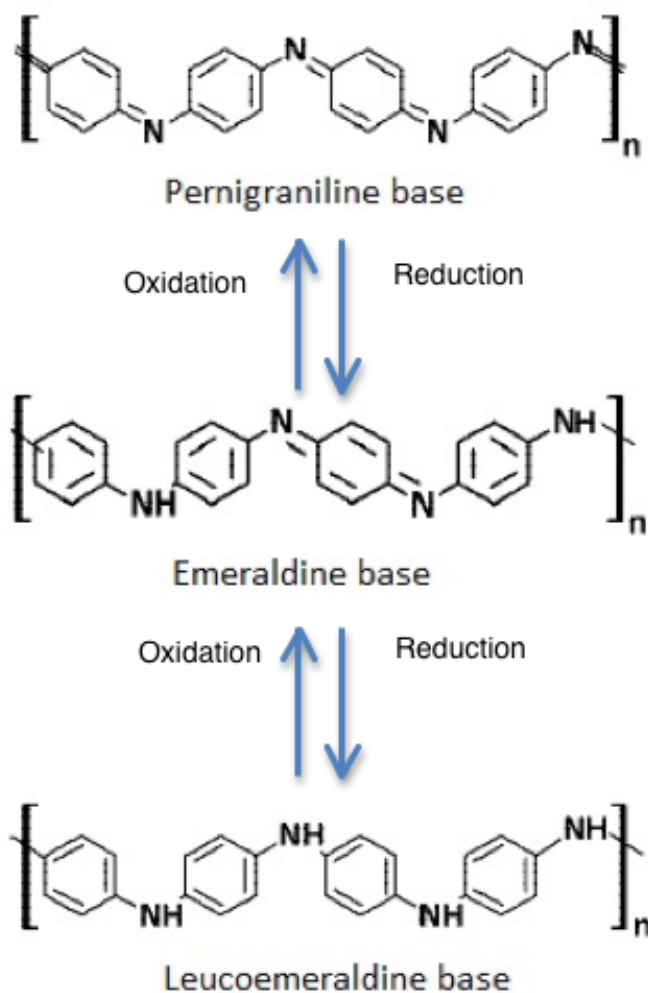


Figure 2 Reversible redox reaction of polyaniline

1.1.2 Doping/dedoping mechanism

Electrical conductivity is highly affected by the structure of the polymer [2] and can be adjusted by changing the oxidation state [11]. Leucoemeraldine base is insulated and we can make it electrically conducting by doping with an acid. By doping with an acid, the inorganic anions incorporate with the $-NH$ groups in the polymer chain [12]. This doping process is also reversible from undoped insulated base to doped conductive salt. Figure 3 gives the leucoemeraldine and emeraldine, doping and dedoping process. Polyaniline has been popular used due to its reversible conductivity.

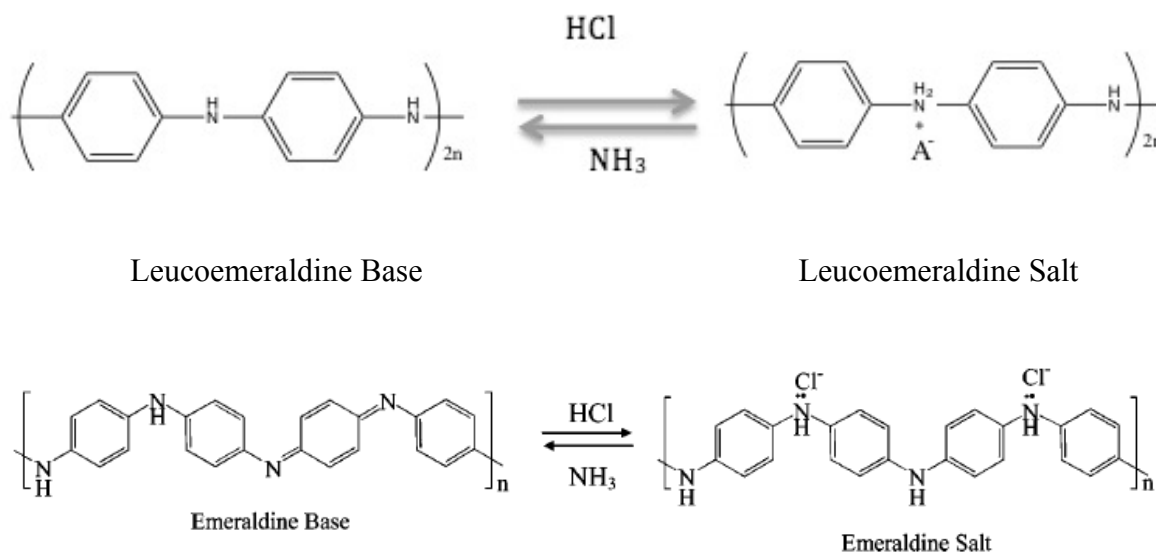


Figure 3 Polyaniline (LEB) and (EB) Doping and dedoping process [9]

Polyaniline has the key characteristic of the conducting polymers, which are the conjugated alternating single and double bonds in a π system along the backbone. Each single and double bonds have a localized strong σ bond and every double bond has a weaker π bond.

But this conjugation is too weak to make charge migrate. So we need the doping process adding charge carriers into the polymer. The charge carrier can be extra electrons and holes that is a position without electrons. As hydrochloric acid (HCl), H^+ is the hole and Cl^- is the anion with electrons. When an electron jumps from an adjacent position, a hole is occupied and another new hole is created. This continuous process allows charge to migrate along the backbone of polymer in a long distance [13]. The protonation form of leucoemeraldine salt will be produced through this conducting mechanism.

1.2 Cellulose Acetate

Cellulose is a type of natural polymer material existing abundantly in the world. Because of its biocompatibility and cheap price, it is a kind of good biological materials being used widely [14]. Cellulose Acetate (CA) is formed by adding acetate ester anion into cellulose polymer chain. CA is colorless, odorless, tasteless, and tough plastic with a density of 1.2-1.4 g cm^{-3} [15]. Figure 4 shows the chemical structure of CA.

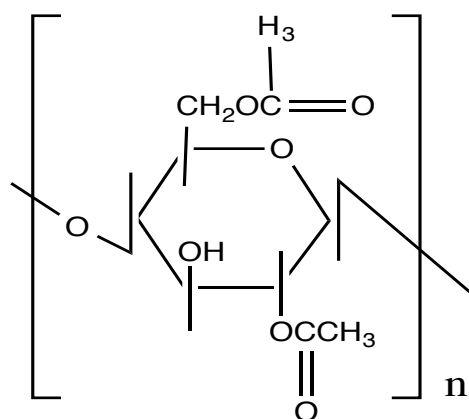


Figure 4 Molecular structure of Cellulose Acetate

High intermolecular forces and the regular structure of the CA lead to a high degree of crystallinity [16-17]. Due to the high crystallinity, CA can combine with other conducting materials, as a kind of matrix, providing holes for charge transport along the composite. For example, as we are considering the conducting polymer, PANI and CA can combine and form composites. In this case, CA is a hole transport layer for polyaniline [18]. Another unique character is that CA is also a kind of hydrophobic polymer when comparing with hydrophilic polymers like PVP. Depending on this property, CA as the matrix can maintain original morphology without bothered by the humidity condition. CA also provides good mechanical strength as the matrix of PANI or other types of materials.

