ADVANCING STRETCHABLE OPTOELECTRONIC DEVICES WITH STRUCTURAL AND MATERIAL DESIGNS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Stretchable electronics are emerging as a new type of devices with their exceeding mechanical compliance compared to the rigid or flexible devices. They can confront demanding mechanical deformations such as twisting, stretching, or conformably wrapping, enabling electronic applications under rigorous mechanical conditions that cannot be addressed by conventional devices. Stretchable electronics are believed to be one of the essential technologies for the next generation electronic device applications. With their significantly improved mechanical “robustness”, the challenges to develop the enabling technologies for stretchable devices also become more difficult to resolve. In this thesis, we focus on developing new structural and material approaches to enable stretchable optoelectronic devices, including stretchable photodetectors and stretchable electroluminescent devices.

Nanowires have driven special interest in the research society due to their unique one-dimensional structure. We presented the fabrication of Zn$_2$GeO$_4$ nanowires and Zn$_2$SnO$_4$ nanowires in a chemical vapor deposition system and their assembly by a solution-processible approach for highly deformable and transparent ultraviolet photodetectors. The solution-processible approach was firstly demonstrated to assemble Zn$_2$GeO$_4$ nanowires and silver nanowires for transparent and flexible photodetectors. The fabricated device showed excellent mechanical stability, high photoresponse and fast switching time. Mechanical properties of the nanowire network structures were further improved to achieve stretchable devices. The first stretchable and transparent ultraviolet photodetector was demonstrated by embedding the nanowire device structures into polymer matrix. Zonyl surfactant was found to be an efficient additive to improve the bonding strength between the nanowire networks and the stretchable polymer matrix, leading to significantly improved transfer efficiency.
The transparent and stretchable silver nanowire networks embedded in polymer matrix were also exploited as the electrodes for stretchable alternating-current electroluminescent (ACEL) devices. The highly stretchable EL devices fabricated with ACEL materials could achieve stable emission under large stretching strains. The unique emission mechanism in ACEL materials was essential for stable device operation under mechanical deformations. With the simple device configuration and highly conformable structures, the stretchable ACEL devices were integrated with dielectric elastomer actuators. An unprecedented self-deformable EL device was demonstrated which could be driven into dynamic shapes under external electrical bias.

Stretchability of the ACEL devices was further improved by using ionic conductors as the transparent and stretchable electrodes. The ionic conductors were fabricated with blends of conductive electrolytes and polymers. Transparency and stretchability of the ionic conductors greatly exceeded those of the electronic conductors. An extremely stretchable ACEL device using ionic conductors as the stretchable and transparent electrodes was demonstrated with the stretchability of 700%.
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<td>ZGO</td>
<td>$\text{Zn}_2\text{GeO}_7$</td>
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<td>$\text{Zn}_2\text{SnO}_4$</td>
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<td>NW</td>
<td>Nanowire</td>
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<td>UV</td>
<td>Ultraviolet</td>
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<td>AgNW</td>
<td>Silver Nanowire</td>
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<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
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<td>EL</td>
<td>Electroluminescence</td>
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<td>ACHEL</td>
<td>Alternating-Current Electroluminescence</td>
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<td>Poly(methyl methacrylate)</td>
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<td>Three-Dimensional</td>
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<td>EPLED</td>
<td>Elastomeric Polymer Light-Emitting Diode</td>
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<td>LEC</td>
<td>Light-Emitting Electrochemical Cell</td>
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<td>PEO</td>
<td>Poly(ethylene oxide)</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>LiTf</td>
<td>Lithium Trifluoromethanesulfonate</td>
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<tr>
<td>TFT</td>
<td>Thin-Film Transistor</td>
</tr>
<tr>
<td>PSR</td>
<td>Pressure-Sensitive Rubber</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid</td>
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<tr>
<td>SCCM</td>
<td>Standard Cubic Centimeters per Minute</td>
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<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
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<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
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<tr>
<td>PVP</td>
<td>Poly(vinylpyrrolidone)</td>
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<tr>
<td>Zonyl</td>
<td>Zonyl-FS300</td>
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<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
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<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate</td>
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<td>QDs</td>
<td>Quantum Dots</td>
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Chapter 1

Introduction

In the emergence of stretchable electronic applications, stretchable optoelectronic devices are still encountering massive challenges to develop the enabling technologies. The problems of complicated fabrication procedures, difficult assembly approaches, and limited mechanical stability in the stretchable optoelectronic devices still need to be addressed. Though flexible devices have been widely demonstrated and achieved significant progress, the mechanical strains tolerable in the flexible structures are too small compared to the required mechanical strains in the stretchable electronics. Different materials, device structures, and corresponding fabrication approaches are required to be developed for the stretchable optoelectronic devices.
1.1 Problem Statement

In 1998, stretchable electrodes were reported based on thin wrinkled metal film on elastomers by Bowden and co-workers. The mechanical conformability of stretchable devices was recognized to possess significant advantages over the simple bendable property in flexible devices. With the special “soft” features, stretchable optoelectronic devices can be applied where demanding deformations are required, such as wearable light detecting systems, electronic eye cameras on curvilinear surfaces, biomedical imaging and monitoring systems, highly conformable and stretchable displays, 3D displays rendering contents physically and interactively etc. With the significantly increased mechanical strains in the stretchable devices, the technologies that have been developed since 1960s for the flexible devices are challenged. Different materials, device structures and fabrication approaches need to be developed to overcome the mechanical strain limitation in the electronic devices.

Based on the underlying idea that any materials in sufficiently thin form are flexible, Rogers and co-workers have developed a wide range of stretchable electronic devices assembled on elastic substrates with stretchable electrical interconnections which were fabricated by patterning the thin and flexible metal films into stretchable structures to accommodate large mechanical strains. With the structural strategy, stretchable photodetectors and LEDs were demonstrated by assembling ultra-small devices onto rubber substrates with the “wavy” electrical interconnections, yielding stretchable device systems. After that, studies on stretchable optoelectronic devices are ignited with different approaches and strategies developed to enable stretchable devices. These studies can be categorized into two strategies based on the approaches to enable device stretchability. The first strategy focuses on “Structure That Stretch”. By configuring the thin materials into “wavy” or buckling structures and bonding them onto elastic substrates, the materials’ flexibility can be utilized to accommodate larger stretching deformations with most of the strains relaxed by the stretchable structures. Advantage of the strategy is that the technologies in conventional device fabrication can be exploited. Great works have been demonstrated by Rogers’s group and Someya’s group based on the strategy. Its limitations lie in the development of effective approaches to pattern the stretchable structures and integrate all
the components with mismatched mechanical properties onto the stretchable substrates. To date, most of the demonstrations are still limited on reporting stretchable electrical interconnections. Stretchable functional components remain difficult with the structural approaches. The other strategy focuses on “Materials That Stretch”. By using intrinsically stretchable active materials, fully stretchable optoelectronic devices can be achieved. Different from the strategy based on stretchable structures, which use conventional rigid functional elements (do not respond to strains) with stretchable electrical interconnection structures (respond to strains), the functional components and the electrodes can be strained simultaneously in response to the mechanical deformations in the fully stretchable devices. Studies in the material approach are still limited due to the daunting difficulty in developing the stretchable functional materials. Reports on fully stretchable EL devices were mainly demonstrated from Pei’s group based on LEC devices. Further efforts are still required in these devices to improve their mechanical stability, operating life-time and switching speed. In this thesis, we focus on exploring different materials and device structures to expand the research scope in fully stretchable optoelectronic devices, aiming to resolve some of the challenges in these devices and improve their fabrication approaches and mechanical performance.

1.2 Objectives and Scope

1.2.1 Explore new materials and structures for stretchable optoelectronic devices.

Electrodes are important components for the optoelectronic devices. Apart from the conductivity, transparency is another important feature in the electrode requirements which allow light transmission to the photosensing layer or light extraction from the emission layer. Conventional photodetectors and EL devices were fabricated using the prototypical ITO as the transparent and flexible electrodes. The brittle nature and high temperature deposition process of the ITO electrodes limit their application in stretchable electrodes. On the other hand, percolating metal NW networks have been demonstrated as promising materials for flexible and transparent electrodes, showing comparable conductivity and transparency with the ITO counterpart. The inherent flexibility of NWs and the percolating NW network structures provide the mechanism to accommodate large mechanical deformations. The mechanical strains induced in the NW networks can be easily relaxed...
by the change in the network structures and flexing in the NWs. The AgNWs are highly conductive metallic 1D structure which can be easily synthesized in solution with the polyol method. The process can be scaled up for low-cost and high-yield fabrication, making the AgNWs strong candidates for stretchable and transparent electrodes. In this thesis, AgNWs will be demonstrated as one ideal material to fabricate the transparent electrodes for stretchable photodetectors and EL devices.

Limited reports have been demonstrated on stretchable photodetectors. The reported stretchable detectors used rigid Si photodetectors connected with stretchable interconnections on elastic substrates. Different materials and device structures are required to be developed for fully stretchable photodetectors. Semiconducting NWs are widely recognized as promising building blocks for photodetectors with their large surface-to-volume ratio. Flexible photodetectors were reported by using NW photosensing channels with their inherent flexibility. However, their application in stretchable photodetector have not been widely recognized and explored. We will demonstrate that NW network structures embedded in stretchable polymer matrix can be applied to achieve fully stretchable photodetectors with good transparency.

Stretchable EL devices have been demonstrated based on LED devices and LEC devices. Due to the multilayer device structures, fully stretchable LEDs still have not been reported. Though different strategies have been exploited to assemble rigid LED devices on elastic substrates with stretchable electrical interconnections, the fabrication approaches were quite complicated and challenging. The new emerging LEC devices were demonstrated as promising alternatives to achieve fully stretchable devices. However, these devices still encounter difficulties in their slow switching speed, short operating lifetime, and poor mechanical stability. On the contrary, ACEL materials have been studied since 1900s with their emission mechanisms well established. Different ACEL materials with tunable emission wavelength have been developed for display and lighting applications. We will demonstrate that the unique emission behavior in the ACEL devices make them ideal candidates for stretchable ACEL devices which help to achieve stable emission performance under large mechanical deformations. In addition, their simple
device architecture will lead to great advantages for integration with other functional devices.

1.2.2 Develop simple and large-scale assembling approaches for stretchable optoelectronic devices.

Stretchable devices based on metal thin films configured into “wavy” or buckled structures require complicated patterning and transferring processes, making them incompatible for low-cost and large-scale fabrication. To overcome the difficulties, a different strategy is explored in our study by utilizing functional NW networks for stretchable optoelectronic devices. The assembly processes for NW structures can be concludes as either the bottom-up approach or the top-down approach. With the bottom-up approach, several solution-based assembly methods have been demonstrated by Liber’s group and Yang’s group, which show the possibility of large-scale assembly (centimeter level, and then wafer level with further improvement) and multi-layers assembly. For example, the fluidic flow-directed assembly technique was applied to align NWs by passing NW suspension through a microfluidic channel and a flat substrate.\textsuperscript{20,21} Blown-bubble film assembly technique\textsuperscript{22,23} was also developed with similar mechanical as the fluidic flow-directed assembly technique. And the Langmuir-blodgett assembly technique\textsuperscript{24,25} was employed to align NWs by uniaxially compressing a NW-surfactant monolayer on an aqueous subphase. In a different way, the top-down technique uses a sequence of lithography and etching process to form NW arrays. A major challenge in the top-down approach is the resolution limitation in the lithography techniques.\textsuperscript{26,27}

In this thesis, percolating NW networks were assembled through a bottom-up approach with simple and solution-based spray-coating method. Compared to the other assembly methods, the spray-coating process delivers a facile and cost effective fabrication approach. The achieved network structures with percolating NWs are essential to achieve stretchable active layers in the optoelectronic devices after embedded into elastic polymer matrix.

1.2.3 Improve mechanical property of the stretchable optoelectronic devices.

Thin percolating metal NWs and ACEL particles embedded in polymer matrix are
promising materials to achieve stretchable EL devices with stable emission performance under moderate mechanical strains (≤100%). To further improve the stretchability of the ACEL devices, stretchability of the transparent electrode using thin metal NW networks will become the main limitation. The material strategy was exploited in our study to overcome the stretching limitation of the thin metal NW networks. Ionic conductors have been investigated as ideal electrode materials for extremely stretchable devices with their excellent stretchability and transmittance.\textsuperscript{28} They have been successfully applied in soft actuators,\textsuperscript{29,30} strain sensors,\textsuperscript{31,32} and transistors.\textsuperscript{33,34} We will demonstrate that ionic conductors can be applied as highly stretchable and transparent electrodes for ACEL devices. The extremely stretchable ACEL devices fabricated with ionic conductors achieved a breakthrough in the mechanical stretchability of stretchable EL devices, reaching a strain record of 700%.

1.3 Dissertation Overview

This thesis focuses on addressing the fabrication challenges and improving the mechanical performance in the stretchable optoelectronic devices. The NWs are interesting building block for deformable devices with inherent mechanical flexibility and various functionalities depending on different NW materials. Transparent and highly deformable photodetectors were firstly demonstrated by using AgNW networks as the electrodes and ZGO NW or ZTO NW networks as the photosensing channels. With the remarkable features of good transparency and stretchability, percolating AgNW networks embedded in polymer matrix were then demonstrated as promising electrodes for stretchable EL devices which are consisted of ACEL particles in elastic dielectric layer as the emission layer. To further improve stretchability of the ACEL devices, ionic conductors were investigated as ideal electrode materials for extremely stretchable ACEL devices.

Chapter 1 presents the challenges and problems existing in the stretchable optoelectronic devices. The objective and scope of this thesis are discussed, focusing on advancing the stretchable optoelectronic devices in their fabrication approaches and mechanical performance with material and structural designs.
Chapter 2 presents review on the approaches and progresses on stretchable optoelectronic devices. We first discuss on stretchable photodetectors which exploit different approaches and materials to achieve stretchability in the devices. After that, the emission mechanisms and the strategies explored to achieve stretchable EL devices are reviewed. Challenges in the stretchable photodetectors and EL devices are discussed.

Chapter 3 presents rationales for our material selection to fabricate stretchable photodetectors and EL devices. The mechanisms and methods to synthesize the materials are introduced. Morphology and structure of the nanomaterials are characterized by SEM and XRD. The methods to characterize the optical and mechanical properties of the devices are introduced. Finally, structure designs and fabrication approaches of the stretchable optoelectronic devices are presented.

Chapter 4 presents the approaches which are developed to fabricate highly deformable and transparent photodetectors. Firstly, a spray-coating method is introduced to assemble thin-film NW networks for flexible NW photodetectors. Both the transparent electrodes and photosensing channels are consisted of spray-coated NW networks. To further improve the mechanical property of the NW photodetectors, a high-efficient transfer method is developed to embed the thin and transparent NW films into stretchable PDMS matrix with the assistance of Zonyl surfactant. The fabricated UV photodetector can be strained to 50% with maintained device performance.