There are various work reported about CA as a matrix, and both metal and organic materials can combine with it for improve mechanical property or for sensor. It is reported [19] that L. Liu etc. found Graphene and CA can interact strongly. CA as the matrix can let the Gr disperse evenly and homogenously in it and formed the composite films with enhanced mechanical property. Joseph. Wang etc. [20] presented the work that Mercury can be coated into CA and synthesized thin film. By applied the film on electrodes, it dramatically enhanced the response when comparing to the traditional Mercury film without CA. Besides, X-L. Ren, D. Chen etc. [21] reported the application of the glucose biosensor fabricated by gold nanorod and CA. In this case, CA is as the matrix for the immobilization matrix of glucose oxidase.

Based on these excellent properties for matrix and widely application of CA, we choose CA to be the material for synthesizing film as actuator.

1.3 Polyaniline Composite Films

1.3.1 Polyaniline/Cellulose Acetate Composite Films

Among the commonly used conducting polymers, PANI has been studied and employed due to its good properties we have mentioned in the former section. PANI hybrids with insulating polymers such as cellulose acetate (CA) show enhanced structural and electronic stability as well as provide good mechanical strength to facilitate the electrons transport through the film [22].

Various methods have also been applied to synthesize PANI composite films like electrochemical and chemical oxidation polymerizations, solution blending etc. [23]. Even though the chemical polymerization method is less stable than the electrochemical polymerization, considering the economic efficiency and operating simplicity, most of the PANI/CA composites are fabricated by chemical polymerization [31]. Figure 5 shows PANI and CA composite formed by chemical oxidation polymerization, and their molecular chain are connected by hydrogen bond.

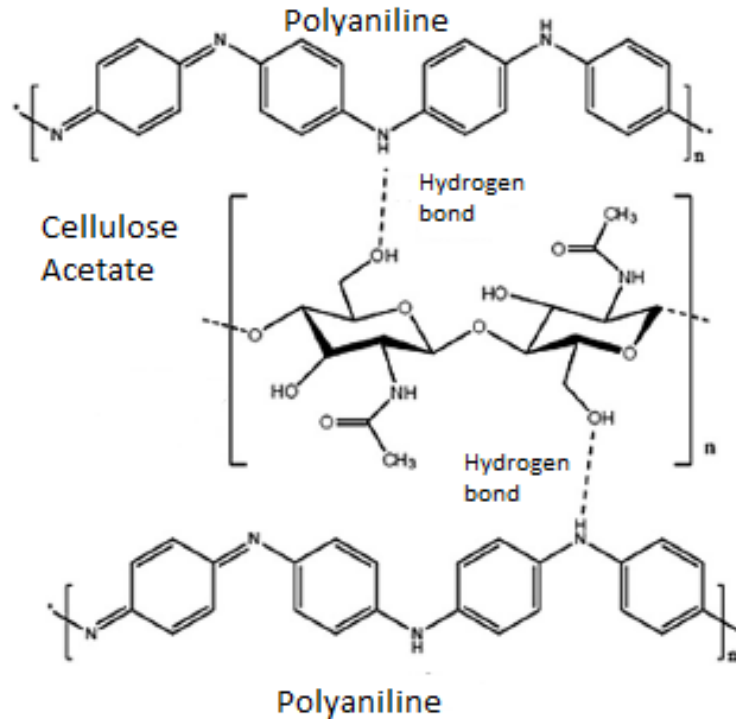


Figure 5 PANI/CA composite molecular structures [10]

Al-Ahmed et al. [15] prepared PANI/CA composite films by using as-prepared PANI and polymerization of aniline during the process. The first way they added the as-prepared PANI into the solution of CA in acetone and directly casting the composite on flat glass plates. Another way is to add viscous CA solution into aniline. The polymerization of PANI happened while forming interconnected structure with CA. Both of them were doped by hydrochloric acid to exhibit the conductivity. They measured the DC electrical conductivity of the doped composite films on different temperatures. J. Planes, A. Wolter et al. [24] used m-cresol instead of acetone as solvent to prepare PANI/CA film and test the transport properties in different length scales. In their work PANI was protonated by camphor sulphonic acid (CSA), phenyl phosphonic acid (PPA). S. Neves, M. D. Paoli [25] has done the work also applied on the Semiconductor photoresponse. They synthesized aniline instead of using as-prepared PANI, and mix it with CA

and acetic acid. Finally film was casted onto a polished platinum substrate. All of these works above were done using the chemical polymerization method and showed good conductivity as the semiconductor. Table 1 summarized the testing method and different materials used for chemical polymerization method.

Materials	Testing method	Application	Reference
0.9g PANI, 1.0g CA, 30ml Acetone	DC electrical conductivity retention on 50, 70, 90 °C	Semiconductor	15
0.5 wt. % PANI (CSA, PPA protonated) in m-cresol, 5 wt. % CA in m-cresol	DC and AC electrical conductivity, magnetoresistance	Semiconductor	12
10 wt. % CA 78 vol. % Acetic acid 1 mol HCl+0.1 mol aniline	Electrochemical impedance spectroscopy	Semiconductor photoresponse	13

Table 1 PANI/CA films produced by chemical polymerization method

There is a novel works reported by using electrospinning method to synthesize PANI/CA films. The traditional methods we mentioned before have disadvantages like hard well dispersed into CA matrix and we can't finely control the production. Also the size of the composite films is in macro scale. This electrospinning method is an effective way of fabricating well-dispersed nanoscale composites with controllable production [9]. One work reported by

Cheng-Hai Hong, Seong-Jong Ki, et al. [10] are using a method for processing PANI/CA nanofibers for bio-composite actuators. Electrospinning is carried out by using a syringe being equipped into a pump and squeezing out the solution through a steel needle to a collection plate. A high voltage supplier generates a high electric field from the tip of needle to the collection plate. When the polymer solution overcome the surface tension, solution droplets are ejected out from the needle tip and finally formed membrane on the plate. Table 2 shows the electrospinning parameters of producing PANI/CA films.

Materials	Electrospinning parameters	Testing Method	Application
CA/Acetone: 20 wt/v% PANI: 0.5 wt. %	Voltage: 20 kV Needle: 16 gage Flow rate: 3.0 ml/h Distance: 20 cm	Harmonic response Current-voltage Displacement	Bio-composite actuator as natural muscles

Table 2 PANI/CA films produced by electrospinning method, *ref. 10*

1.3.2 Polyaniline/Other Polymer Composite Films

By reviewing former works done by other people, they produced PANI/CA films either using as-prepared PANI and CA or synthesizing aniline or natural cellulose while films forming process. Most of them were using as semiconductors. Besides these works, PANI can react with other kinds of insulating polymers and synthesize versatile films.

PANI/Heptamethyleneimine (HPMI) porous asymmetric films was made by J. Bao, J-M, Sansinena [14] and cut into strips 40mm in length and 2mm wide. The strips as the chemomechanical actuator, bending-recovery behavior was showed by putting strips above the organic vapor like tetrahydrofuran (THF), hexane, ethyl ether and different bending-recovery angles and times was studied. Nanoscale PANI fibers made by Shbnam Virji, Jiaying Huang, et al. [15] using a new interfacial polymerization method and the size are uniformly around 30-120 nm in diameter. PANI nanofiber gas sensor was assembled by drop-casting the filtered solution onto interdigitated electrode sensor substrate.

PANI/NMP thin film was made by H.L. Wang and B.R. Mattes [17] for gas separation. This application was first achieved in 1991 [18], which the films showed great O₂/N₂ selectivity after doped with hydrochloric acid. For H.L. Wang's work, they used 20% PANI (EB)/NMP solution to fabricated the films with thickness around 43-51 microns. Selectivity was measured by using pairs gas He/N₂, O₂/N₂, CO₂/CH₄ on different temperatures. The permeability of these three pairs gases increased by increasing temperature.

From all above, PANI can cooperate with CA and other polymers like HMP, HFIP and synthesize film from nano scale to macro scale. These films can be coated onto a substrate to consist a gas sensor or directly casted as an actuator for organic vapors. Table 3 summarized PANI films application by different materials and methods.

Materials	Processing method	Application	Reference
3.7g NMP, 0.31g HPMI, 1.0g PANI(EB)	Poured onto a glass plate and spread into a wet film using gardener's blade	Chemomechanical actuator: organic vapors (THF)	28
2 mg/mL of PANI(EB)/HFIP	Filtered solution drop-cast onto interdigitated electrode sensor substrate	Gas sensor: NH ₃ , HCl, N ₂ H ₄ , CHCl ₃ , CH ₃ OH	29
20% PANI (EB)/NMP solution	Heat treated for 2 hours and then casted on the glass plate	Gas separation: He/N ₂ , O ₂ /N ₂ , CO ₂ /CH ₄	30

Table 3 PANI/Other polymer composites films

1.4 Chemomechanical and Electrochemical Actuator

Generally, an actuator is a kind of mechanism that can transfer the energy from pressure, electric current or chemical into mechanical motion upon specific environment. Earliest polymer actuators were reported in the year 1949. The actuator was collagen filaments when they were put in acid solutions, shrinking will happened; while will be expanded when putting into alkali solution [32]. The acid and alkali solution are the specific environment for the collagen filament actuator.

Conducting polymer actuators have been studied for a long time because of the excellent properties of polymer with low potential and broad applications in microactuators and artificial muscles [33-34]. Conducting polymer actuators can be electrical and chemical stimulated and are called electrochemical actuators and chemomechanical actuators respectively.

1.4.1 Chemomechanical Actuator

Chemomechanical actuator can be chemically triggered by external conditions and isothermally transfer chemical energy into mechanical work [35, 36]. Mechanical motion can be macroscopic or microscopic. For example, conducting polymer fibers are fabricated on a matrix and exhibit macroscopic mechanical movement like bending and recovery. The advantage is we don't need any transducer or power supplies to measure this.

As PANI demonstrates high environmental stability, low cost and relatively high conductivity, it is one of the most promising conducting polymers for fabricating actuators. One of the most popular applications for PANI actuator is in the field of biological detection and artificial muscles. Various works have been done on these. In the work [28], PANI actuator was fabricated by using commercial PANI (EB) powder and NMP solution. Film was formed by pouring the solution on top of a glass substrate and heat-treating it for 2 hours under nitrogen atmosphere. Methanol was used to remove the residue NMP solvent. Porous asymmetric membranes were made and cut into strips of 40 mm long and 2 mm wide. Finally the strip actuators went through bending and recovery movement stimulated by physical sorption and desorption of organic vapors. There is no chemical reaction happened during this process. It is a reversible process. Exposure to organic vapors will change the conformational structure of the

conducting polymer chain and result to displacement of the membrane. After sorption of organic vapor molecules the membrane extend and result to volume change along the cross section. After remove the membrane out of organic vapor, gas molecular leave away from the PANI chain and volume back to original state. Figure 6 shows the sorption and desorption of organic vapor. For this case, it took about 1.5 s for PANI membrane bending and 2.7 s for recovery. Under different organic vapor, the maximum bending angle and recovery time are also different.

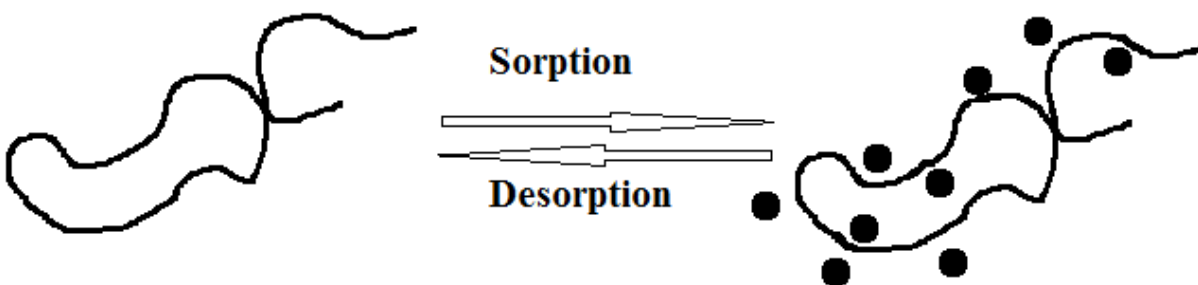


Figure 6 Polymer chain Sorption and desorption of organic vapor

Beside PANI films actuator, polypyrrole/perchlorate (PPy/ ClO_4) actuator were synthesized by anodic oxidation of pyrrole also showing Chemomechanical response under certain adsorbates [37]. This is a novel actuator because by using different adsorbate, the direction of bending is opposite instead of different bending angle level on the same side. The PPy was cut into 25 mm length and 5 mm width. For the polar volatile organic solvent such as alcohols, ketones and ethers, the bending happened to the same side; but for organic or inorganic water vapor, the bending happened to the opposite side. The phenomenon illustrate that the mechanism for the bending is related to a reversible van der Waals adsorption of different gases.

All the actuators illustrated above are triggered by various vapors, another kind of chemomechanical actuator can be stimulated in acidity environment [38-39]. An early work described by Katchalsky [40] is the reversible viscosity change of polyacrylic acid solution under different pH. Because of protonation of the carboxylate groups and hydrogen bonds dismissing, repulsion exists between the carboxylate anions, thus polymer chain elongate at high pH value.

Polymer hydrogels show the excellent performance on assembling actuator due to the size and shape of gel being easily changed by environmental trigger [41]. Hydrogels are cross-linked with lots of pores inside of the network. Thus these pores allow other molecules binding and exchange. We can explain this mechanism through Figure 7 below. There are a bunch of sites (marked as A) on polymer chain for the guest molecules (marked as G) binding. When the guest molecules are binded non-covalently with sites along the polymer chain, water molecules will cover the guest molecules quickly, thus expansion happened. A work has done by Molina. M, Rivarila. C. et al. [42] about macroporous hydrogel as a Chemomechanical actuator. PANI nanoparticles were synthesized by interfacial polymerization [43]. Hydrogel composites were formed by hydrogels absorbing PANI nanoparticles and swelling happened under electromagnetic radiation.