Chapter 5 presents the material and device structure design which are developed to enable stretchable and self-deformable EL devices. Highly stretchable ACEL devices were fabricated using ZnS:Cu in PDMS as the stretchable emission layer and AgNWs thin film embedded in PDMS matrix as the transparent and stretchable electrodes. The unique emission mechanism of the ACEL devices was demonstrated to be critical to achieve stable emission behavior under large mechanical deformations. Advantages of the simple device architecture and solution-processible fabrication approach of the stretchable ACEL device were further harvested to integrate the EL devices with DEAs. An innovative self-deformable device was demonstrated.
Chapter 6 presents a novel transparent conductor which is developed to improve the stretchability of the stretchable ACEL devices. Ionic conductors possess extremely high stretchability and transmittance compared to the conventional electronic conductors. The ionic conductors were prepared with simple blending processes in polymer matrix. The unique characteristics of the ACEL devices with small capacitance and alternating-current operation were demonstrated to be the important features which enable the application of ionic conductors as the transparent and stretchable electrodes. The simple and solution-processible approaches in the extremely stretchable ACEL devices may lead to revolutionary EL fabrication, such as fully printable EL devices.

Chapter 7 concludes the approaches which are developed to achieve and advance the stretchable photodetectors and EL devices. Suggestions on the future works in stretchable optoelectronic devices are provided.

1.4 Findings and Outcomes

Our research leads to several novel outcomes:

1. Transparent and stretchable photodetectors were demonstrated for the first time. The photodetectors could be fabricated by an all-solution processible method. An efficient transfer method was developed to embed the NW structures into PDMS, imparting stretchability to the NW devices.

2. Highly stretchable ACEL devices with stable performance under stretching strains were demonstrated. The unique emission mechanism in the ACEL device was demonstrated to be critical to achieve stable emission performance under mechanical deformations.

3. Dielectric elastomer actuators were fabricated using AgNW networks as the compliant electrodes. The good transparency, high conductivity, thin structure, excellent mechanical compliance and self-clearing capability in the AgNW networks made them ideal candidates for the DEA electrodes. An unprecedented self-deformable EL device was demonstrated by integrating the DEA with the highly stretchable ACEL device.
4. Extremely stretchable ACEL devices were demonstrated by using ionic conductors as the stretchable and transparent electrodes. With the excellent stretchability in the ionic conductors, the extremely stretchable ACEL devices could achieve a stretchability of 700%.

References


Chapter 2

Literature Review

Stretchable optoelectronic devices are a new type of mechanical deformable electronics which are gaining increasing interests and believed to be one of the essential technologies for the next generation electronic applications. Apart from the simple bendable feature, the stretchable optoelectronic devices are required to withstand more demanding mechanical deformations with stretching strains beyond 10%. The excellent mechanical conformability in these devices enables them to maintain functionality under rigorous conditions with mechanical deformations such as flexing, twisting, stretching, and folding etc, leading to unprecedented applications that cannot be addressed with the conventional technologies. In this chapter, recent progresses in the stretchable optoelectronic devices are covered with focus on the approaches and materials that were developed to circumvent the difficulties in the enabling technologies.
2.1 Stretchable Photodetectors

Photodetectors are important electronic devices which can detect light stimuli and convert it into electrical signals. They have important applications in imaging system, biological threat detection, infrared night vision systems, flame detection and ozone hole sensing etc.\textsuperscript{1-3} Stretchable and conformable photodetectors which can be applied on arbitrary curvilinear surface or complied with large mechanical deformations will enable new integration systems such as wearable monitoring devices and electronic eye systems. Unfortunately, there are still limited studies demonstrating stretchable photodetectors due to the complicated patterning and assembling procedures to impart stretchability to the conventional photodetectors through the structural approaches, and the daunting difficulties of developing new functional materials to enable intrinsically stretchable photodetectors. These studies will be covered and discussed in the first section of this chapter.

2.1.1 Photodetector arrays with stretchable interconnections

The strategy to achieve stretchable photodetectors which can tolerate large stretching strains (>50\%) was firstly demonstrated by Rogers and coworkers. The light sensing element is based on Si with $n$-type and $p$-type doping. The photosensing mechanism for Si photodiode is illustrated in Figure 2.1a. In the depletion region, the photogenerated electrons will be swept to the $n$-side and the photogenerated holes will be swept to the $p$-side by the internal electrical field, leading to photocurrent in the device under photo-excitation. As the photodetectors are fabricated with Si thin film, the devices are rigid. Additional strategy is required to reduce strains on the photodetectors under mechanical deformations. As shown in Figure 2.1c, conventional planar device processing method was applied to pattern a passive matrix of photodiodes connected by thin metal interconnections. The patterned photodiodes array was transferred onto elastic substrate under strains. After releasing, most of the compression strains could be released through the thin metal interconnections which buckled into arc shapes in response to the mechanical
deformations.\textsuperscript{4} The strain encountered in the rigid photodetectors could be maintained below 0.2\% under the global strain of 30\%, analyzed with X-ray computed tomography and finite element method calculations.\textsuperscript{5} Consequently, device functionality could be maintained in the rigid photodetectors. Similarly, conformable photodetector arrays could also be achieved by patterning the thin metal interconnections into wavy structures (Figure 2.1c), which could accommodate the strains by changing the magnitude and length of the wavy structures.\textsuperscript{5}

\textbf{Figure 2.1} (a) A schematic of the Si photodiode. (b) A schematic of the energy band structure of the Si photodiode under light illumination. (c) A photograph (left) and SEM image (right) of photodetector arrays on hemispherical PDMS.\textsuperscript{4} Reprinted by permission from Macmillan Publishers Ltd: [Nature] [4], copyright (2008). (d) A schematic of the photodiode array connected by serpentine wires (left top) and optical image of a photodiode (left bottom). The right photograph is the photodiode array under hemispherical deformation.\textsuperscript{5} Reprinted by permission from Macmillan Publishers Ltd: [Nature] [5], copyright (2013).
2.1.2 Intrinsically stretchable photodetectors with NW networks

Different from the structural strategy discussed above, our group has demonstrated a fully and intrinsically stretchable photodetectors with NW networks. The sensing mechanism in the NW photodetectors is based on the light induced electron-hole pair separation, as shown in Figure 2.2a. With the large surface-to-volume ratio which contributes to largely prolong the lifetime of the photogenerated carriers and the direct pathway in the 1D structure which shorten the carrier transit time, NWs have been recognized as promising photosensing materials with high sensitivity. The photoconductive gain ($G$) in the NWs can be evaluated by the following equation:

$$G = \frac{\tau}{\tau_t}$$

where $\tau$ is the lifetime of the photogenerated carriers, and $\tau_t$ is the carrier transit time.

Figure 2.2b shows a schematic drawing of the NWs under illumination and dark conditions.\textsuperscript{8} The oxygen adsorption ($O_2+e^{-}\rightarrow O_2^-$) and desorption ($O_2^-+h^+\rightarrow O_2$) at the surface of the NWs are the important process contributing to increase the lifetime of the photogenerated carriers and thus leading to their high photosensitivity. However, due to the prolonged lifetime of the photogenerated carrier, switching time of the photodetectors will also be increased in the single-NW devices, as shown in Figure 2.2c. It has been widely reported that Schottky barrier can be utilized to modulate the sensing behavior of NW photodetectors.\textsuperscript{9-11} As the modulation only takes place at the Schottky barriers instead of the whole NW surface, it contributes an effective mechanism to improve the switching speed of the NW photodetectors.\textsuperscript{10} The NW-NW junction barrier in the network structure (Figure 2.2d) can be treated as two back-to-back Schottky barriers,\textsuperscript{12} contributing to enhance the response speed of the NW photodetectors. Besides, the NW network device can be easily fabricated with solution-processible methods such as spin-coating, vacuum filtration, drop-casting and spray coating \textit{etc}, delivering a cost-effective and large-scale assembly solution which is more promising compared to the expensive and delicate fabrication procedures required for single-NW photodetectors. The NW network structure is also important to achieve stretchable photodetectors which can accommodate large mechanical deformations through strain relaxation in the network structures.
Figure 2.2  (a) Energy band diagram of the NWs under photon excitation. (b) Oxygen desorption and adsorption process in the NW photodetector when the excitation light is on and off. Reprinted (adapted) with permission from (Soci, C., Zhang, A., Xiang, B., Dayeh, S. A., Aplin, D. P. R., Park, J., Bao, X. Y., Lo, Y. H. & Wang, D. Nano Letters 2007, 7, 1003-1009.). Copyright (2007) American Chemical Society. (c-d) Photodetectors with single NW and NW network as the photosensing channels.

In order to achieve uniform NW percolating films, a lithography filtration method, as shown in Figure 2.3a, was used to filtrate the NW solutions through polycarbonate membranes. The electrodes and photosensing channels for the photodetectors were patterned with different PDMS membrane masks during the filtration process. The NW patterns were then placed into a glass Petri dish and filled with liquid PDMS which will penetrate into the porous NW films and embed the NW structures. After curing of the PDMS, the devices were peeled off from the filter membrane with the NW films transferred and embedded in the stretchable PDMS matrix. As shown in Figure 2.3b, the NW photodetectors demonstrated excellent stretchability which could be strained up to 100%.
Figure 2.3 (a) Schematic drawing showing the fabrication procedure of stretchable photodetector array by lithographic filtration method. (b) Photographs showing the photodetectors under 50% and 100% stretching. Reproduced with permission from reference [13].

2.2 Stretchable EL Devices

Deformable EL devices drive special interests as they are expected to bring a plethora of new possibilities for the envisioned display-centric word in the near future which cannot be achieved with recent device technologies. With the special “soft” features, stretchable EL devices can be applied where demanding deformations are required such as 3D displays which can render contents physically and interactive displays which can provide users tactile interaction beside visual information. Prototype applications were demonstrated by MIT tangible media groups using 2D actuation arrays and a top projector to achieve dynamic shape displays. Another example was demonstrated by Sif Khan and known as the MegaFaces in 2014. These interesting and other unprecedented applications will not be limited on their huge and bulky platforms with the developed technologies for stretchable EL devices.

2.2.1 Emission mechanisms for stretchable EL devices

Light-emitting diodes (LEDs)

The electroluminescent mechanism of LEDs is based on charge injection and radiative recombination at the p-n junction. Figure 2.4a shows a schematic of a typical LED device structure which comprises a p-type layer and an n-type layer forming the p-n junction at
the interface (Figure 2.4b). Bottom and top electrodes are deposited on opposite sides of the device to form electrical contacts with at least one transparent electrode for light extraction. Under forward bias, electrons will be injected from the $n$-type layers into the $p$-type layers. The injected minority carriers will radiatively recombine with the majority carriers in the opposite side of the $p$-$n$ junction, leading to light emission.

**Figure 2.4** (a) A schematic showing the device configuration of a LED device. Energy band structures of the $p$-$n$ junction: (b) under thermal equilibrium; (c) under forward bias.

Both organic and inorganic materials have been investigated for LED devices. Though the quantum efficiency and longtime stability in the OLEDs are still lower compared to the ILEDs, the OLEDs are superior in certain features such as their good mechanical flexibility and low fabrication cost. The LEDs with stretchable emission structures based on organic materials have been successfully demonstrated utilizing the excellent flexibility in ultrathin OLED.\(^{18}\) On the contrary, ILEDs generally require high-temperature fabrication processes to deposit the single-crystalline inorganic layers, making it incompatible with most of the flexible or stretchable substrates. Alternative approaches are to develop effective methods to transfer the ILEDs from high-temperature compatible substrates onto flexible\(^{19,20}\) or stretchable substrates.\(^{21,22}\) Moreover, the transferred ILEDs are still required to be integrated with stretchable and transparent electrode before fully stretchable ILEDs can be achieved.

**Light-emitting electrochemical cells (LEC)**

The light-emitting electrochemical cell was introduced by Pei and co-workers in 1995 by doping the conjugated polymer with electrochemical reactions to form $p$-$i$-$n$ junction in the emissive layer.\(^{23}\) The LEC devices have simple device structure with a single
electroluminescent layer, as shown in Figure 2.5a. They have shown promising performance with rather simple device structures and low-cost fabrication processes. Intensive study has been conducted in the field and a number of review papers on LECs are available in the literatures.\(^{24-29}\) The emission mechanism of LEC devices is similar to LED devices which are based on charge injection from the \(p\)-type or \(n\)-type layers, followed by radiative recombination. Different from conventional LEDs, the LECs only consist of a single emissive layer with mixtures of dissolved salts, ionic conductors and electroluminescent materials. The \(p-i-n\) junctions can be \textit{in situ} formed by external electrical bias which leads to electrochemical doping of the EL materials in the opposite sides, as illustrated in Figure 2.5b. The \(p-i-n\) junctions can be locked and preserved by restricting mobility of the dopants after the junction formation with different strategies such as temperature cooling or polymerization of the ionic dopants. Compared to the conventional LEDs, the LECs possess advantages of reduced complexity in the device fabrication, automatically achieved efficient and balanced charge injection, and applicable thick emissive layers for low-cost fabrication process. These features make the LEC an ideal candidate for stretchable EL devices. First of all, the single-layer device architecture helps to circumvent the difficulties in the multi-layer device configuration in LED devices. Stretchable materials with corresponding functionalities for the different layers are still needed to be developed for the stretchable LED devices. Mechanical matching between these layers are also a critical challenge to resolve in order to maintain good interfaces between these layers under mechanical strains. Secondly, the highly doped polymers in the LECs have good conductivity at the electrode and polymer interfaces, leaving the undoped polymer as the effective emission region. As a result, there is no rigorous requirement on the work function of the electrodes to achieve effective charge injection. It should be noted that, LEDs require high work function anode and low work function cathode. And in most cases, additional charge transport layers are required between the emissive layer and electrodes in order to achieve balanced charge injection, leading to more complicated device architectures. On one hand, the thick polymer structure of the LEC devices simplifies the deposition process with more adoptable methods such as spin-coating, drop-casting and screen-printing \textit{etc}. On the other hand, it improves the mechanical properties
of the emissive layer with reduced defects and non-uniformities which induce stress concentrations and degrade the material stretchability in the thin film structure.\textsuperscript{24}

Collectively, the LECs possess inherent structural advantages for stretchable EL devices compared to the conventional LEDs. However, these devices still need to improve their switching speed and long-term stability before wide applications are possible. Besides, the LECs are similar to the LED devices in the emission mechanism (based on charge injection and subsequent radiative recombination). Performance of the devices is highly sensitive to the variations in the electrode conductivity. The characteristic has become a limiting factor for the LECs to achieve stable device performance under large stretching strains. As it is still challenging to fabricate stretchable and transparent electrodes for EL devices with stable conductivity under high stretching strains,\textsuperscript{30,31} the stretchable LECs still suffer from dramatically degraded performance under high stretching strains.\textsuperscript{32,33} The problem is still very difficult to resolve without the development of new materials or strategies for highly conductive, stable, transparent and stretchable electrodes.

Figure 2.5 (a) Schematic illustration of the simple EL device architecture comprising a single emissive layer, top electrode, and transparent bottom electrode. (b) Formation of a $p$-$i$-$n$ junction in the LEC device under external electrical bias.

Apart from the EL devices discussed above, electrophoretic devices which change between the white and black color on the movement of the charge pigments by external applied bias\textsuperscript{34-36} and electrochromic devices which utilize materials that change their optical properties in their oxidizing or reducing states\textsuperscript{37,38} are rarely investigated in the stretchable structures. Nevertheless, it is believed that their great potentials will be recognized soon.
for stretchable display applications with their extremely low power consumption, simple device architecture and cost-effective fabrication procedure.

2.2.2 Partially stretchable EL devices

Electrodes with stretchable structure

Stretchable EL devices assembled with rigid ILEDs and stretchable electrical interconnections on elastomers are representative samples that conventional techniques can be recombined to achieve exceeding new applications by changing the underlying strategies. 21, 22, 39-42 In these devices, the light-emitting elements are bonded device islands which encounter very small strains under mechanical deformations (the maximum strain in the ILEDs is ~0.17% with 24% strain applied on the whole device). Most of the strains are relaxed by the highly stretchable interconnections designed to isolate the light-emitting elements from significant strains. The challenges in these devices are narrowed down to the fabrication of stretchable electrical interconnects and integration of the rigid light-emitting elements. Successful demonstrations were reported by Rogers and coworkers. 40 Stretchable interconnects were fabricated by designing thin metal films in their serpentine or “wavy” structures bonded onto elastic substrates, as shown in Figures 2.6a and 2.6b. The wavelength and amplitude of these “wavy” structures can change in response to the applied strains. Strains on the interconnections are mainly induced on the structures so that the flexible metal thin film can easily accommodates the reduced deformations. Multiple-step lithography and etching processes were required to pattern the anchor points (for easy device transfer after fabrication on rigid substrates) and “wavy” interconnecting structures (for stretchable electrical connections). After gold electrodes were evaporated, the stretchable electrodes were transferred onto an Ecoflex elastomer. Purchased LED devices (dimensions of 1 mm×0.6 mm× 0.2 mm in length, width and thickness correspondingly) were then carefully aligned to the electrical contacts and bonded onto the elastic substrate by transfer printing. The EL device arrays could be uniaxially stretched to a peak strain of 200% with no significant variation in the performance of the EL devices.

Similar idea was also demonstrated to fabricate biaxially stretchable EL devices with different patterning processes, which is showed in Figure 2.6c. 39 Different from the
previous design with a “wavy” structure, the devices used an arch-shape interconnect which could buckle out of plane from the underlying substrate. Instead of being transferred onto a relax substrate, the devices were bonded onto a prestrained PDMS balloon after the device structures were patterned. After the substrate was released, the thin electrical interconnects resulted in buckling structures with non-coplanar layouts in response to the compressing strains. The compressing strains were converted into flexing strains which can be accommodated by the metal thin film. As long as the deformation was limited by the strains below the prestrain values, the interconnects could be repetitively stretched and released with the device performance maintained invariant even after 100,000 deformation cycles. Compared to the in-plane “wavy” structures, the buckling interconnects required much lesser space on the elastomer to accommodate similar strains, reducing the pixel size of the packed LEDs. Moreover, with the stretchable interconnects designed in the orthogonal directions, the devices could sustain different modes of deformations such as biaxial strains, twisting, shear and related strains.
Figure 2.6 (a) The circuit model of the LED arrays for stretchable EL devices, consisting of blue and red LEDs connected reversibly. (b) The blue or red LEDs were controlled to turn on or off by reversing the applied bias under unstretched states (left photographs) and under 140% strain (right photographs). Reproduced with permission from reference [41]. (c) An optical image of an array of µ-ILEDs connected by non-coplanar serpentine metal bridges on a PDMS substrate. The right image is a schematic illumination of a single device with a representative device shown in the inset photograph. (d) An optical image of the stretchable EL device conformably attached onto a sharp pencil tip. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] [39], copyright (2010).

Electrodes with stretchable materials

Though the stretchable electrodes based on patterned structures have shown good performance for the stretchable EL devices, their fabrication required multiple patterning and etching steps to achieve the designed structures on rigid supporting substrates. Efficient transfer methods were also needed to be developed to tether the fabricated devices on elastic substrates after the complicated lithography and etching processes. The vacuum evaporation, photolithographic patterning and mechanical bonding process make the fabrication processes difficult to scale up with cost-effective approaches. To avoid the difficulties, different strategies are required.
The direct usage of stretchable materials was demonstrated to be a straight-forward method which can circumvent the fabrication difficulties of the stretchable structures. Single-wall carbon nanotube (SWNT) paste was reported by Sekitani et al as a promising material for stretchable electrodes.\textsuperscript{43} The conductive inks were prepared by mixture of SWNT and ionic liquid in 4-methly-2-pentanone to form black paste-like gels. After successively mixed with a fluorinated copolymer (vinylidenefluoride–tetrafluoroethylene–hexafluoropropylene) which was also dissolved in 4-methly-2-pentanone, the resultant composite gel became conductive rubber after dried. The composite gel could be directly patterned onto elastic substrate by screen printing through shadow masks in the gel form, forming intrinsically stretchable electrical interconnects after dried. Conductivity of the rubber could be tailored by varying the SWNT contents in the composite. Increasing the SWNT amount could significantly improve conductivity of the rubber. The stretchability of the conductive rubber would be decreased with a trade-off effect. With the SWNT content higher than 6 wt\%, conductivity of the rubber was above 50 S/cm while the stretchability would decrease below 40\%. Figure 2.7a shows the stretchable conductor printed on elastic PDMS substrate. The OLEDs fabricated separately with the conventional process were laminated onto the stretchable interconnects to achieve rubber-like stretchable LED display, as demonstrated in Figure 2.7b. Compared to the stretchable metal thin film structures, the idea of printable conductive gel on elastic substrate was proved to significantly reduce the fabrication difficulties. Inspired by the strategy, many ideas have also been reported to fabricate stretchable electrodes with different stretchable conducting materials. For example, Kim et al had fabricated stretchable electrodes with reduced electrical conductivity under increased stretching strains, as shown in Figure 2.7c.\textsuperscript{42}\textsuperscript{44-50} Nickel powders mixed in PDMS were used as the conductive ink which was exposed to high magnetic field to align the nickel powders vertically to the polymer surface before the PDMS curing. The conductor showed unique property with rapidly decreased resistance under increased tensile strains, attributed to the increased conducting paths with more nickel powders in contacts under strains. Many other filler, such as nanotubes, nanoplates, nanoparticles and textiles, were also demonstrated to be promising materials that could be embedded into the elastic polymer matrix for stretchable electrodes.
Figure 2.7 (a) A photograph showing the stretchable elastic conductor printed on a PDMS substrate using a SWCNT paste (left inset photograph) with linewidth of 100 µm (micrograph image on the right inset). (b) A photograph of a stretchable display fabricated by assembling active-matrix OLED arrays. The stretchable display can be attached onto arbitrarily curved surfaces. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] [51], copyright (2009). (c) Blue LED devices connected by elastic conductor with negatively strain-dependent resistance. Reproduced with permission from reference [42].

2.2.3 Fully stretchable EL devices

The devices discussed above depend on stretchable conductors either by structural or material strategies, leaving the challenge of obtaining stretchable light-emitting elements unresolved. To achieve fully stretchable EL devices, the difficulties of developing stretchable light-emitting elements become impossible to avoid. As discussed above, due to the structure complexity, it is rather demanding to achieve stretchable LED devices in their multi-layer structures. Stretchable materials for the corresponding layers have not yet been fully developed. Nevertheless, the successful approach which used structural designs
to achieve stretchable interconnects with metal thin film was also proved to be applicable on the LED devices. The material difficulties might be overcome with the stretchable structures while the challenges were turned onto the stretchable structure fabrication. As shown in Figure 2.8a, to meet the extreme flexing conditions that would be confronted in the stretchable structures, ultra-thin PLEDs were fabricated onto a 1.4 µm PET foil which was adhered on a rigid substrate. The ultrathin PLEDs were fabricated in similar procedures with the conventional PLED devices. The PEDOT:PSS was used as the transparent electrodes, poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV) derivative or poly[2-methoxy-5(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) was used as the light-emitting polymer, and LiF/Al was used as the back contact. After being peeled off from the rigid substrate, the resultant device thickness was around 2 µm. With the significant reduced thickness, the device could accommodate flexing with radii of curvature under 10 µm. The ultrathin PLEDs were then pressed and attached onto prestrained elastomeric adhesive tapes. Similar to the arch-shape interconnecting structures in Figure 2.6c, the thin devices could form bulking structures to relax the compressing strain when the prestrained tapes were released. The final devices could be crumpled (Figure 2.8b) or stretched to the maximum strain state at the prestrained position (100% stretching strain, Figure 2.8c).
Figure 2.8 (a) Schematic drawing of the ultrathin PLEDs. (b) Photographs of the ultrathin PLEDs under crumpling test. (c) Photographs of the ultrathin PLEDs adhered onto prestrained elastomer tape. The PLEDs bulked to accommodate the strains after the elastomer was relaxed and the devices can be stretched back to the prestrained state. Reprinted by permission from Macmillan Publishers Ltd: [Nature Photonics] [18], copyright (2013).

In a different way, difficulties in the stretchable LEDs were circumvented with new materials developed to fabricate fully stretchable LECs, which possess simpler device architecture. Pei’s group has been developing the technologies in stretchable LECs and reporting leading works in the area. Figure 2.9a illustrates the fabrication procedure of the stretchable LEC device. The transparent and stretchable electrodes were fabricated by embedding thin AgNW film into stretchable polymers. Briefly, AgNWs were firstly spray-coated onto a glass substrate, forming random NW network. To achieve better conductivity and transparency in the NW networks, AgNWs with larger length are beneficial. After the coating process, copolymer of siliconized urethane acrylate (UA) oligomer and ethoxylated bisphenol A dimethacrylate (EBA) were poured onto the
percolating NW network, following by subsequent curing with ultraviolet light. Though the embedding polymers might not be limited to PUA polymer, properties of the polymers such as the glass transmission temperature, stretchability, transparency and bonding force with the NW network to be transferred will need to be considered for the polymer selection. With weak bonding interactions between the polymers and conductive networks, insufficient transfer will occur and lead to dramatic conductivity degradation in the thin and transparent layers. After the stretchable and transparent electrodes were achieved, the electroluminescent layer consisting of a blend of a yellow light-emitting polymer (a poly(para-phenylenevinylene) copolymer known as SuperYellow), ethoxylated trimethylolpropanetriacrylate (ETPTA), PEO and LiTf was subsequently spun after the stretchable electrodes was protected by a thin layer of PEDOT:PSS. The SuperYellow is a light-emitting material with high molecular weight which can maintain its functionality under large strains. The ETPTA and PEO are the stretchable ionic conductors that transport ions from the LiTf. Top stretchable electrodes were prepared with the same process and laminated onto the emissive layer to complete the device fabrication.

With the device structures fully constituted of stretchable materials, the PLEC device can accommodate large mechanical deformations with stretching strains up to 120% before device failure, as shown in Figure 2.9b. The PLEC could achieve the emission intensity of 320 cd/m² at the applied voltage of 16 V, as shown in Figure 2.9c. The external quantum efficiency of the PLEC devices was calculated to be 4%, comparable to state-of-the-art performance of EL devices based on SuperYellow fabricated with other electrodes. Emission intensity of the device reduced with the increased stretching strains, as illustrated in Figure 2.9d. The brightness reduced for ~85% at 120% strain (compared to the initial brightness at 0% strain) which was attributed to the increased resistance in the stretchable electrodes. Cycling stretchability of the devices was limited at 30%. The device performance deteriorated dramatically when the stretching strain was 40% or higher, which was contributed to the limited stretchability of the light emitting layer and gradually degraded electrical conductivity of the electrodes. Pinholes were observed in the EL layers after stretching and the density of the pinholes increased as the stretching cycles increased, indicating the limited stretchability of the EL layers.
Figure 2.9 (a) A schematic showing the fabrication process of the stretchable PLECs. (b) Images of a PLEC device wrapped around a cardboard with 400-μm thick and stretched to a maximum strain of 120%. (c) Current density and luminance characteristics of the PLEC under different driving voltages. (d) Change of the luminance and current density of the PLEC with increased strains (biased at 12 V). (e) Cycling stability of the PLEC device at 30% strain. Reprinted by permission from Macmillan Publishers Ltd: [Nature Photonics] [32], copyright (2013).

2.2.4 Unprecedented applications with stretchable EL devices

The excellent mechanical conformability in the stretchable EL devices make them possible to keep conformable contacts with static or dynamic curvilinear surfaces, easily comply to external pressures with maintained functionality, be driven to arbitrary shapes with internal
forces and other promising properties. Some of the unprecedented applications in stretchable EL devices are reviewed as followed.

Wirelessly powered implantable light-emitting systems

Applications of the stretchable EL devices includes biomedical devices which can be implanted onto parts of the human body to accelerate wound healing, activate photosensitive drugs, or image of the internal tissues. A system with the design of stretchable EL device connected with a spiral inductor coil was demonstrated by Kim et al., as shown in Figure 2.10a.\textsuperscript{41} The inductor coil can inductively couple the electrical field in radio frequencies and convert it into voltage output to power the connected ILEDs. As shown in Figure 2.10b, with the “soft” nature, the wireless ILED system could be laminated conformably onto a mouth model and covered with dermis. The ILEDs could be lighted up by the primary coil through inductive coupling for potential applications of implantable and biocompatible systems.
Figure 2.10 (a) A schematic of the wireless μ-LED device design. The spiral inductor coils are used to power the connected μ-LED wirelessly. Inset pictures show the enlarged top interconnects and wireless coil design. (b) Optical images of the wirelessly powered μ-LED laminated onto a mouse model (left) and covered with dermis (right). Reproduced with permission from reference [41].

User-interactive electronic skin

By integrating the OLED arrays with thin-film transistor and pressure sensor, Wang et al. have demonstrated a user-interactive electronic skin which could provide direct and quantified visualization of the applied pressure on the devices. Figure 2.11a shows the schematic of the integrated devices. The OLED device was connected between a nanotube TFT (independently control the on and off states of the OLED) and a PSR. Conductivity of the PSR increased with the applied pressures, leading to increase of the emission intensity from the OLED to provide instant quantified visualization on the applied pressures, Figures 2.11c and d. The user-interactive system will find interesting applications in automotive control panels, interactive input devices, robotics and health monitoring devices.
2.3 Challenges in Stretchable Photodetectors

As discussed in the review, studies in the stretchable photodetectors are still quite limited. Different materials, device structures and fabrication approaches are required to be developed. The reported structural approach uses complicated patterning and transferring processes to achieve stretchable interconnects with metal thin films,\textsuperscript{4,5} which is rather difficult to develop into cost-effective and large-area assembly. With an alternative strategy, stretchable photodetector was demonstrated by patterning functional NWs with a lithography filtration method.\textsuperscript{13} The stretchable photodetector used thick and opaque NW films (dozens of micrometers) for both the stretchable electrodes and photosensing
channels. Switching speed in the thick NW film with fully embedded structure was significantly prolonged with the reduced oxygen concentration around the NW surfaces. Switching speed of the stretchable NW photodetectors requires to be improved. Moreover, efficient transfer method has not been demonstrated to embed thin and transparent NW network into the PDMS matrix. Most of the reports on stretchable NW structures in PDMS are based on thick and opaque NW films.\cite{13,44} Efficient transfer methods need to be developed to embed thin NW films into the polymer matrix for stretchable and transparent device structures.