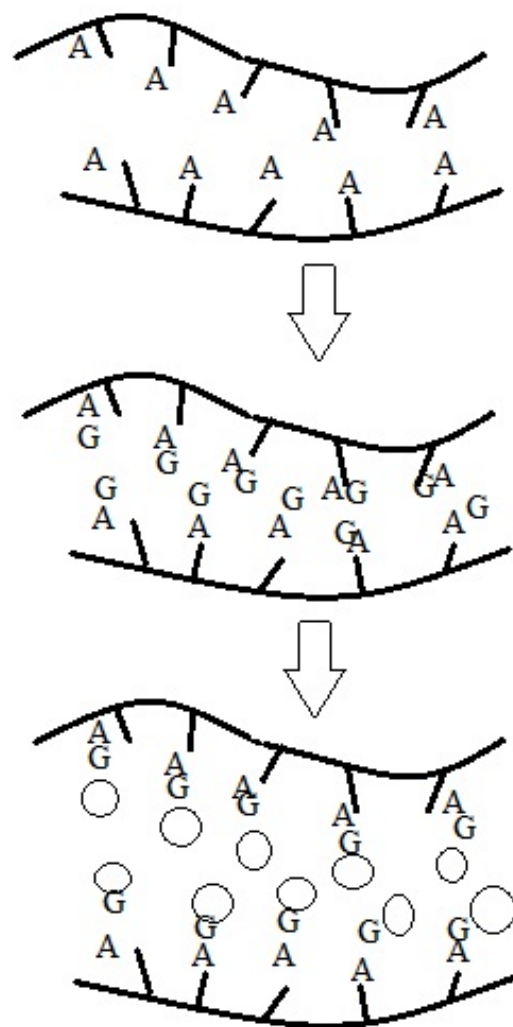


Figure 7 Expansion of polymer hydrogel by guest molecules

Chemomechanical actuators have various shapes or forms. They can be films, bulk gels or solution. Each of them also has different stimulus for working. We provide many actuators synthesized by other research to illustrate the mechanism and working environments. Table 4 provides examples from relevant work in the literature

Materials		Stimuli	Change form	Reference
Film	PANI (EB) powder, 20% NMP solution	Organic vapors: THF; Hexane; diethyl ether, ethyl acetate	Bending with different angle	[28]
	PPy/CIO ₄	Organic or inorganic water vapor, Polar volatile organic solvent	Bending on different side	[15]
Gel	PANI nanoparticles/LTHG	Electromagnetic radiation	Hydrogel swelling	[37]
Solution	polyacrylicacid solution	PH	Viscosity of solution	[40]

Table 4 Chemomechanical actuators

1.4.2 Electrochemical actuator

The electrochemically driven conducting polymer actuators have been promoted a lot recent year. Conducting polymers have the π -conjugated system. That means single and double bonds alternatively exist in the polymer chain. They are intrinsically insulating and can be conductive through doping process. Dopants incorporate within polymers causing the charge movement and polymer chain conformation change. Because of the doping process is reversible, the volume change such as expansion and contraction [44-46] are also cyclic. Based on this property, electrochemical actuator can be assembled by constructing the multilayers with conducting polymer film [47], because this will form the asymmetric structure and allow volume

changing unevenly. The flexible films can be polymer thin films [48], adhesive tapes [49] and metal layers [48]. The thin films are the most widely used because the adhesive tapes or the metal are with relatively higher weight, and will reduce the efficiency about the actuator. We illustrate some electrochemical actuators with different layers below. Figure 8 and Figure 9 separately illustrates single layer/triple layers of electrochemical actuators.

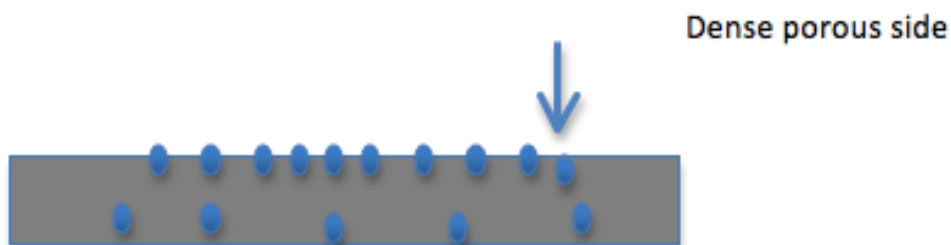


Figure 8 Single layer actuator

A single layer electrochemical actuator is achieved by Jose-Maria Sansinena and etc. [47] using phase inversion method. They fabricated the PANI asymmetric membranes using the monolithic PANI. The cross-section of this membrane shows porous structure with unevenly distribution. Due to this asymmetric distribution and with the electrochemical doping process, volume expansion happened in the polymer chain, thus we don't need to use multilayers to promote the bending. The membrane was cut into strips and voltage was applied to the actuator. The bending angle of this PANI electrochemical actuator was measured and the maximum is over 90° . Bending-recovery was observed under up to 20Hz.

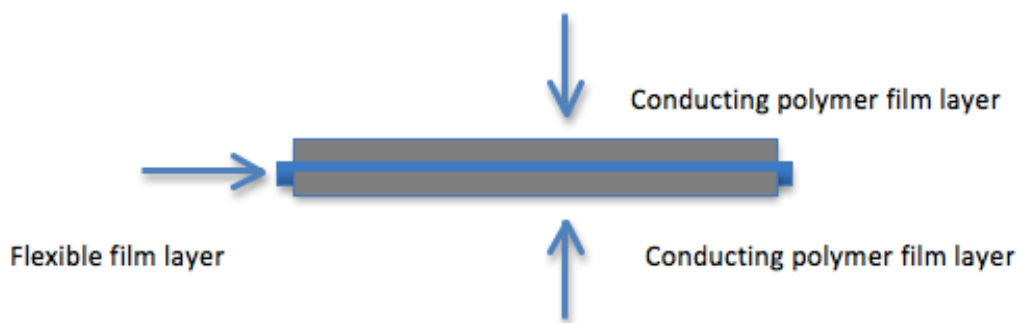


Figure 9 Tri-layers actuator

Triple-layered electrochemical actuator was reported by Gaoyi Han and Gaoquan Shi [50]. They synthesized this Polypyrrole (DBS)/ polythiophene / Polypyrrole (ClO_4) actuator by using the PTh as the flexible mechanical layer to support doped PPy (ClO_4) and PPy (DBS) as the driving layers. Bending was showed when put this actuator in the electrolyte solution background. Two mechanisms can be explained for this actuator's movement. The first is that oxidation happened in the doping process. Electrons are activated and move along polymer backbone. Water molecules are captured and cause the film swelling. Another is accounted for electromechanical bending. With large anions as dopant for oxidation process, the film bends to the large anions side; while small anions for the reduction process, the film bends to the small anions side.

Multiwall carbon nanotubes were used by YeoHeung Yun, Vesselin Shanov, etc. [51] to synthesize multilayers the electrochemical actuator by using Chemical vapor deposition method. Multiwall carbon nanotubes were applied on the patterned Si substrate. This electrochemical

actuator was stimulated by an applied voltage and caused the displacement thus we can measure it by a displacement sensor.

Conducting polymers	Flexible polymers as matrix	Number of layers	Reference
Monolithic PANI	–	1	[13]
Polypyrrole /(ClO ₄), Polypyrrole /(DBS)	Polythiophene	3	[24]
Multiwall carbon nanotubes	Si	Mutil	[23]

Table 5 Electrochemical actuators by different layers

Chapter 2: Material Synthesis and Characterization

2.1 PANI/CA Actuator Synthesis

2.1.1 Chemical Used

In my thesis, I used polyaniline (leucoemeraldine base) and cellulose acetate to synthesize the composite thin films used to prepare chemomechanical actuator and acetone, ethanol, 1-butanol 2-propanol to test the actuators' selectivity. Chemicals used to prepare and test are listed below in Table 6.

Chemical Name	Chemical Formula	Molecular Mass (g/mol)	Density (g/mol)	Company
Polyaniline (leucoemeraldine base)	$(C_6H_8N_2)_n$	–	–	Sigma-Aldrich
Cellulose Acetate	$C_6H_7O_2(OH)_3$	~ 50,000	1.3	Sigma-Aldrich
Hydrochloric Acid	HCl	36.46	1.2	Sigma-Aldrich
Acetone	CH_3CH_2OH	58.08	0.791	Pharmco-Aaper
Ethanol	CH_3CH_2OH	46.06	0.789	Pharmco-Aaper

1-Butanol	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	74.12	0.812	J.T.Baker
2-propanol	$(\text{CH}_3)_2\text{CHOH}$	60.1	0.786	J.T.Baker

Table 6 Chemical Properties used in synthesis

2.1.2 PANI/CA Actuator Synthesis processing

There are three steps to synthesize a PANI/CA actuator: solution preparation, casting and strip cutting. Figure 10 clearly shows the casting solution preparation process.