### 2.4 Challenges in Stretchable EL Devices

Similarly, many challenges and hurdles still exist in the enabling approaches for stretchable EL devices. The stretchable ILEDs based on rigid and discrete emission elements encounter the problems of large pixel sizes as a large portion of the substrate is consumed by the electrical interconnects to enable stretchable structures. Many research topics will also need to be covered in the strategy such as the manipulation between materials with largely varied mechanical properties, adhesion and interface science between the different layers for endurable device operations. More importantly, a cost-effective approach is required for the patterning, transferring and bonding processes. On the other hand, intrinsically stretchable EL devices based on PLECs show significantly simplified fabrication procedures with all-solution processible approaches. A critical challenge in the stretchable PLECs is their dramatically deteriorated device performance under high stretching strains. Stretchable conductors with good transparency and stable conductivity under strains are the major challenge. Further improvements are also required in the newly developed LEC devices, especially stabilization of the dynamic junctions after the $p$-$i$-$n$ junction formation, which is directly related to the key figures of the devices in their response time, efficiency and long-time stability.

### 2.5 PhD Studies in Contest with Literature

In this thesis, we focus on investigating new materials and device structures to enable stretchable photodetectors and EL devices, aiming to resolve the challenges as discussed
above. For the stretchable photodetectors, we develop an all-solution assembly method to fabriecate photodetector arrays. The low-temperature spray-coating method is cost effective which can be easily scaled up for large-area device fabrication. High efficient transfer method is developed to embed thin and transparent NW structures into PDMS for stretchable and transparent photodetectors. NWs that are partially embedded in the polymer matrix can be effectively transferred for stretchable device with the developed method, contributing to improve the switching speed of the NW photodetectors.

The ACEL devices are investigated as promising alternatives to achieve stable emission behavior under large mechanical strains. The ACEL devices possess the advantages of simple device architecture, no rigorous requirement on the electrode materials, and thick emission layer for easy deposition process, which are preferable features for stretchable EL device fabrication. Besides, ACEL devices have been commercialized since 1960s with their emission behavior, device performance and material systems well established. The stretchable ACEL devices can be fabricated with all-solution processible methods which deliver simple device fabrication and enable integration with other functional device components, resolving the challenge of complicated device fabrication approaches in stretchable EL devices. The unique emission mechanism in the ACEL devices provides the advantage to achieve stable EL performance under large strains, which can circumvent the difficulties in LEC devices or other devices that require highly stable and conductive transparent electrodes. Stretchability of the emission layer in the ACEL devices can also be easily improved using different elastic polymer to embed the emissive particles, enabling further improvement in the stretchability of the ACEL devices.

References


Chapter 3

Experimental Methodology

Material and device structure designs are important approaches to realize stretchable optoelectronic devices. This chapter first presents the rationale for our material selection to achieve stretchable photodetectors and EL devices. The techniques applied to characterize the morphology and structure of the nanomaterials, the electrical, optical, and mechanical properties of the devices are then introduced. Finally, the device structures and the fabrication approaches of the stretchable devices will be discussed in detail.
3.1 Rationale for Materials Selection

3.1.1 Ternary oxides NWs for stretchable UV photodetectors

Photosensing behavior of the semiconducting NWs is one of the most promising NW applications that has been extensively investigated. The high surface-to-volume ratio and 1D electrical pathway are recognized to make the NWs ideal candidates for photodetectors with high photosensitivity.\(^1\) As discussed in Chapter 2, the photoconductive gain \((G)\) in the photoconductors is determined by the lifetime of the photogenerated carriers \((\tau)\) and the carrier transit time \((\tau_t)\): \(G = \tau/\tau_t\). With the large surface-to-volume ratio which contributes to largely prolong the lifetime of the photogenerated carrier and the 1D pathway in the active area which contributes to reduce carrier transit time, NWs have demonstrated excellent photosensitivity.\(^1\)-\(^9\)

Ternary oxides NWs are large bandgap materials (ZGO has the bandgap of \(E_g=4.6\) eV; ZTO has the bandgap of \(E_g=3.6\) eV), which are particularly interesting in UV light detection for applications such as biological threat detection, optical communication, and missile tracking etc. The conventional Si photodetectors have encountered the limitation of low efficiency and high dark current in UV light detection. The generated electron-hole pairs by the UV radiation are close to the highly recombinative surface states in the Si photodetectors.\(^10\) Costly and bulky high pass optical filters are required in these devices to avoid optical crosstalk due to the small bandgap in silicon \((E_g=1.1\) eV). Application of large bandgap semiconductors can eliminate the insertion of optical filters, providing miniaturized UV photodetectors. Recent reports on the large bandgap nanomaterials such as In\(_2\)Ge\(_2\)O\(_7\) nanowires,\(^11\) \(\beta\)-Ga\(_2\)O\(_3\) nanostructures,\(^12,13\) and Zn\(_2\)GeO\(_4\) NWs\(^14,15\) have shown promising performance in UV light detection. Investigation in the ternary oxides NWs for stretchable UV photodetectors will provide promising solutions to tackle the challenges with the conventional Si photodetectors.

Another interesting feature of the NWs is their intrinsically mechanical flexibility. The NWs can be easily assembled for large-area devices with bottom-up approaches such as, drop-casting, spin-coating, vacuum filtration and spray-coating etc, which can deliver solution-processible and cost-effective fabrication approaches. They have been widely
applied for flexible photodetectors with simple fabrication approaches and promising photosensing performance.\textsuperscript{16-21} The intrinsic flexibility and low-temperature assembly approaches in the NW photodetectors possess great potential to enable stretchable devices with simple and solution-processible fabrication methods.

3.1.2 ACEL materials for stretchable EL devices

Different from the LED or LEC devices, emission mechanism in the ACEL devices is based on field-induced excitation of the luminescent centers in the phosphors. Emission in the ACEL devices includes multiple steps: charge injection into the phosphor layers, acceleration of the charge carriers under high electrical field, impact excitation of the luminescent centers by high-energy electrons, radiative relaxation of the luminescent centers in the host materials, as shown in Figure 3.1b. With the unique emission mechanism, the ACEL devices have simple device architecture with a single emissive layer sandwiched between two electrodes, as shown in Figure 3.1a. Besides, the ACELs do not require rigorous requirement on the electrode work functions for charge injection. The devices consist of thick emissive layers in the range of 50-100 µm. These features are the key factors making the ACEL device an ideal alternative to achieve fully stretchable EL device. The ZnS doped with different elements such as Cu, Al and Mn et al is known to achieve different emission colors. A comprehensive review on the materials with their preparations and properties for ACEL devices can be found in the book edited by D. R. Vij.\textsuperscript{22}

Figure 3.1 (a) A schematic of the ACEL device architecture comprising a single emissive layer, top electrode, and transparent bottom electrode. (b) Emission process in the ACEL devices under electrical field excitation.
Emission brightness of the ACELs using powder phosphors can be expressed by the following relation:

\[ B = B_0 \exp\left(-b/V^{0.5}\right) \]

where \( B_0 \) and \( b \) are constants that are determined by the particle size of the phosphors, concentration of the EL powders in the dielectric materials, the dielectric constant of the embedding medium and the device thickness.\(^{23}\) Figure 3.1b is the energy band structure interpreting the emission model in the EL powders.\(^{24,25}\) The ACEL devices are capacitively coupled to the external electrical bias with small displacement current. Emission behavior of the device is mainly determined by the applied bias with less dependence on the resistance variation in the electrodes.\(^{26}\) The emission behavior is quite different from the LED devices or LEC devices which are highly dependent on the electrode conductivity to achieve large charge injections (dozens to hundreds of mA/cm\(^2\)) for light emission. The unique emission behavior provides the ACEL devices remarkable benefit to achieve stable device performance under large mechanical deformations which will be demonstrated in Chapter 5 and 6.

### 3.2 Synthesis

#### 3.2.1 Ternary oxides NW growth

The ternary oxides NWs were synthesized by a CVD system through the VLS mechanism. Equipment setup for the synthesis is an Elite furnace equipped with vacuum pump, gas gauge, and two mass flow controllers for precise control of pressure and gas flow during NW growth, as shown in Figures 3.2a and b.
Figure 3.2 (a) Schematic of the chemical vapor deposition system.\textsuperscript{27} Reprinted (adapted) with permission from (Yan, C. & Lee, P. S. The Journal of Physical Chemistry C 2009, 113, 14135-14139). Copyright (2009) American Chemical Society. (b) Temperature gradient of the furnace. Position of the source materials and substrates in the furnace.

The VLS is a 1D growth technique by the assistance of metal catalyst. It was first demonstrated by Wager and Ellis in 1964\textsuperscript{28} for single crystal silicon growth. Direct observation of VLS NW growth was also demonstrated by Wu and Yang on a high-temperature \textit{in situ} TEM,\textsuperscript{29} which provided direct evidence and better understanding on the growth process. The VLS process can be explained by the schematics in Figure 3.3. The small metal catalyst, for example Au, was first coated on a substrate. The catalyst forms metal alloy by absorbing vapors in a high temperature environment in the alloying process. With increasing vapor condensation and dissolution, the metal alloy becomes supersaturated and begins the nucleation process in which chemical components in the alloys are driven to precipitate and nucleate at the interface. Once the nanocrystal nucleates at the liquid/solid interface, further condensation/dissolution of vapor into the alloy system will increase the amount of crystal precipitation from the alloy. The precipitation prefers to diffuse to the existing solid/liquid interface, primarily due to the fact that less energy will be involved with the crystal step growth as compared with secondary nucleation events in a finite volume. The existing interface will then be pushed forward (or backward) to form a nanowire.\textsuperscript{29}
Figure 3.3 Schematic images of the VLS growth process of NWs.

Source materials for the NW growth were prepared by homogenously mixing the chemicals with desired molar ratios. The source powders were then transferred into a 30 mm diameter quartz tube and inserted into the furnace. Pure Ar or Ar mixed with Oxygen was used as the carrier gases for different sample preparation. The flow rate and composition ratio of carrier gases were controlled by two accurate mass flow controllers. Si substrates coated with thin Au film (~10 nm, sputter coating) were used to collect the nanowires in the low temperature region.

**Synthesis of ZGO NWs**

Carbon powder, ZnO, and GeO$_2$ in molar ration of 4:2:1 were used as source materials which were placed at the temperature region of 1000 °C. The Au coated Si substrates were placed at the temperature region of 400-500 °C for NW collection. Temperature of the furnace was ramped to 1000 °C at a rate of 15 °C/min and kept under the temperature for 60 min. The carrier gas was argon mixed with 17 sccm O$_2$ with pressure maintained at 2 mbar in the furnace. After the NW growth, the furnace was allowed to naturally cool down to room temperature. The synthesized samples were collected and sent for characterization.

**Synthesis of ZTO NWs**

Carbon powder, ZnO, and SnO$_2$ in molar ration of 4:2:1 were used as source materials. Growth process of the ZTO NWs were similar to the ZGO NWs growth except that the oxygen flow rate is set at 15 sccm and the Au coated Si substrate were placed at 300-400 °C for the ZTO NW growth.
3.2.2 Stretchable polymer matrix

Silicone elastomers are important classes of viscoelastic materials. They share the similar molecular backbone consisting of alternating silicon and oxygen polymeric chains, as shown in Figure 3.4a. Due to the very flexible silicon-oxygen bonds (Figure 3.4b), the polymer chains in the silicone elastomer enable high level of elasticity. Silicone elastomers have wide applications in the industry or daily life with their good thermal stability, high stretchability and biocompatibility. The silicone elastomers can be vulcanised by mixing two parts of compositions which undergo hydrolysis reaction with catalysts and cross-link to form the siloxane polymer. Depending on the repeat unit (n) and the degree of cross-linking, the physical properties of the silicone elastomers, such as the tensile strength, elongations and shore hardness, can be varied.

Commercially available silicone elastomers, PDMS (Dow Corning, Sylgard 184) and Ecoflex (Smooth-on, Supersoft 0050), are used for our device fabrications. The PDMS is one of the promising materials for stretchable electronics with good biocompatibility, high stretchability at room temperature, excellent optical transparency and ease of molding down to the nanometer scale.\textsuperscript{10,11} The elastomer possesses a tensile strength of 980 psi and elongation of 120%. The PDMS elastomer can be fabricated by mixing the PDMS base and curing agent in the weight ratio of 10:1 which can be cured at 60 °C in two hours. The Ecoflex Supersoft 0050 is another silicone elastomer with a tensile strength of 315 psi and elongation of 980%. The Ecoflex can be fabricated by mixing two parts of precursors of Supersoft 0050A and 0050B in the weight ratio of 1:1 which can be cured at room temperature in \textasciitilde30 min.

\begin{figure}[h]
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\includegraphics[width=0.8\textwidth]{figure3_4}
\caption{(a) Chemical structure of the polysilicone. (b) Flexible Si-O bonds under strains.}
\end{figure}
3.3 Characterization

3.3.1 SEM

Morphology of the NW was characterized by SEM (JEOL 6340F, JEOL 7600F), which can provide high resolution down to nanometers, larger magnification and higher depth of field, making it an important instrument for topography and morphology characterization of nanomaterials. Resolution of the SEM system is limited primarily by the wave nature of the electrons, as shown in the Abbes Equation:

\[
d = \frac{0.61\lambda}{NA}
\]  

(1)

where \(d\) is the minimum resolvable distance, \(\lambda\) is the wavelength of the energy source and NA is the numerical aperture of the system. As the energy of the electrons is determined by the operating voltage of the SEM, increasing the electron accelerating voltage will reduce the \(\lambda\) and increase the resolution. However, the high energy electrons might travel deep into the sample surface depending on samples, reducing the signals from the sample surfaces. Figure 3.1 shows a schematic of the SEM system. Electron beam in the SEM system can be electromagnetically shifted by the scanning coils to produce scanning patterns. The scanning rate and scanning area can be controlled electronically to control the magnification on the images.

![Figure 3.5 A schematic of the SEM system.](image)

3.3.2 XRD

Crystal structures of the NWs are investigated by X-ray diffraction (Shimadzu XRD-6000, Cu Ka radiation). Mechanism of the X-ray diffraction is shown in Figure 3.6, the X-ray is
scattered by the crystal lattices and creates interference patterns in the reflected waves. Maximum intensity is observed in the interference patterns when the diffraction angle $\theta$ satisfy the Bragg’s law:\footnote{31}

$$N\lambda=2d\sin \theta$$

where $N$ is the wavelength number, $\lambda$ is the wavelength of the x-ray, $d$ is the lattice constant of the crystal.