1. Casting solution preparation:

0.1g of LEB PANI was put into a glass vial with 10ml HCl, dark grey solution was made and kept the glass vial overnight. After acid doping process, centrifuged the solution and the acid on the top was removed. Added water to the remaining precipitates, and centrifuged the solution again and got the precipitate. This procedure was repeated for 6 times and we got the acid-treated PANI. Then we dried it in air at room temperature. 12ml acetone was then added to the acid-treated PANI. The mixture was sonicated for 1 hour in order to let PANI distributing evenly in acetone. We added 0.5 g cellulose acetate in the mixture, then dissolved the mixture properly by sonicate the mixture extra time. The ratio of PANI/CA equal to 1:5; the total polymer concentration in acetone was 5%.

2. Casting process:

Because PANI doesn't dissolve in acetone and CA, we need to make sure PANI grain evenly distributes in the solution (Figure 11 (a)). The mixture was poured on a clean flat glass slide and we can use a blade to make it evenly. Thin films (Figure 11 (b)) was formed and kept it dried in ambient.

3. Actuator making:

When the thin film was dried out, we split it from matrix glass by using the sharp blade. Cut the thin film into strips having dimensions of 3mm width and 40mm length (Figure 12). The actuator now is ready to use.

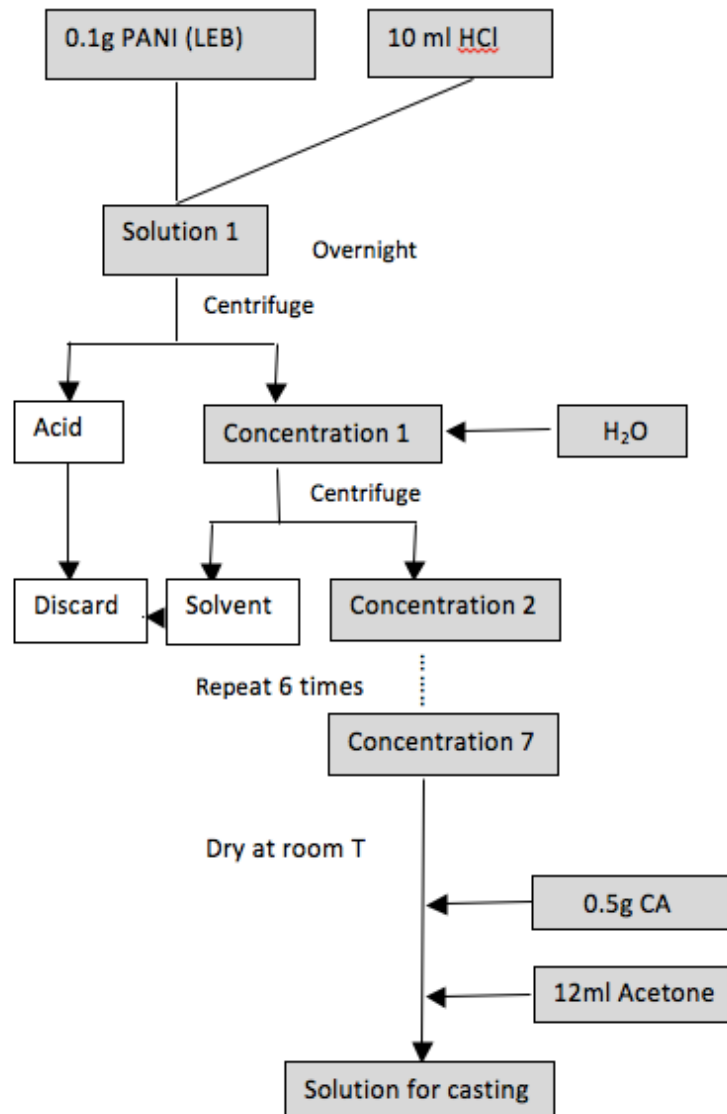


Figure 10 Process of synthesizing

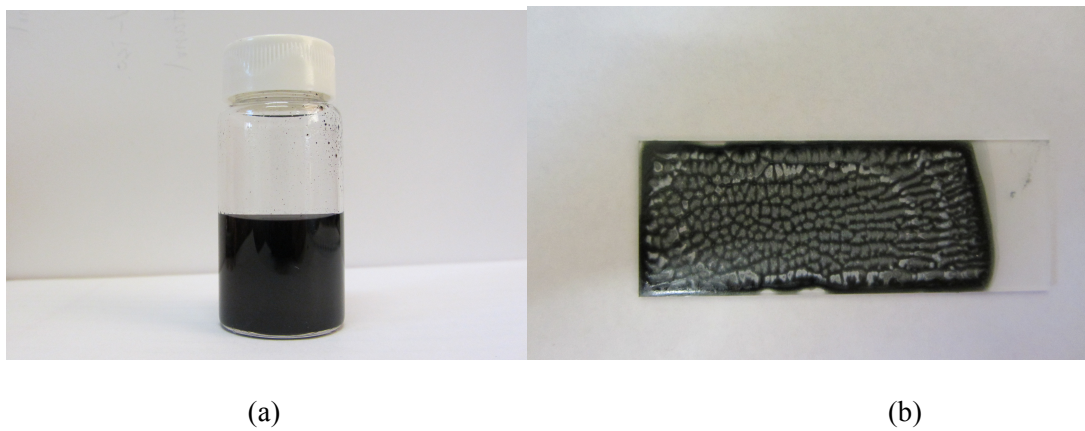


Figure 11 Process of making casting solution



Figure 12 Strips with dimension 3mm width and 40mm length

2.2 PANI/CA Actuator Characterization and Testing

2.2.1 Scanning Electron Microscopy

The SEM analysis for the PANI/CA films was carried out to observe the morphology about casted films. Before we inserted the sample into SEM chamber, we need to gold coating. The coating process conducted under Argon atmosphere. With a high voltage, the argon atoms was starting vibrating, the gold atoms from the gold foil was leaving to cover all the sample surface.

A LEO 1550 Schottkey Field Emission Scanning Electron Microscope was used to analyze the gold coated film surfaces. The walking distance is 8mm; EHT is 20kV; and the back scattered signal was used to obtain all the images. We looked both side of the films.

2.2.2 Energy Dispersive X-Ray Spectroscopy

The Energy Dispersive X-Ray (EDS) Spectroscopy, which was carried out on the Scanning Electron Microscopy tool (LEO 1550 SEM), is a quantitative analysis technique. It can measure the elements in the sample quantitatively and form a spectroscopy to show the concentration of the elements.

2.2.3 Fourier transform infrared spectroscopy

We used a Nicolet Model Magna 760 FTIR spectrometer with the Thermo Spectra-Tech Infinity ReFlachromat 32X lens. The PANI/CA films were placed on a gold plated and the background were subtracted from it. We collected the data from the range 4000-500 cm^{-1} .

2.2.4 Bending angle and time in acetone background

As the PANI/CA actuator ready to use, we use a beaker containing acetone and cover the beaker for a period of time to let the acetone vapor saturated in the beaker. Then we simply make a small hole on the cover, use a tweezers hold the tip of one side and insert the strip into beaker. Make sure the strip doesn't touch acetone liquid. When we insert the strip into beaker containing acetone, it starts to bend in the saturated acetone vapor. Once the strip leaves the acetone vapor, it recovers to its original shape. At the same time we insert the strip into beaker, we use a stopwatch to record the bending and recovery time. An angulometer paper is printed out and sticks it on the beaker's back to measure the bending angle.

2.2.5 Selectivity

For this time, we prepare four beakers with acetone, ethanol, 1-butanol and 2-propanol respectively. All of these four kinds of chemicals are volatile, and keep the beakers covered and leave them for a period of time to make all the chemical vapors saturated in the beakers. Then as the work we've done in the section 2.2.4, we put the strip into the beaker through hole on the cover separately. Observe the movement of the strip.

Chapter 3: Result and discussion

3.1 Scanning Electron Microscopy

We conducted the SEM under different magnifications. From Figure 13-15, the magnifications are 1kx, 3kx and 10kx respectively. The parameters are: working distance is 8mm; EHT is 20kV; signal is backscattered signal. Because we want to see the surface of this PANI/CA film, back scattered signal can provide topographic details so we selected it.

From all the three images, we can see the PANI/CA thin film is porous. The hole size diameter is about 1-2 micrometer. From Figure 14, the magnification is 3kx, we can observe the distribution of the holes is on the top of the film. From Figure 15, we can also see the hole inside of the structure. Because of this porous structure, the PANI/CA film can absorb vapor and causing the polymer chain deformation and bending.

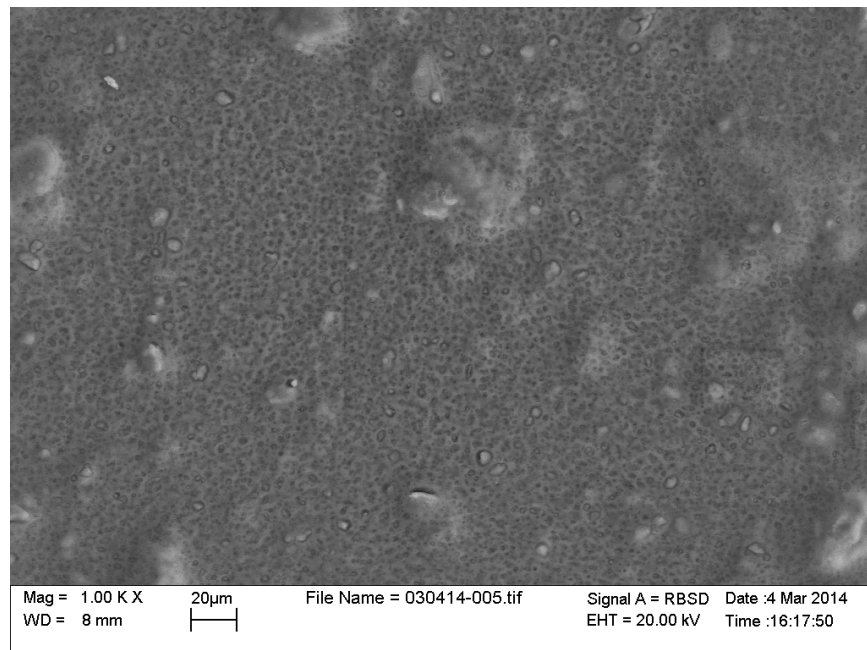


Figure 13 SEM of PANI/CA film (Mag=1.0kx, WD=8mm, EHT=20kV)

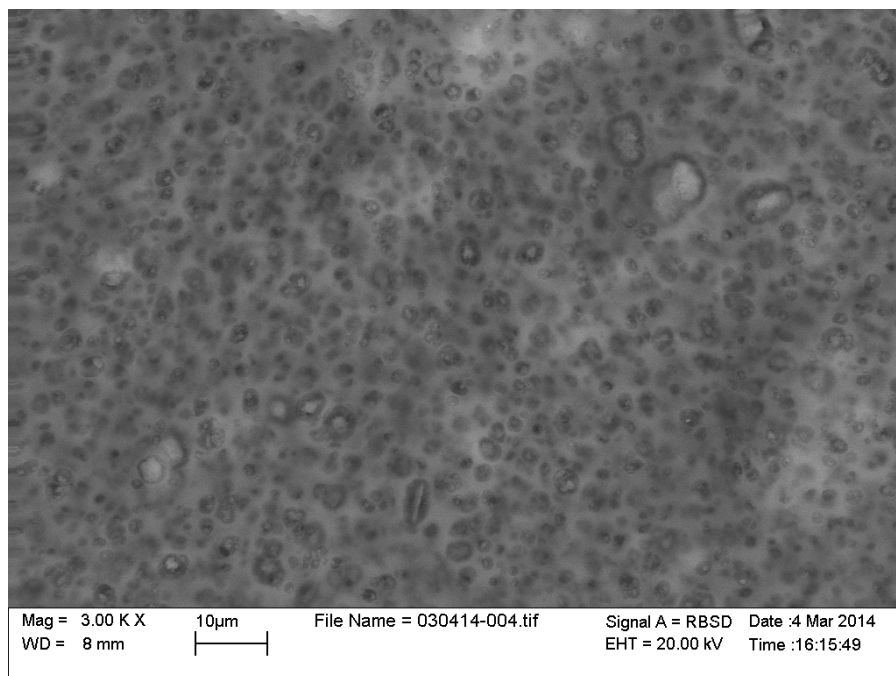


Figure 14 SEM of PANI/CA film (Mag=3.0kx, WD=8mm, EHT=20kV)

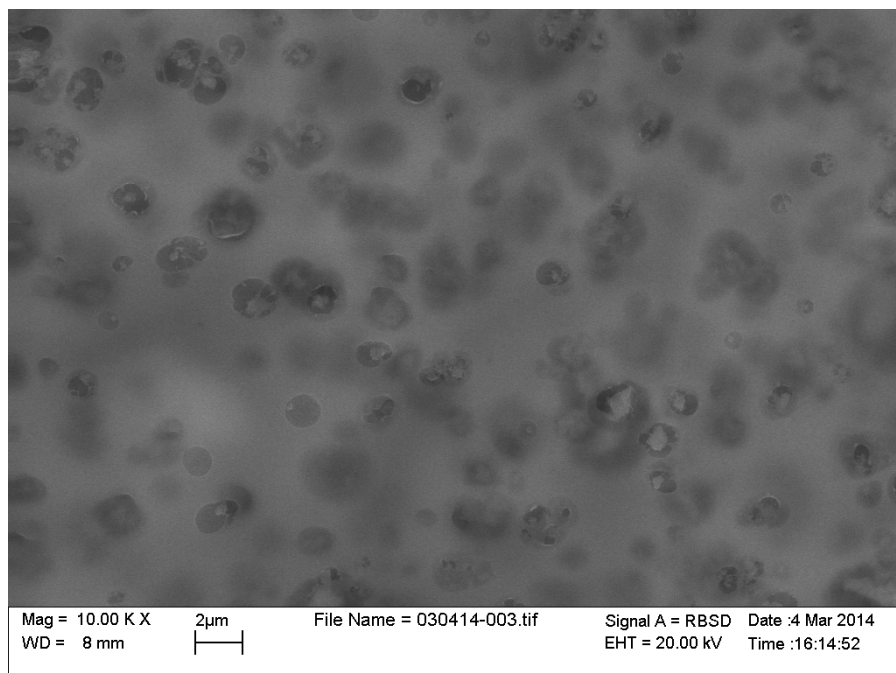


Figure 15 SEM of PANI/CA film (Mag=10.0kx, WD=8mm, EHT=20kV)

3.2 Energy Dispersive X-Ray Spectroscopy

From the EDS spectra, we know the elements concentration about PANI/CA film. The first step we use hydrochloric acid as the dopant to react with PANI, now we can see the elements chlorine from the spectra and that means doping is successfully happened during the first step of making casting solution.