![X-ray diffraction on crystal lattices.](image)

The Shimadzu power XRD system is used to characterize the as-synthesized NWs on Si substrates (500 µm) in the range of 20-80° with the X-ray incident angle set at 0.5°. The obtained diffraction data was exported into the software “Match” for further analysis.

### 3.3.3 Optical measurement

Electroluminescence of the devices was characterized by a spectrometer, which includes a monochromator (Acton SP-2356) and thermoelectric-cooled CCD (Princeton PIXIS: 100), as shown in Figure 3.7a. Emission from the devices was collected by a 7-core fiber and coupled into the monochromator. Gratings in the monochromator dispersed the incoming light to a focus plane with a highest resolution of 0.30 nm in the system. The thermoelectric-cooled CCD was cooled down to -75 °C when recording the spectra in order to reduce the background noise. The maximum enquiry speed of the CCD is ~10 ms/frame. Luminance of the devices was measured by a Konica CS-200 spectroradiometer (Figure 3.7b).
Figure 3.7 (a) A photograph of the spectrometer. (b) A photograph of the Konica CS-200 spectroradiometer.

3.3.4 Stretching test

Stretching test of the sample was performed on a home-made motorized linear translation stage at room temperature. The translation stage was controlled by a CL-01A stepper motor controller, which could be programmed to achieve different translation operations on the stage. Performance of the devices under different stretching strains was measured by elongating the devices to corresponding positions on the stage. Mechanical stability test of the device was carried out by programming the controller for repetitive translations between the strained and relaxed positions. Figure 3.8a is a photograph of the stretching stage. Figure 3.8b shows an ACEL device under stretching test.

Figure 3.8 (a) A photograph of the home-make stretching stage. (b) A photograph of the ACEL device under stretching test.
3.4 Device Fabrication

3.4.1 Spray-coating of nanowire

Spray-coating of the nanowire was carried out with a hand-held spray-gun (Figure 3.9a, right) which has a nozzle size of 0.5 mm. Compressed gas was fed into the spray gun at the pressure of ~0.5 MPa. The spray-coating process is carried out when the compressed gas is released and driven through the small nozzle, producing the spray plume containing air-solution mist. Generally, the NWs were dissolved in IPA with a concentration of 0.1-0.5 mg/ml. The fast evaporation rate of IPA is beneficial to simplify the coating process. Heating was not required on the substrates during the spray-coating process, making it feasible to use a wide-range of flexible or stretchable substrates. The spray-coating process provides a simple solution-processible approach to achieve homogenous coating of NWs networks, as shown in Figure 3.9b.

![Figure 3.9](image)

**Figure 3.9** (a) A schematic of the spray-coating process and a photograph of the spray-gun. (b) A SEM image of the NW networks fabricated by spray-coating process.

Compared to other solution coating process, the spray-coating approach possesses advantages of high throughput, low requirement on the solution stability and substrate conditions, capability of patterning with shadow masks, making it ideal for the AgNW
electrode fabrication. Table 3.1 provides comparison between the spray-coating method with other solution coating methods.

**Table 3.1 Compare between different solution coating methods**

<table>
<thead>
<tr>
<th>Solution coating methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Spray coating</td>
<td>- High throughput and fast coating process</td>
<td>- Spray coating conditions vary systematically</td>
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<td></td>
<td>- Suitable for large-area and complex shaped substrates</td>
<td>- High surface roughness</td>
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<td>- Capability of patterning with shadow mask</td>
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<td>Spin coating</td>
<td>- Reliable and reproducible</td>
<td>- Require flat surface</td>
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<td></td>
<td>- Suitable for thin film coating (&lt;100 nm)</td>
<td>- Not scalable</td>
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<tr>
<td></td>
<td>- Fast coating process</td>
<td>- Require material recycling</td>
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<td></td>
<td>- Uniform coating</td>
<td>- Sensitive to solution properties and surface conditions</td>
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<td>Dip coating</td>
<td>- Simple and flexible</td>
<td>- Require large amount of coating liquid</td>
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<td></td>
<td>- Suitable for large-area and complex shaped substrates</td>
<td>- Low deposition rate</td>
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<td>- Feasible for double-side coating</td>
<td>- Require good stability in the solution</td>
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<td>- Suitable for multiple layer deposition</td>
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<tr>
<td>Roll coating</td>
<td>- Suitable for large-area coating</td>
<td>- Require high solution viscosity</td>
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<td></td>
<td>- High speed coating process</td>
<td>- Require material recycling</td>
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<td>- Suitable for single- or double-sided coating</td>
<td>- Require flat surface</td>
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<td>- Thickness can be easily adjusted with different rollers</td>
<td>- Not suitable for thin-film coating (coating thickness generally larger than 1 µm)</td>
</tr>
<tr>
<td>Vacumm filtration</td>
<td>- Fast coating process</td>
<td>- Not scalable</td>
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<td>- Capability of patterning with shadow mask</td>
<td>- Require film transferring from the filter paper</td>
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<td></td>
<td>- Suitable for thick film coating (coating thickness can be larger than 100 µm)</td>
<td>- High surface roughness</td>
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3.4.2 Fabrication of flexible photodetector

The functional NWs for photosensing channels (ZGO NWs) were grown on Si substrates by the chemical vapor deposition (CVD) system as described above. The NWs were removed from the substrates with sonication for 15 min and dispersed in IPA at a concentration of ~0.1 mg/ml. The purchased AgNWs (Seashell Technology) have the diameters of 120-150 nm and lengths of 20-50 µm. The AgNWs can be synthesized with the widely adopted polyol method, as illustrated in Figure 3.10a.\textsuperscript{32,33} The AgNWs solution was diluted to 0.5 mg/ml in IPA before use. Figure 3.10b illustrates the fabrication procedure of the flexible photodetectors. The ZGO NWs were firstly spray-coated onto the PET substrate through a shadow mask, forming the photosensing channels. Subsequently, AgNWs were coated analogously through another shadow mask, forming the transparent and conductive percolating AgNW networks. The resultant photodetectors had a channel length of 0.15 mm and channel width of 1.2 mm. Typically, 2 ml of ZGO NW solution and 1 ml of AgNW solution could be used to coat onto a substrate area of 2×2 cm.

![Figure 3.10](image)

**Figure 3.10** (a) Synthesis of AgNWs with the polyol method. (b) Fabrication process of the flexible photodetectors by spray-coating method.

3.4.3 Fabrication of stretchable and transparent conductor

The AgNW networks were fabricated with the spray-coating process. The SEM image of the transparent and conductive AgNW networks is shown in Figure 3.9b. The AgNW
networks were annealed at 200 °C for 20 min to remove the PVP capping agent on the NW surface and create fusion between the AgNWs. Sheet resistivity of the AgNW film was significantly reduced after the annealing process. Liquid PDMS mixed with different amount of fluorosurfactant Zonyl-FS300 was poured onto the AgNW coated substrate, degassed for 30 min in a vacuum desiccator to allow the liquid to penetrate and wrap around the NW network. After that, the samples were transferred into an oven to cure the PDMS overnight at 110 °C. The resultant AgNWs/PDMS conductors were peeled off from the glass substrate for further characterization. The fabrication process is illustrated by the schematic images in Figure 3.11.

![Schematic images](image)

**Figure 3.11** Processes for embedding AgNW networks into PDMS for transparent and stretchable electrodes.

### 3.4.4 Fabrication of stretchable ACEL device

The transparent and stretchable electrodes for the ACEL devices were fabricated with AgNW networks on PDMS substrate, which will be embedded into the elastic polymer matrix with subsequent layer deposition. The PDMS elastomer was prepared by mixing the base and curing agent (Sylgard 184, Dow Corning) in the weight ratio of 10:1. The liquid mixture was degassed and thermally cured at 60 °C for two hours. The ZnS:Cu micro-particles (Shanghai KPT company) were mixed with the PDMS liquid in a weight ratio of 2:1. The ZnS:Cu/PDMS composite was deposited onto the bottom electrode by spin-coating at a spin rate of 2000 rpm for 120 s. The composite was also thermally cured at 60 °C for two hours. After curing of the emissive layer, the top electrode was fabricated analogically with a thin layer of AgNW network. Finally, another PDMS layer was spun
onto the AgNW network to embed the conductive network and complete the device fabrication. A schematic of the device structure is shown in Figure 3.12.

![Schematic of the device structure](image)

**Figure 3.12** A schematic of the architecture of the ACEL device.

### 3.4.5 Fabrication of self-deformable EL device

As shown in Figure 3.13a, an elastic substrate (3M VHB tape) was firstly prestrained and fixed onto a rigid frame. The AgNW solution was sprayed on both sides of the elastomer film to form the bottom and top electrodes for the DEA device through a shadow mask. The stretchable EL device was integrated onto the DEA with the fabrication procedures described above. The ZnS:Cu/PDMS ratio was 1:2 to reduce effective elastic modulus of the emission layer, as large elastic modulus will hinder actuation performance of the device. Silver paste was coated at the edges of the AgNW networks as electrical contacts to the external circuit.
3.4.6 Fabrication of extremely stretchable ACEL devices

Preparation of ionic conductor: The PMMA (average Mw= ~350,000), LiClO₄, PC, and acetonitrile were purchased from Sigma-Aldrich and used as received. 0.75 g of LiClO₄ was firstly dissolved in 2 g of PC. After the LiClO₄ was fully dissolved, 7.86 g of acetonitrile was mixed with the solution. One and a half gram of PMMA was slowly added into the blended solution and stirred at 1000 rpm overnight. Viscous and clear gel-like solution was obtained after the PMMA was fully dissolved.

Fabrication of the extremely stretchable ACEL devices: The ionic gel prepared as described above was deposited onto a 3M VHB tape (thickness of 1 mm) with the thickness of ~100 µm by doctor-blade coating. The ionic conductor was then dried in an oven for 6 hours at 60 °C to allow the acetonitrile fully evaporated, leading to a solid polymer film for subsequent layer deposition. A commercially available silicone elastomer, Ecoflex 00-50 was used as the polymer matrix to enable high stretchability in the emissive layer. The silicone elastomer was prepared with 1 part Ecoflex 00-50 A and 1 part Ecoflex 00-50 B (Smooth-On). ZnS:Cu micro-particles were mixed with the Ecoflex solution in the weight ratio of 1:1. The prepared ZnS:Cu/Ecoflex composite was then coated on the ionic conductor by doctor-blade coating with the thickness controlled at ~200 µm. The composite was allowed to cure under room temperature for 2 hours. Another ionic gel layer
in the thickness of ~100 µm was subsequently coated as the top electrode. Copper tape or graphite paper was used to electrically connect the ionic conductors with the external power source. The VHB tape with the thickness of 0.5 mm was laminated on top to seal the whole device structure and complete the device fabrications.

![Schematic of device configuration](image)

**Figure 3.14** A schematic showing the device configuration of the extremely stretchable ACEL device.

### 3.5 Overview of Methodologies

In this chapter, we first discuss the rationale for our material selections for the stretchable photodetectors and EL devices. The NWs provide high photosensitivity for the photodetectors and possess great advantages to achieve stretchable structures with simple and cost-effective assembly approaches. The simple device architecture and unique emission behavior in the ACEL device make it ideal candidate for stretchable EL device fabrication with stable emission performance under large mechanical deformations.

The growth mechanism of NWs and the NW growth system were introduced, followed by discussion on the stretchable polymer used to impart stretchability to the device structures. SEM and XRD were used to characterize the morphology and structure of the synthesized NWs. The optical and mechanical properties of the stretchable devices were characterized with a spectrometer, a spectroradiometer, and a motorized stretching stage.
Spray-coating of NWs was developed as a promising assembly method to fabricate NW devices. Fabrication of the flexible and transparent UV photodetector were first introduced. Based on the NW assembly method, a surfactant assistant approach was introduced to fabricate stretchable and transparent conductors by embedding the AgNW networks into PDMS. The device design and fabrication approach for stretchable EL devices with the solution-assembly AgNW electrodes and ACEL particles were presented. Finally, the fabrication approach of the extremely stretchable ACEL devices was introduced by using the ionic conductors as the stretchable and transparent electrodes.

References


Chapter 4

Highly Deformable and Transparent Photodetectors

Transparent and highly deformable electronic devices are of great interest for emerging applications in conformable and wearable devices. The capability to fabricate optically transparent and mechanically deformable photodetectors paves the way to the next-generation integrated “see-through” devices. In this chapter, a solution-assembly method will be demonstrated to integrate NWs for transparent photodetectors. The solution-assembly approach is firstly demonstrated on flexible substrate with un-embedded NW network structures for flexible photodetectors. Photosensing properties of the flexible photodetectors are investigated. With the developed solution-assembly method for NW device fabrication, an efficient transfer method is introduced to embed the NW network devices into stretchable polymer matrix, improving the mechanical properties of NW networks and obtaining stretchable, transparent photodetectors.
4.1 Introduction

Stretchable devices are emerging as “soft” electronics which can be mechanical deformed and conformably wrapped onto surfaces with arbitrary curvilinear. They possess exceeding mechanical compliance compared to the conventional rigid or flexible devices, enabling applications where rigorous mechanical conditions need to be confronted. Among these soft devices, stretchable photodetectors can convert light stimuli information into electrical signal. They can be integrated with biological systems such as monitoring devices on textiles, electronic eye cameras with special curvilinear surfaces, wearable infrared light detection systems for night vision, and many other applications as well. However, research works which have been demonstrated to enable stretchable photodetectors are still quite limited. Reported studies include hemispherical imaging systems which patterned thin and wavy metal thin films for stretchable interconnects and assembled conventional rigid silicon photodetection elements onto elastic substrates.\(^1\)\(^2\) However, the fabrication process for these stretchable photodetection systems required complicated lithography and transfer steps. The approach to achieve stretchable and transparent photodetectors are yet to be developed, which will have important applications for integration with smart window, foldable display and other transparent electronic devices.

Semiconducting NWs have attracted special interest for photodetection applications,\(^3\)\(^-\)\(^9\) which are also widely recognized as promising materials for flexible devices with their inherent flexible 1D nanostructure.\(^10\)\(^11\) The NWs can be deposited onto flexible or stretchable substrate by low temperature coating process such as: inkjet-printing, spin-coating, drop-casting or spray-coating \textit{etc.}, which are critical to meet the aspects of cost-effective fabrication and large-scale assembly. The ITO is normally exploited as the transparent electrodes in previous reports on transparent photodetectors. However, the ITO electrodes are brittle and require high temperature for deposition, which have become the limiting factors to improve the device flexibility and develop low-temperature processible approaches for device fabrication. On the other hand, percolating metal NWs have been attracting increasing interest as promising alternatives for transparent electrode fabrication with their good conductivity, solution processability, high transparency and excellent flexibility.\(^12\)\(^-\)\(^17\) The AgNW is an ideal candidate which can be easily synthesized in large
scale through the polyol process. The AgNWs percolating films have been demonstrated with excellent conductivity of $\sim 10 \ \Omega/\text{sq}$ with the transparency of $\sim 90\%$.