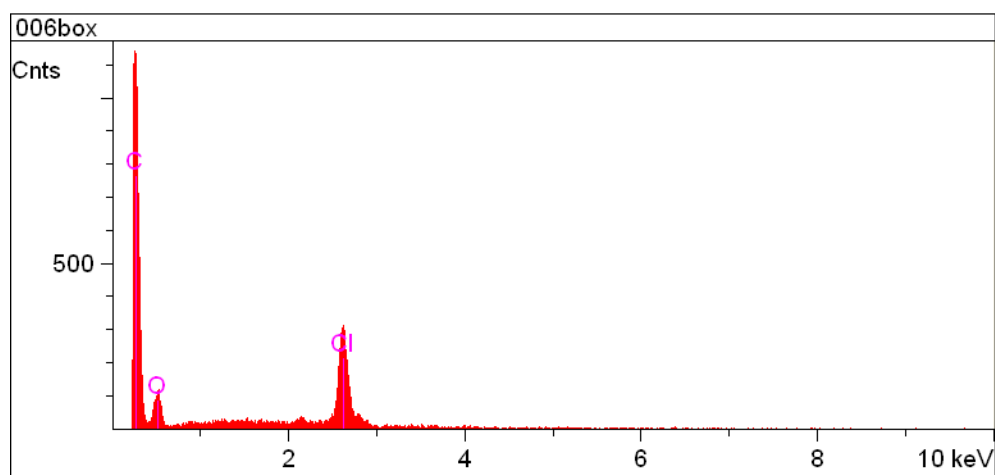


Figure 16 EDS of the porous PANI/CA film

3.3 Fourier transform infrared spectroscopy

The band at 835 cm^{-1} is responding to out of plane bending vibration of benzene ring. The band at 1533 cm^{-1} is responding to stretching vibrations of N-benzene-N and N=Q=N, Q is the quinoid moieties in the PANI polymer backbone. The bands at 1137 cm^{-1} is responding to vibration of N=Q=N ring. The band at 1270 cm^{-1} is for stretching of C-N bond. The band at 2913 cm^{-1} is for C-H present in CH_2OH group in composite structure. A broad band around $1089\text{-}1137\text{ cm}^{-1}$ is responding to -C-O-C- . Another band at 1764 cm^{-1} is for C=O bond stretching.

In analyzing above, all the band appeared in the spectra are indicating PANI and CA are interconnecting and formed the composite.

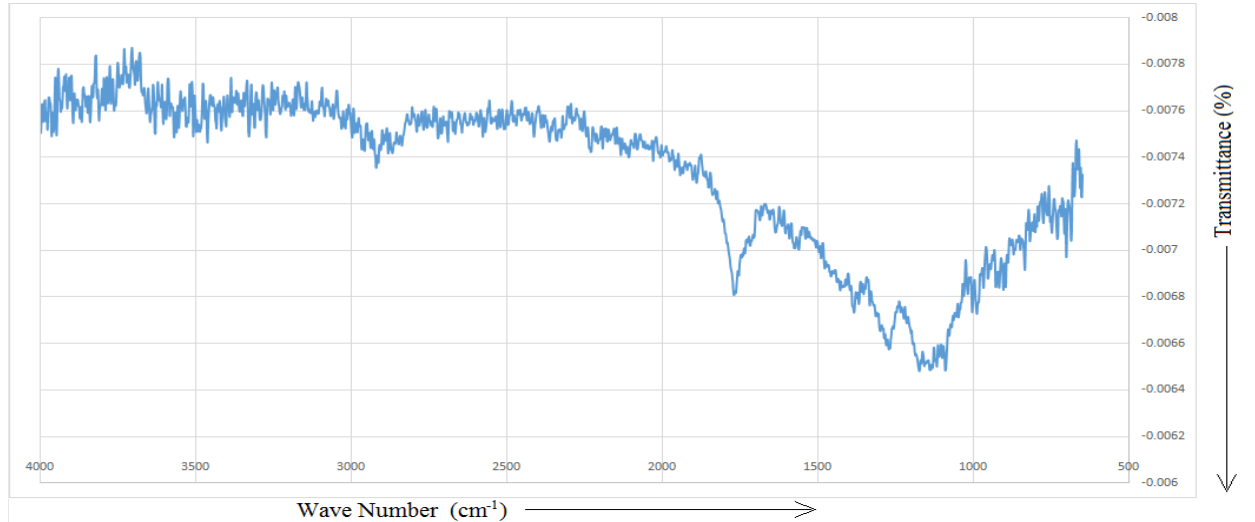
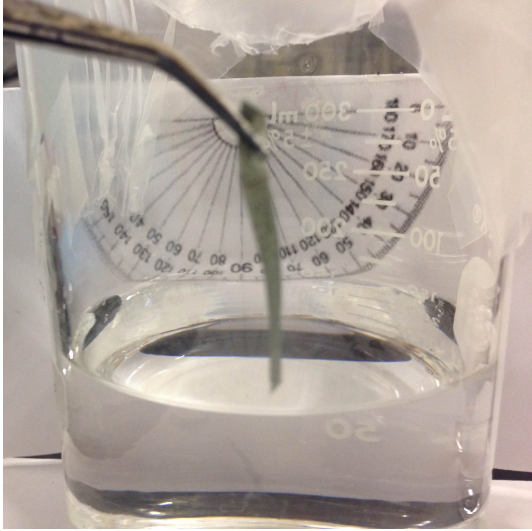


Figure 17 PANI/CA thin film FTIR spectra

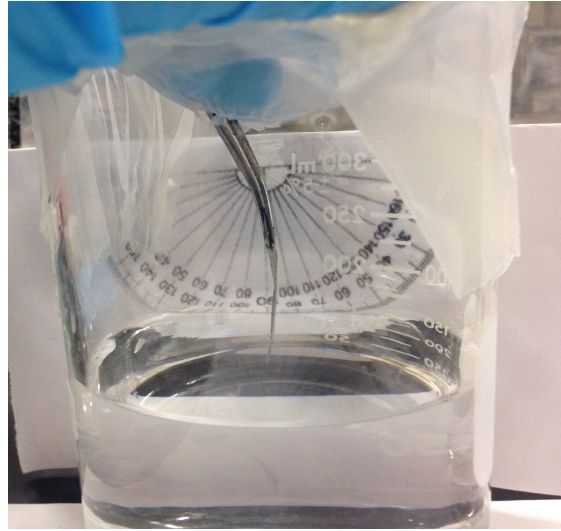
3.4 Bending angle and time

Figure 18 shows the whole bending-recovery process. (a) is when the strip before put into the headspace of acetone; (b)(c) are the strip entering acetone vapor; (d) is the strip removed out of acetone vapor.