Hereby, we first develop a solution-assembly method to demonstrate that high-performance flexible and transparent photodetectors can be fabricated with all the device structures consisting of functional NW networks. The solution-assembly method meets the requirement of low-temperature processability which is critical for its compatibility with flexible and elastic substrates for highly deformable devices. Directly depositing thin NW networks on top of flexible or stretchable substrates can provide an efficient approach to achieve flexible device structures. However, additional strategies are required to improve the mechanical performance in the exposed NW network structures which can be easily displaced under larger mechanical deformations, such as stretching. To tackle the problem, a surfactant-assisted transfer method was demonstrated to transfer NW films into the PDMS polymer matrix. After embedding the thin and transparent percolating NW films into the stretchable polymers, stretchability of the NW structures could be significantly enhanced. A stretchable and transparent UV photodetector based on all-NW structures was demonstrated for the first time.

### 4.2 Experimental Methods

#### 4.2.1 Flexible and transparent photodetector fabrication

The ZGO NWs were firstly synthesized on Au coated Si substrates by a CVD method. The AgNWs and ZGO NWs were assembled with a spray-coating method for the flexible and transparent photodetectors. Detail fabrication procedure on the device was described in Chapter 3, Section 3.4.2. The channel length and channel width of the resultant photodetectors were 0.15 mm and 1.2 mm respectively. Different dimensions in the device configuration can also be achieved with different shadow masks.

#### 4.2.2 Stretchable and transparent photodetector fabrication

The surfactant assistant transfer method was first developed with the fabrication of transparent and stretchable AgNW conductors which can be found in Chapter 3, Section
3.4.3. Stretchable and transparent photodetector was then demonstrated by combining the developed approaches.

Similar to the flexible NW photodetector fabrication, the synthesized ZTO NWs were first dispersed into IPA after removed from the substrate. The NW solution with a concentration of ~0.1 mg/ml was sonicated for 15 minutes before used for the spray-coating process. After patterning the ZTO NW network and AgNW network, liquid PDMS mixed with Zonyl was poured onto NW networks to bury the device structures. After the PDMS was fully cured, stretchable and transparent photodetectors could be achieved by peeling the PDMS composites from the substrates.

4.2.3 Characterization

Morphologies of the sample were characterized with a field-emission SEM (FE-SEM, JSM 7600F). Diffraction patterns of the NWs were measured on a Shimadzu XRD-6000 instrument. Transmittance spectra of the photodetectors were measured on the Shimadzu spectrometers (UV-2550 and UV-3600). A Keithley 4200-SCS parameter analyzer with PreAmp models was used to characterized the electrical properties. A UV lamp with the wavelength of 254 nm and 365 nm was used to applied light stimuli to the photodetectors. The bending test on the flexible photodetectors and stretching test on the stretchable photodetectors were both carried out on a home-made translation stage, as described in Chapter 3. The photodetector performance was measured when the stage compressed the flexible photodetectors to different bending angles or stretched the stretchable photodetectors to different strains.

4.3 Result and Discussion

4.3.1 Flexible and transparent photodetectors
Figure 4.1 (a) A schematic showing the device structure of the transparent and flexible photodetectors. Photographs of the transparent and flexible photodetectors (b) placed on a paper and (c) bended by hands. Reproduced by permission of The Royal Society of Chemistry. (d) Device configuration of Si photodiode for UV detection with high pass optical filter. (e) Large bandgap NW photodetector for UV detection without the requirement of optical filter.

A schematic of the NW photodetector is shown in Figure 4.1a. The flexible and transparent photodetectors consist of AgNW networks as the transparent electrodes and ZGO NW network as the photosensing channels. The large bandgap in the ZGO NWs \( (E_g=4.6 \text{ eV}) \) eliminates the requirement of high pass optical filter, which is necessary for the low
bandgap materials (such as Si, $E_g=1.1$ eV) to prevent false detection, as illustrated in Figures 4.1d and e. The photodetectors were patterned into a five by five array on the flexible PET substrate. Excellent transparency could be achieved in the photodetector. Letters could be clearly seen through the flexible photodetectors, as shown in Figure 4.1b. The NW photodetector had good mechanical flexibility which can be subjected to repetitively bending and releasing cycles, as shown in Figure 4.1c. No obvious deformation or pealing of the device structures could be observed after the bending test. Due to light scattering by the NW networks, haze appearance was observed on the device structures.

The SEM images of the AgNWs and ZGO NWs were shown in Figures 4.2a and b respectively. After the VLS growth, white and furry product with large amount of ZGO NWs was achieved on the silicon substrate (around 10 mg of nanowires was produced on a 1×1.5 cm substrate). As shown in Figure 4.2b, the ZGO NWs were quite homogenous with a high aspect ratio (diameter of ~100 nm and length of ~100 µm). Figure 4.2c shows a top SEM image of the photodetector at the interface of the device’s channel and electrode. The NW network on the right side of the dashed line composed of pure AgNWs. The region on the left side of the dashed line consisted both AgNWs and ZGO NWs, establishing interconnects between the electrode and photosensing channel. The XRD patterns in Figure 4.2d confirm that pure ZGO NWs have been achieved by the VLS growth, which have a rhombohedral crystal phase (JCPDS: 011-0687, $a=14.231$ Å, $b=9.53$ Å). The synthesized ZGO NWs with high crystallinity are believed to have important contribution to the high photosensitivity of the NW devices, which will be further discussed below.
Figure 4.2 Morphology characterization by SEM: (a) AgNWs; (b) ZGO NWs; and (c) NW networks assembled by spray-coating method, locating at the interface region of the device’s electrode and photosensing channel. (d) XRD characterization of the ZGO NWs. Reproduced by permission of The Royal Society of Chemistry.

The NW photodetector shows a high transmittance of ~80% in the wavelength range of ~300-1000 nm. It should be noted that the transmittance of the pure PET substrate is around 90%, as shown in Figure 4.3a. Only the directly transmitted light through the device was measured by the ultraviolet-visible spectroscopy. Consequently, the device transmittance value might also be underestimated as the scattered light transmitted through the device was not considered. Figure 4.3b presented the electrical characteristic of the photodetector under UV light (250 nm) and dark condition. It is noticed that an asymmetric I-V characteristic exists in the device when the UV light is on, which is attributed to that the contact conditions between the electrodes and channels might be different at the opposite sides of the devices. A nonlinear I-V curve can be observed in the photodetector which indicates that energy barriers exist in the device. The photodetector has a low dark current of around 10 fA with the bias of 10 V. Two possibilities are considered to contribute to the low dark current in the ZGO NW photodetectors. First of all, the intrinsic ZGO NWs have low carrier intensity of $1.78 \times 10^{17}$ cm$^{-3}$ (reported by Liu.
et al.\textsuperscript{22}). Secondly, Schottky barrier exists between the AgNW and ZGO NW due to mismatch between the conduction band edge of ZGO NWs (located at around -3.80 eV) and the work function of AgNWs (located at around -4.30 eV). Besides, energy barriers will also exist between the ZGO NW junctions through the large channel length (0.15 mm). The two energy barriers contribute to suppress the dark current to a small value. Significant change in the current is observed in the photodetector when the 250 nm UV light (~0.2 mW/cm\textsuperscript{2}) is on. The current reaches at 30 pA, 3000 times higher compared to the dark current. The on/off ratio is close to the best result reported in the literature,\textsuperscript{20-24} while the fabrication approaches are much simpler and promising for large-scale assembly in this study. The photocurrent increases significantly and reaches the maximum value in less than 5 s after illuminated with the UV light, as presented in Figure 4.3d. The dark current can also be recovered promptly after the UV light is off, below 2.6 s. It should be noted that the respond and recovery times of the photodetector are overestimated here and the fastest measurement time is limited by the equipment due to the extremely low dark current in the NW photodetectors. Nevertheless, the respond time in the NW network device is improved compared to the reported device fabricated with single ZGO NW (12 s).\textsuperscript{20} The improved respond time and photosensitivity in the NW network devices are attributed to the combined effects of the Schottky barriers and NW junction barriers in the NW network structures as discussed above. Under light illumination, the Schottky barrier height will be lowered and its width will be narrowed.\textsuperscript{25-27} Similar effects were also reported on NW junction barriers in the network structures.\textsuperscript{21} Current transport behavior in the photodetector is dominated by the modulation of the barrier height and width in the network structure under light illumination. Under dark condition, the carrier transport is significantly suppressed by the energy barriers. When the UV light is on, the barrier height and width will be reduced, leading to a gating effect which contributes to largely increase the current in the device. In addition, the modulation only takes place at the interface instead of the whole NW surface, contributing addition mechanism to improve the switching speed of the photodetectors.\textsuperscript{26}
Photoresponse of the NW device was measured when the photodetector was bended to different angles to examine the mechanical property of the flexible devices, as shown in Figure 4.4a. The bending angle (2θ) is defined in Figure 4.4b inset. Small variation in the photocurrent is observed under the mechanical deformations with a ~12% decrease in the photocurrent when the bending angle is increased to 90°. The decrease could be due to that the induced tensile strain in the NW networks will lead to displacement at the NW junctions, affecting the photocurrent as a result. The displacement may also increase the resistance of the network structures, leading to the photoresponse drift under bending. The effect is more obvious under higher bending states. However, the contact conditions could be recovered after the bending was released and good cycling stability could be achieved in the flexible device with the repetitively bending and relaxing test. As shown in Figure 4.4b, the dark current was almost constant in the photodetectors after bended to an angle of 90° for 50,
100 and 150 cycles. Small variation in the photocurrent is observed which decreases 1.2% after 150 bending cycles compared to the initial photocurrent before bending. In conclusion, a highly flexible and transparent photodetector with good stability has been successfully fabricated with comparable mechanical properties against previous works.\textsuperscript{10,11,28} Remarkably, the fabrication approach is much simpler and easier with solution-processability and large-scale assembly. The results also suggest that the developed approach is encouraging for fabrication of other NW based flexible and transparent devices.

Figure 4.4 (a) Photosensing behavior of the flexible device under different bending angles. (b) Mechanical stability test of the flexible photodetectors after bending for different cycles.\textsuperscript{18} Reproduced by permission of The Royal Society of Chemistry.
4.3.2 Stretchable and transparent photodetectors

Figure 4.5 Top SEM characterizations on the surfaces of (a) AgNWs/PDMS composite without Zonyl; (b) glass substrate after the AgNWs/PDMS without Zonyl was peeled off; (c) AgNWs/PDMS composite with ~11 wt% Zonyl; (d) glass substrate after the AgNWs/PDMS with ~11wt% Zonyl was peeled off; (e) Chemical structures of PDMS and Zonyl. Interactions between the AgNWs and PDMS with and without Zonyl are illustrated on the right. Reproduced by permission of The Royal Society of Chemistry.
With the developed spray-coating method to fabricate flexible and transparent NW photodetectors, further improvement on the mechanical property of the NW devices is investigated. Conductive fillers (such as AgNW networks) have been demonstrated to possess significantly improved stretchability after embedded into PDMS.\textsuperscript{9,30} However, the conductive films used in these studies are in the thick and opaque structures (several μm in thickness), efficient embedding and transferring methods have not been demonstrated to achieve thin and transparent conductive NW structures in PDMS. Consequently, we firstly explored on transferring thin and transparent AgNW films into PDMS. Homogenous AgNWs network was firstly coated onto the glass substrates and used to investigate the NW transfer efficiency by PDMS elastomer. The transfer with pure PDMS polymer was firstly studied. As shown in Figure 4.5a, limited amount of AgNWs is observed on the PDMS surface after the embedding and transferring process. Most of the NWs are fully buried under the surface of the polymer. The transferred NWs distribute sparsely in the polymer matrix with limited interconnection observed between the NWs. Resistance of the AgNW networks are dominated by the junction resistance at the NW interconnections. The limited interconnections in the NW networks lead to high resistance in the electrode composite which exceeded the measurement range of our equipment. An alternative approach was also studied by increasing the AgNW film thickness, attempting to compensate the interconnection loss during the transfer process. No substantial reduce in the resistivity was observed in the AgNW/PDMS composite though the transparency had dramatically reduced to ~40% due to the increased film thickness. Surface of the supporting substrate was investigated after the transfer process with pure PDMS. As shown in Figure 4.5b, a large amount of AgNWs remained on the substrate after the transferring, indicating that large damage has been induced in the conductive NW network.

The surface energy of PDMS is around 20 mJ/m\textsuperscript{2}.\textsuperscript{31} The interaction between the NWs and the PDMS matrix is weak (Dupre equation: \( W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \), where \( W_{12} \) is the work of adhesion between the two surfaces, \( \gamma_1 \) and \( \gamma_2 \) are the surface energy of the two different materials, and \( \gamma_{12} \) is the interfacial tension) and insufficient to transfer AgNWs from the surface of the substrates. The NWs can only be transferred by the PDMS matrix when most
part of the NW is covered by the polymer, as illustrated in Figure 4.6a. It is also evidenced in Figure 4.5a which shows that most of the NWs in the electrode composite are fully covered and located underneath the PDMS surface. The result suggests that stronger interaction between the NWs and the polymer matrix is necessary to achieve efficient transfer process. Zonyl has been used to improve the interaction between PEDOT:PSS and PDMS with its amphiphilic nature. Zonyl has both fluorinated and ethylene glycol segments, as shown in Figure 4.5e. The ethylene glycol group in Zonyl will lead to strong chemical coupling with the AgNWs surface through O-Ag bonding. Improved bonding strength between the polymer matrix and AgNWs surface is expected with the present of Zonyl. Figure 4.5e shows the chemical structures of PDMS and Zonyl. The interactions between the AgNWs and PDMS with and without Zonyl are also presented on the right of Figure 4.5e. Indeed, significant improved transfer efficiency was obtained after adding Zonyl into the PDMS, verified both by the increased amount of NWs on the surface of the resultant electrodes (Figure 4.5c) and the increased conductivity in the elastic electrodes. Comparing Figure 4.5d to Figure 4.5b, it is also obvious that all the NWs have been transferred into the stretchable polymer matrix with the high-efficient transfer process.
Figure 4.6 (a) A Schematic illustrating the transfer of AgNWs by PDMS with and without Zonyl. (b) The SEM images on the surface of the AgNW/PDMS composite electrodes with different weight ratio of Zonyl.

The PDMS with small weight ratio of Zonyl (7.7%) had shown increased transfer efficiency compared to pure PDMS. As shown in Figure 4.6b, more NWs have been transferred after the peeling process compared to pure PDMS. However, ideal transfer has not been achieved and exfoliation sites are observed on the surface of the elastic electrode, as indicated by the red arrows in the SEM image. When the weight ratio of Zonyl was increased to ~11%, the best transfer efficiency was achieved. All the NWs had been
transferred into the stretchable polymer with no exfoliation sites observed on the surface. The conductivity of the resultant elastic electrodes remained almost identical to the initial conductivity on the glass substrate. It was shown that after the weight ratio exceeded ~11%, increase of the Zonyl weight ratio did not help to increase efficiency in the transfer process. On the contrary, larger amount of Zonyl would further prolong the PDMS cross-linking time and lead to an inferior rough surface in the final electrode composite. Plenty of wrinkles were presented on the surface of the elastic electrodes.