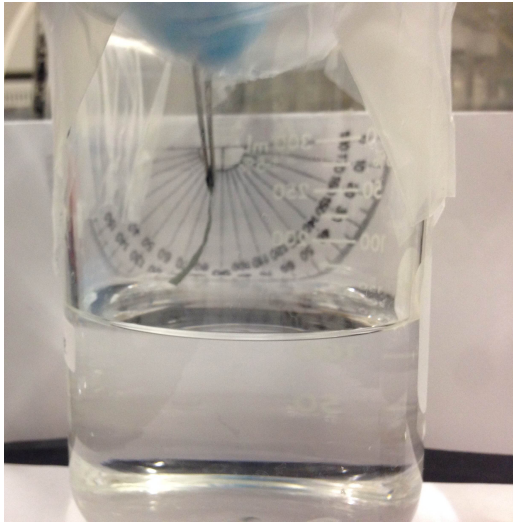
From the angulometer readings (see background), we can observe the maximum bending angle is about 45 degree. From the strip starts to bend, it will take about 4 seconds to reach the maximum angle and will take less then 7 seconds to recovery. This cycle can repeat more than 10 times and we can keep this actuator in air for a long time without reducing its performance. Figure 19 show the bending angle with time.



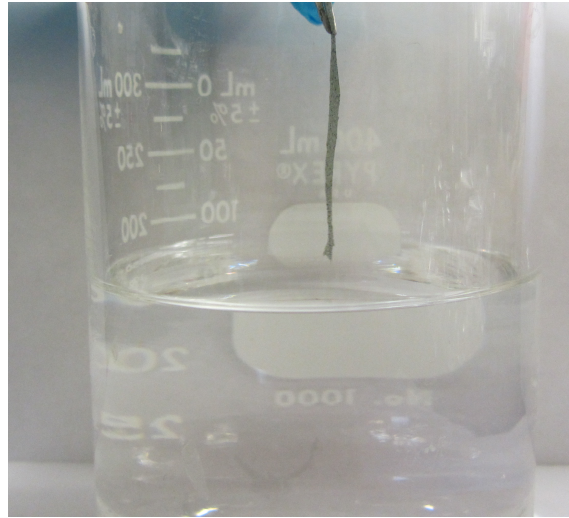
(a)



(b)



(c)



(d)

Figure 18 Bending-recovery processes

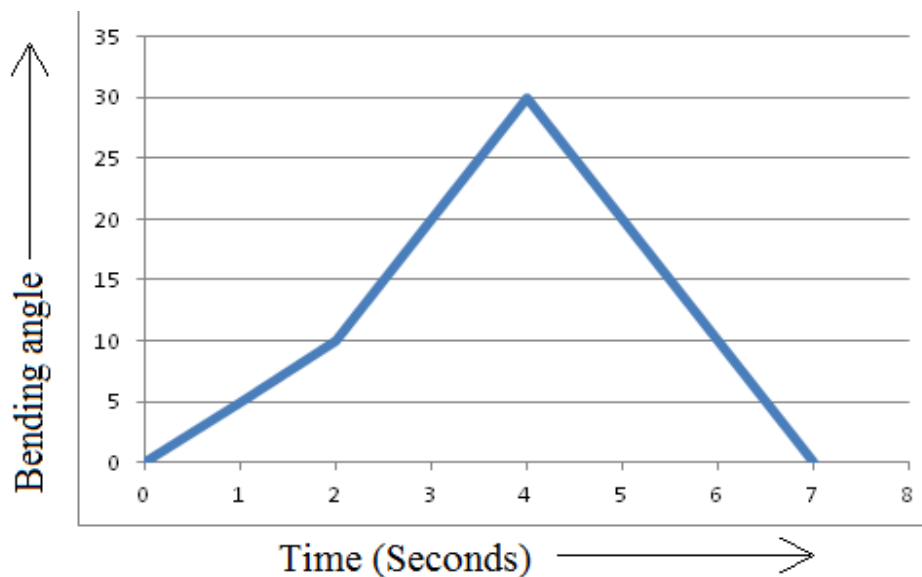
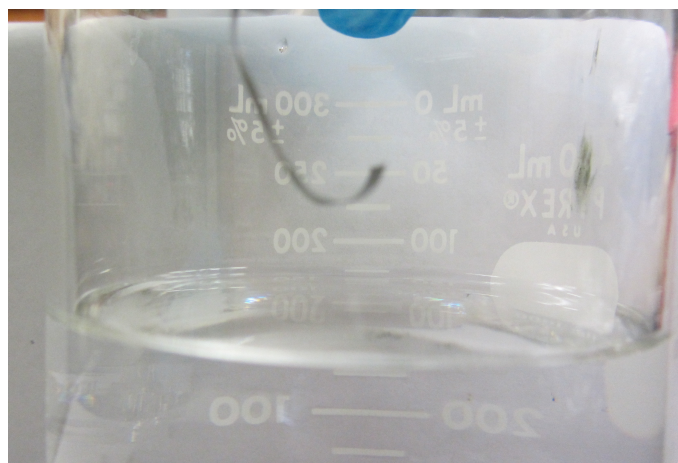


Figure 19 Bending angle variation with time

3.5 Selectivity

As shown on Figure 20, same operation applied to ethanol (b), butanol (c) and 2-propanol (d) vapors in the beakers. There is no movement for the strips no matter how long we expose them to the vapors. So the PANI/CA actuator only works on acetone vapor, and have the selectivity about acetone vapor. Figure 20 are the beakers containing different chemicals: acetone (a), ethanol (b), butanol (c) and 2-propanol (d).



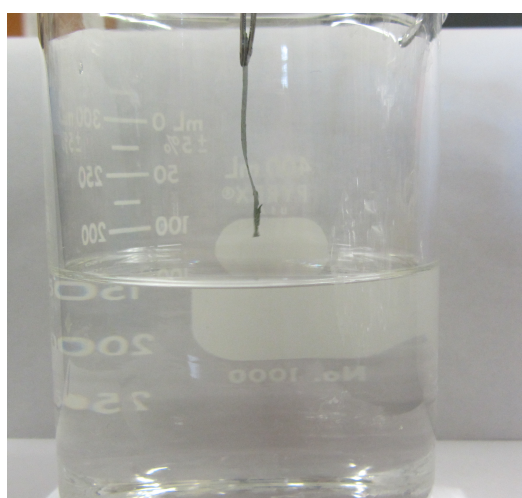
(a) acetone



(b) ethanol



(c) 1-butanol



(d) 2-propanol

Figure 20 Selectivity under different background vapor

Conclusion

We synthesized the polyaniline and cellulose acetate thin films and cut them into strips, which is a kind of chemomechanical actuator. We characterized the actuator's morphology by SEM; the result shows the actuator is porous on the surface or inside of the film. This will allow gas molecules to be absorbed into the film and this leads to the bending of the film. EDS and FTIR were also used to characterize the synthesis of actuator. Main elements and structures are showed on the spectra, which mean the polyaniline, and CA composite films were successfully synthesized and ready for making actuator. Bending angle and time were tested and exhibit good performance. The maximum bending angle is 30 degree and the time for a cycle is about 7 seconds. The selectivity was conducted by using acetone, ethanol, 1-butanol and 2-propanol. The bending movement only appeared on the acetone vapor background, which means PANI/CA actuator has selectivity of acetone.

Future work

We synthesized the PANI/CA actuator successfully and with good performance on bending and selectivity based on the characterization and testing. For the future, we can enhance the mechanical property and test the strain-stress. We can enhance the PANI dispersion and make it disperse more evenly in the acetone and CA solution. The actuator we made is on the macro scale, but we can try to synthesis the film in a better way to make it on the nanoscale. This will dramatically improve the bending angle and other performance. Based on the selectivity of acetone, we can apply it in the field of flexible sensor as well. The application of this actuator or sensor by future work, we can easily test the acetone without complicated electrical equipment.

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