Figure 4.7 (a) The transmittance spectrum of the stretchable and transparent electrode. Inset shows the photograph of the stretchable and transparent electrode beside a commercial ITO glass. The scale bar is 1cm. (b) Resistance change of the stretchable and transparent electrode under different tensile strains. (c) Mechanical stability test of the stretchable and transparent electrode with different stretching cycles. (d) Photographs showing a LED device lighted up by the integrated stretchable and transparent electrode in the electrical circuit. The LED device maintains light emission when the elastic conductor is stretched to 80% strain. Reproduced by permission of The Royal Society of Chemistry.
Transparency of the elastic electrode under different wavelength is shown in Figure 4.7a. The stretchable and transparent electrode has a low sheet resistivity of 4.5 Ω/sq. And the transmittance is around 80% at the wavelength of 550 nm, comparable to commercial ITO/glass which typical has a sheet resistance of 10 Ω/sq and transmittance of ~85%. Improvement in the transparency of the elastic electrode can be achieved if longer AgNWs are used for the electrode fabrication which can further reduce the junction resistance between the NWs.\(^{19}\) Electrical properties of the elastic electrode were measured when it was stretched to different strains. The resistance change \(\Delta R/R_0\) (\(\Delta R=R-R_0\), where \(R\) is the resistance under strains, \(R_0\) is the initial resistance before deformation) upon stretching is shown in Figure 4.7b. The stretchable electrode demonstrated good conductivity even with tensile strains increased to 100%. With tensile strains below 50%, resistance in the stretchable electrode increased slowly, which was mainly attributed to the increased length in the conducting path (\(R=\rho L/A\), \(R\) is the resistance, \(\rho\) is the resistivity of the conductor, \(L\) is the length of the conducting path, and \(A\) is the cross-section area of the conductor). After the tensile strains exceeded 50%, the resistance increased steeply and the \(\Delta R/R_0\) reached 32.8 at the tensile strain of 100%. When the elastic electrode was released, the resistance variation was similar to the variation under increased strains. Mechanical stability test on the elastic electrode was carried out on a new sample with the tensile strains limited between 0-50%, as presented in Figure 4.7c. The stretchable electrodes maintained conductive after the stretching cycles. Increase in the resistivity was observed in the stretchable electrode as the stretching cycles increased, which could be attributed to the NW displacement in network structures under the mechanical deformations, which is still difficult to avoid in the stretchable and transparent electrodes with NW network structures.\(^{34,35}\) To demonstrate stretchability of the elastic electrodes, a LED device was connected in a circuit with the stretchable electrode, as shown in Figure 4.7d. The LED could remain the light emission when the stretchable electrode was elongated to 80% strain. As expected, increased resistivity was observed in the elastic electrode under the high stretching strain, indicated by the reduced brightness in the LED device. Nevertheless, the stretchability and mechanical stability of the elastic conductor with the embedded NW structures were much better comparable to previous studies with AgNW networks directly deposited on PDMS substrates.\(^{36,37}\) And the performance of our elastic conductor was
comparable to other distinguished works reported with different stretchable polymer matrix used for the embedding and transferring process.\textsuperscript{34,35}

![Image](image_url)

**Figure 4.8** (a) A schematic showing the device architecture of the stretchable UV photodetector. (b) A photograph of the stretchable UV photodetector. (c) Electrical characteristic of the unstrained UV photodetector when the UV light is on and off. (d) Photoresponse of the stretchable device with periodical on/off (60 s/60 s) UV light.\textsuperscript{29} Reproduced by permission of The Royal Society of Chemistry.

Based on the developed high-efficient transfer method, more complicated device structures such as NW photodetectors which have been demonstrated in the first part of this chapter can also be effectively transferred into the polymer matrix to achieve stretchable devices. Similar to the flexible NW photodetectors fabrication, transparent electrodes of the device were firstly fabricated with the AgNWs network, which were followed by the photosensing NW networks deposition with another shadow mask. Other NW device configurations can also be realized by simply changing the shadow masks. The ZTO NWs were synthesized and used as the photosensing materials with their well-known high photosensitivity and UV light selectivity.\textsuperscript{38} The schematic of the device was shown in Figure 4.8a. Spacing between the strips is around 0.5 mm. Photograph in Figure 4.8b shows a fabricated elastic
UV photodetector which shows high transparency. I-V curve of the elastic photodetector is presented in Figure 4.8c. The linear I-V curve indicates that good ohmic contact is achieved between the AgNWs (work function is located at around -4.3 eV) and the ZTO NWs (conduction band edge is located at around -4.94 eV).\textsuperscript{39} Photoresponse behavior of the unstrained device is presented in Figure 4.8d. The UV photodetector showed fast and stable respond to the UV light which was repetitively on/off with the period of 60/60 s.

Mechanical property of the stretchable device was examined with the photodetector stretched uniaxially along the channel direction, as shown in Figure 4.9a. Photoresponse of the detector under different stretching strains is presented in Figure 4.9b. Photoresponse behavior could still be maintained in the stretchable device with the tensile strain up to 50%. The photocurrent was observed to decrease with the increasing tensile strains. Photosensing mechanism in the NW photodetector is based on the photogenerated electron-hole pairs under light illumination, which contribute to increase the carriers in the NW channels. Lifetime of the photogenerated carriers (τ) and the transit time of the carriers (τᵣ) are the two major parameters affecting the photocurrent of the device under light stimuli. Photoconductive gain \( G \) of the photodetector can be given by the following equation:\textsuperscript{5,40}

\[
G = \frac{\tau}{\tau_i} = \frac{\mu V \tau}{l^2}
\]  

(1)

where \( \tau_i = \frac{l^2}{\mu V} \) (\( l \) is the channel length of the device, \( \mu \) is the carrier mobility and \( V \) is the applied voltage). \( G \) is also proportional to the photocurrent \( I_{ph} \) (\( I_{ph} = I_{illumination} - I_{dark} \)):\textsuperscript{8,41}

\[
G = \frac{I_{ph}}{P_{opt} / h\nu}
\]  

(2)

where \( P_{opt} \) is the absorbed optical power, \( q \) is the elementary charge, \( h \) is the Planck constant, and \( \nu \) is the frequency of the absorbed photon. After combining Equation 1 and Equation 2, one can derive that:

\[
I_{ph} = \frac{P_{opt} q \mu V \tau}{hvl^2}.
\]  

(3)

From equation 3, the photocurrent has a reciprocal relation with the square of the channel length when the incident light intensity and the applied voltage remain constant. Variation in the photocurrent under different channel length is plotted in Figure 4.9c. Good
agreement between the experiment data and the fitting line (based on the relation between the photocurrent and channel length deduced above) was obtained.

Switching behavior of the elastic photodetector under different strains is shown in Figure 4.9d. It could be observed that the photodetector responded promptly when the UV light was on. The maximum photocurrent could be achieved in less than 0.8 s. Recovery time of the photodetector was around 3 s, which was defined as the time required for the photocurrent to decrease to $1/e (37\%)$ of the maximum value. No dependence was observed between the switching time and the stretching strains. The switching time was improved compared to reported study on stretchable photodetector with fully embedded NW structures. The response/reset time was reported to be ~30/6 s at 0% strain which will further increase with increased tensile strains. It is understood that the switching behavior of the NW photodetectors will be significantly affected by the surrounded oxygen concentration. The fully embedded NW networks in the polymer matrix would lead to an oxygen deficient condition, hindering the response speed of the NW photodetectors. Increasing the tensile strain will equivalently reduce the oxygen concentration around the NWs surface (the polymer chains will be laterally compressed onto the NW surfaces to reduce the contact area between the NW surfaces and air), contributing to increase the switching time in the elastic photodetector. In comparison, the elastic NW photodetectors fabricated with the developed high-efficient transfer method consist of plenty NWs with exposed surface above the elastic PDMS matrix, providing more oxygen on the NW surfaces for fast switching speed. And the change in the oxygen concentration around the NWs is negligible under tensile strains as most of the NW surfaces are exposed to the atmosphere, leading to a stable switching behavior under mechanical deformations. Switching speed of the elastic NW photodetectors was close to ZTO NW devices on SiO$_2$/Si substrate, which showed a response/recovery time of 0.46 s/ 0.42 s.
Figure 4.9 (a) Photographs of the elastic NW photodetector under different tensile strains. (b) Photoresponse of the elastic NW photodetector under different tensile strains (c) Experiment data and the fitting curve under different tensile strains. (d) Switching behavior of the elastic NW photodetector within a single on/off cycle under different tensile strains. Reproduced by permission of The Royal Society of Chemistry.

4.4 Conclusions

In summary, transparent and flexible photodetectors with all-NW structures were successfully demonstrated. The photodetector arrays were fabricated with a solution-assembly method. The NW photodetector showed a good transparency at around 80% in the visible light range. Excellent flexibility and electrical stability were also achieved in the NW network device, which could be repetitively bended to an angle of 90°. The features of 1D structure, high material purity, and good crystallinity of the ZGO NWs contributed to high photosensitivity in the NW photodetectors. Photocurrent of the ZGO NW detectors reached 3000 times of the dark current. The Schottky barriers between the Ag-ZGO NWs and the energy barrier in the NW-NW junctions in the NW network structures contributed to improve the switching speed of the NW photodetectors.
With the developed approach to assemble NW devices, we established an effective transfer method to embed the transparent NW thin film structure into stretchable polymer matrix for transparent and stretchable photodetectors. The underling mechanism was to impart stretchability to the NW networks with the elastic polymer matrix which help to protect the NW networks under mechanical deformations and provide restoring force to the NW networks after the strains are released. To resolve the challenge of weak interaction between the NWs and the PDMS polymer matrix which leaded to nonideal transfer, Zonyl fluorosurfactant was used to improve the chemical interaction between the NWs and the polymer. A stretchable conductor fabricated with AgNW thin film was firstly demonstrated with the developed high-efficient transfer method. The conductors had a sheet resistivity of 4.5 $\Omega$/sq and transmittance of 80% at 550 nm. With the developed approaches for NW devices assembly and high-efficient NW transfer, a transparent and stretchable UV photodetector could be successfully fabricated. The photodetector tolerated tensile strain up to 50% with good photosensing performance maintained in the device. With the partial embedded NW structures, switching speed of the photodetector could be improved compared to fully embedded device structure, showing the respond time below 0.8 s and the reset time of around 3 s. The developed solution-assembly approach can be widely applied for other NW device fabrication. The elastic and transparent photodetector may find broad applications which can be integrated onto textiles or dermal for wearable and implantable electronic devices.

References


Chapter 5

Highly Stretchable and Self-Deformable ACEL Devices

Stretchable EL devices are a new type of mechanical deformable electronics which are gaining increasing interests and believed to be one of the essential technologies for the next generation lighting and display applications. Apart from being bendable like the traditional flexible EL devices, the stretchable EL devices are required to withstand more demanding mechanical deformation and accommodate stretching strains beyond 10%. The excellent mechanical conformability in these devices enables them to maintain stable performance under rigorous mechanical conditions such as flexing, twisting, stretching, and folding etc. The stretchable EL devices can be conformably wrapped onto arbitrary curvilinear surface and respond seamlessly to the external or internal force, leading to unprecedented applications that cannot be addressed by the conventional technologies. A solution-assembly approach has been developed in the previous chapter to fabricate transparent and stretchable NW films for both electrodes and photosensing channels. In this chapter, the developed approach will be applied to fabricate stretchable and transparent electrodes for the deformable EL device. Combining with the simple device architecture and unique emission mechanical in the ACEL devices, a highly stretchable EL device will be demonstrated with stable emission performance under the stretching strains up to 100%. The stretchable ACEL device can also be easily integrated with a DEA
device to demonstrate an unprecedented EL device which can be driven into dynamic shapes under electrical bias.
5.1 Introduction

Stretchable and soft EL devices which possess good mechanical compliance property will inspire numerous new applications which cannot be achieved with traditional technologies on rigid or flexible devices. For example, stretchable displays, biomedical imaging and monitoring devices, and conformable visual readout on skins etc. Pioneering works which were demonstrated to successfully fabricate stretchable EL devices were reported by Rogers and coworkers,1,2 Pei and coworkers,3-5 and Someya and coworkers.6,7 Different strategies, such as using intrinsically stretchable materials or patterning stretchable structures with conventional materials, were studied in these reports. Difficulties to employ stretchable structures in the conventional materials persist in that complicated patterning and transferring processes are required which are not cost-effective and not suitable to scale up for large device fabrication. Using intrinsically stretchable materials can circumvent the challenges to pattern stretchable device structures. However, difficulties also exist in the stretchable EL devices fabricated with intrinsically stretchable materials, such as their significantly reduced emission intensity under stretching and limited mechanical stability under large strains.

In this chapter, we will demonstrate that a simple and all-solution processible approach can be developed to fabricate highly stretchable EL devices with intrinsically stretchable emission layer. Excellent mechanical and electrical stability can be achieved with the ACEL devices which can tolerate stretching strains up to 100%. Moreover, with the simple device architecture and easy fabrication process in the stretchable EL devices, they can be integrated with DEAs to achieve unprecedented self-deformable EL devices. The DEAs are attracting increasing interest as “smart materials” which can generate large mechanical motions under electrical bias. They possess extraordinary advantages in their high actuation performance (area strain can reach above 200%), thin device profile and simple device architecture compared to other kinds of actuators, such as piezoelectric actuator8 and ionic gel actuators9 etc. They have been successfully demonstrated in applications such as wearable tactile display devices,10,11 smart artificial muscles,12,13 and high-speed electromechanical transducers.14,15 Comparisons between the DEAs and other types of actuators are provided in table 5.1. We will demonstrate that the DEAs can also be
integrated with the stretchable ACEL devices to impart dynamic shape changes to the EL devices. The novel and unprecedented functionality in the active-deformable EL devices will provide new opportunities for the envisioned display-centric world in the near future. For example, the active-deformable EL device can be integrated to fabricate volumetric displays which render 3D contents physically and deliver interactive feedback to the users. 16-19

Table 5.1 Compare between different actuators

<table>
<thead>
<tr>
<th>Types of actuator</th>
<th>Maximum strain (%)</th>
<th>Elastic energy density (J/cm$^3$)</th>
<th>Coupling efficiency (%)*</th>
<th>Speed</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEA</td>
<td>380</td>
<td>3.4</td>
<td>85</td>
<td>&lt;0.5 ms</td>
<td>20,21</td>
</tr>
<tr>
<td>Ionic gels</td>
<td>&gt;40</td>
<td>0.06</td>
<td>—</td>
<td>~1 s</td>
<td>22,23</td>
</tr>
<tr>
<td>Piezoelectric ceramic (PZT)</td>
<td>1.7</td>
<td>1</td>
<td>81</td>
<td>~60 µs</td>
<td>24,25</td>
</tr>
<tr>
<td>Electromagnetic</td>
<td>50</td>
<td>0.025</td>
<td>—</td>
<td>~100 µs</td>
<td>26</td>
</tr>
<tr>
<td>Natural muscle</td>
<td>100</td>
<td>0.04</td>
<td>—</td>
<td>&gt;5 ms</td>
<td>26,27</td>
</tr>
</tbody>
</table>

* Coupling efficiency=energy converted into mechanical work per cycle/electrical energy applied per cycle.

5.2 Experimental Methods

5.2.1 Stretchable and self-deformable ACEL device fabrication

The developed method to deposited homogenous NW thin film for functional device structures (discussed in Chapter 4) was used to fabricate the stretchable and transparent AgNW electrodes for the EL devices. Different from the embedding and transferring method in Chapter 4, the AgNWs could be directly embedded into the PDMS with subsequently deposited device structures. The spray-coated AgNWs conductive films could also be used for the DEA electrodes which were required to maintain good conductivity under actuations. The ZnS:Cu ACEL particles mixed with PDMS were used as the intrinsically stretchable EL materials. Detail fabrication procedures on the stretchable ACEL devices and active-deformable ACEL devices can be found in Chapter 3, Section 3.4.4 and 3.4.5.
Effect on the ZnS:Cu/PDMS ratios was investigated by changing from 1:2 to 3:1. Luminance from the devices with the same thickness and voltage was measured and shown in Figure 5.1a. Luminance from the device increased by increasing the ZnS:Cu/PDMS weight ratios. The maximum luminance was observed at the ZnS:Cu/PDMS ratio of 2:1. When the weight ratio was further increased beyond 2:1, no substantial increase in the luminance was observed in the device. On the contrary, the viscosity of the ZnS:Cu/PDMS composite largely increased, making it difficult for the emission layer deposition. Saturation in the luminance can be understood by that insufficient polymer is provided to separate the ZnS:Cu particles under the high weight ratio of ZnS:Cu/PDMS composite, which is analogous to increase the ZnS:Cu particle size in the composite. Efficiency of the ACEL powders is affected by the particle size and increases in proportion to $1/d^{0.5}$ (d is the particle size). Increase in the particle size will lead to decrease in the efficiency of the ACEL powder, which was also reported in ACEL devices with different binders for the emission layer. Effect of the different emission layer thickness was also studied, as shown in Figure 5.1b. Increase the film thickness could help to increase the luminance of the ACEL device. However, the required voltage would also increase linearly to the film thickness.

**Figure 5.1** (a) Luminance of the ACEL device under different weight ratios of phosphor and PDMS. (b) Luminance of ACEL device with different film thickness, the electrical field is remained constant.
5.2.2 Characterization

Top and cross-section SEM images of the samples were taken by FE-SEM, JSM 7600F. Photoluminescent spectra were measured by a spectrofluorophotometer (Shimadzu RF-5301PC). Stretching test of the sample was performed on a home-made motorized linear translation stage in room temperature. A Keithley 2400 source meter and a functional generator (Yokogawa FG 300) connected with a power amplifier (Trek PZD 2000) were used to applied voltage bias for the highly stretchable ACEL devices. Emission from the device was collected by an optical fiber connected to an Acton SP-2300 monochromator. Emission spectra from the devices were measured by a Princeton Pixis 100B spectroscopy CCD detector on the monochromator. Luminance of the devices was measured by a Konica CS-200 spectroradiometer.

5.3 Result and Discussion
5.3.1 Highly stretchable ACEL device

Figure 5.1a is a schematic drawing showing the device architecture of the stretchable ACEL devices. As a widely used ACEL material, ZnS:Cu is commercially available. ZnS with different active dopants or dopant concentrations can provide different emission colors. After mixed with the stretchable PDMS polymer matrix, highly stretchable EL materials could be achieved with the ZnS:Cu/PDMS composite after cross-linking. The excellent chemical stability of the PDMS provided the advantage to ease the deposition process for different functional layers in sequence. A layer of cross-linked PDMS was used to cap the whole device structure which could reduce oxygen concentration around the AgNWs electrodes and protect them from oxidation. Besides, the PDMS capping layer would isolate the EL layer from moisture which might quench the luminance centers by reacting with the EL phosphors. Figure 5.2a provides a schematic of the ACEL devices under stretching (right side of the figure). The ACEL device comprises of both stretchable transparent electrodes and stretchable emission layers. Stable emission behavior can be expected in the ACEL device under large mechanical deformations such as stretching or twisting. A fabricated device is presented in Figure 5.2b (left), showing semitransparent appearance. Light extraction could be achieved on both sides of the devices as the top and
bottom electrodes were both composed with the transparent AgNW thin films. Green emission could be observed from the device when powered by the Keithley 2400 source meter, right image in Figure 5.2b.

**Figure 5.2** (a) Schematic images of the stretchable ACEL device (left) and the stretchable ACEL device under stretching and twisting (right). (b) Photographs of the stretchable ACEL devices when the device is off (left) and on (right). Reproduced with permission from reference [31].

The electrodes of the stretchable EL devices could be patterned to achieve EL arrays which could be independently addressed and controlled. For example, three parallel strips of AgNW electrodes were deposited as the bottom electrodes of the EL device by spray-coating the AgNWs through a shadow mask. After the emission layer coating, another homogenous AgNW network was spray-coated to form the top electrode. As shown in Figure 5.3a and b, the emission strips can be turned on and off independently.
Figure 5.3 Photographs of the stretchable ACEL device: (a) Electrical bias is applied on the middle strip; (b) Electrical bias is applied on two strips.

Figure 5.4a shows the top SEM image of the AgNW network coated on the PDMS surface. A homogenous percolating AgNW network was obtained on the PMDS after the spray-coating process. Instead of using the embedding and transferring method developed in Chapter 4, the AgNW conductive films can be buried and embedded in the PDMS after subsequent layer deposition. The approach is infusive with a simple and scalable fabrication process for the stretchable ACEL device, which is also critical for its integration with DEA devices. Cross-section of the AgNW network embedded in PDMS is shown in Figure 5.4b. It is obvious that the top PDMS layer has combined with the bottom PDMS layer after penetrating through the intermediate AgNW layer. With its low surface energy (~20 mJ/m²), the PDMS easily penetrated through the openings in the AgNW networks and partially dissolved the underneath PDMS to form strong bonding strength between the two layers after cross-linking. Compared to other bonding methods, such as oxygen plasma bonding, hot-press lamination, and corona discharge bonding etc., the bonding process here will provide much stronger bonding force at the interface to enable stable mechanical property in the stretchable devices. The ZnS:Cu particles used in this study have a an average diameter of 29 µm, as shown in the SEM image of Figure 5.4c. The emission layer shows a thickness of ~41 µm (Figure 5.4d), which is mainly determined by the ZnS:Cu particle size.
Figure 5.4 The SEM images of the stretchable ACEL device: (a) AgNWs network on the PDMS substrate; (b) cross-section of the electrode with the AgNW layer embedded in PDMS; (c) morphology of the ZnS:Cu phosphor; (d) cross-section observation of the device with the emission layer sandwiched between the two AgNW electrodes. Reproduced with permission from reference [31]

A rectangular pulse function (magnitude of +/- 120 V, frequency of 2.5 kHz) was applied to power the stretchable ACEL device. The device was subjected to different mechanical deformations: bended to an angle of 180° (or folded face-to-face, Figure 5.5a) and twisted (Figure 5.5b). Excellent mechanical stability was achieved in the ACEL device with no degradation observed in the emission intensity under the mechanical deformations. As shown in Figure 5.5c, the ACEL device was tested under larger deformations by elongating the device to different strains (≤100% stretching strains, before the break down of the PDMS). Remarkably, stable emission behavior was maintained in the stretchable ACEL device.
The EL spectrum in the stretchable ACEL device has a FWHM (full-width-at-half-maximum) of 80 nm. And the emission peak is at 495 nm which is attributed to the relaxation through the dopant levels, as shown in Figure 5.6a. The active dopants (Cu) in the ZnS hosts provide a more effective recombination path for the excitons, as interpreted in the band structure of ZnS:Cu (Figure 5.6b, inset). Most of the excitons will relax through the active dopants, leading to green emission from the device, as evidenced by the PL spectrum in Figure 5.6b.

**Figure 5.5** Photographs of the stretchable ACEL device (a) folded; (b) twisted; (c) stretched to different strains.\textsuperscript{31} Reproduced with permission from reference [31]
Characteristics of the emission intensity under different voltage bias are plotted in Figure 5.7a. Light emission can be detected from the device when the excitation voltage increases above 60 V, after which the brightness of the device increases with the increase in the electrical bias. In ACEL devices, the brightness of the device and the electrical bias follow the equation below:\(^2^{8}\)

\[
L = L_0 \exp\left(-\frac{\beta}{V^{1/2}}\right) \tag{1}
\]

where \(L\) is the luminance, \(V\) is the voltage, \(L_0\) and \(\beta\) are the constants determined by the devices.\(^3^{3}\) The probability to accelerate the electrons into the energy which can lead to excitation of the luminance center will increase steeply after the electrical bias exceeds a certain value (60 V in our device). As a result, the luminance increases rapidly with increase in the electrical bias. The experiment data fits well with Equation 1. When the frequency of the electrical bias increases, the luminance can also be enhanced. It can be understood that more excitation cycles are provided to produce emission from the phosphors with the increased frequency. Switching behavior of the stretchable ACEL device is studied and presented in Figure 5.6b. Luminance of the device could increase to the maximum value within 130 ms after the electrical bias is applied. The stretchable ACEL device could be turned off within 88 ms after the electrical bias is removed. The ACEL device could operate stably under the on-off tests, as shown in the inset of Figure 5.6b.
Figure 5.7 (a) Luminance characteristic of the elastic EL device under different frequencies and voltages. (b) Time response of the elastic EL device. Inset is the emission behavior of the elastic EL device under repeated on-off cycles. (c) Mechanical stability test of the elastic EL device under different strains. (d) Stretching stability test of the EL device between the strains of 0% and 80%.\textsuperscript{31} Reproduced with permission from reference [31]

Mechanical stability of the stretchable ACEL device was examined by elongating the device to different strains (up to 100%). Below 30% strains, emission intensity of the device slightly increased, reaching $\sim$111% of the initial intensity (at 0% strain) at the stretching strain of 30%. The emission intensity began to decrease after the stretching strains are beyond 30%. The final emission intensity at 100% maintained at around 87% of the initial intensity. Variation in the emission intensity is attributed to the combined effects of the increase in the emission area, decrease in the emission layer thickness, and decrease in the conductivity of the AgNW electrodes under the stretching strains. Increasing the emission area will lead to smaller phosphor density in the emission layer.
Consequently, the luminance will be reduced, as discussed in Figure 5.1a. On the contrary, reducing the emission layer thickness will enhance the electrical field on the emission layer, leading to higher brightness in the ACEL device. When the stretching strains is small (<30%), enhancement in the electrical field might dominate to increase the device brightness. With the stretching strains further increased, reduce in the phosphor density and the electrode conductivity will dominate to reduce the device brightness. Notably, emission in the stretchable ACEL device is much more stable compared to other intrinsically stretchable EL devices based on EPLEDs. The EPLEDs have encountered the difficulty of significant declined luminance under large stretching strains, which can only maintain ~10% of the initial intensity under 100% stretching strains. The large degradation in luminance was mainly due to the reduced conductivity in the transparent electrodes under large stretching strains, which is still difficult to avoid (resistance in the stretchable transparent AgNW networks increases for 20 times at the stretching strains of 100%). The unique emission mechanism in the ACEL device helps to circumvent the difficulties. In the stretchable ACEL device, emission brightness is mainly determined by the voltage bias ($L = L_0 e^{-\beta / V^{1/2}}$) with small current required in the devices. Variation in the electrode resistance is small compared to the device resistance, limiting its effect in changing the device brightness under stretching strains. Consequently, stable emission brightness can be maintained in the ACEL device. With the excellent mechanical stability, the stretchable ACEL device can also be repetitively stretched to a large strain of 80%, as shown in Figure 5.7d. Brightness of the device can maintain 62% of the initial intensity after 1000 stretching and releasing cycles.

### 5.3.2 Integrating stretchable ACEL device with DEAs for self-deformable EL devices.

The electrical actuation performances of the DEAs fabricated with AgNW electrode were firstly investigated. The amount of AgNWs solution (with the same concentration of 0.3 mg/ml) was varied from 1.5, 2 to 2.5 ml for the DEA device fabrication. It could be observed that the area strain of the DEAs increases with the increased amount of AgNWs solution for the electrode fabrications, as shown in Figure 5.8b. The area strain is defined as $(A_a - A_o) / A_o$, where $A_a$ is the area of the DEAs under actuation and $A_o$ is the original area before actuation. Actuation mechanism in the DEA devices is based on the Maxwell stress...
Chapter 5

\( p = \varepsilon \varepsilon_0 E^2 \), \( \varepsilon \) is the relative permittivity of the elastomer, \( \varepsilon_0 \) is the permittivity of free space, and \( E \) is the applied electrical field) caused on the elastomer by the accumulated opposite charges on the two electrodes under electrical bias. The elastomer will be compressed along its thickness under the Maxwell stress, leading to lateral expansion of the elastomer, as shown in Figure 5.8a. The DEAs fabricated with more AgNWs solution are expected to maintain the electrode conductivity under larger mechanical deformation when the devices are actuated. Consequently, better actuation performance can be observed in the devices. As shown in Figure 5.8c, the DEA fabricated with 2.5 ml AgNWs solution achieved 67% area expansion at 5 kV. The area expansion was further increased above 106% at 5.5 kV (the area expansion was underestimated as buckling existed in the DEA resulted due to the silver paste confinement at the edge of the AgNW electrodes).

**Figure 5.8** (a) A schematic of the actuation mechanism in the DEAs. (b) Electrical actuation performance test of the DEAs with different amount of AgNWs. (c) Photographs of the DEA under different actuating voltages. The scale bars are 0.5 cm.

Figure 5.9a is a schematic showing the structure of the self-deformable EL device. Performance of the self-deformable EL device after integration with the DEAs was investigated, as shown in Figure 5.9b. The rectangular pulse function (magnitude of +/-
120 V, frequency of 2.5 kHz) was used to power the stretchable ACEL device. Dynamic shapes were achieved in the self-deformable EL device when different biases were applied on the DEA. Similar to the actuation behavior in the DEAs before EL device integration, area expansion in the self-deformable EL device increased with the ramping voltages. With the excellent mechanical stability in the stretchable ACEL device, stable emission was maintained in the self-deformable EL device when actuated to different area expansions, as shown in Figure 5.9c. Slightly reduced area expansion was observed in the integrated device (the area expansion reduced to 55% compared to the area expansion of 67% before integration under the same actuation voltage of 5 kV). It can be attributed to the increased elastic modulus in the integrated device. Under the same Maxwell stress, the actuation performance will be hindered with the increased elastic modulus. Similar to the DEAs before integration, buckling in the emission layer was also observed in the self-deformable EL devices under the high actuating voltage of 5.5 kV.

**Figure 5.9** (a) A schematic showing the structure of the self-deformable EL devices. (b) Electrical actuation performance of the self-deformable EL device. (c) Photographs of the self-deformable EL device under different voltages. The scale bars are 0.5 cm.
5.4 Conclusions

In this chapter, we further explored application of the stretchable and transparent AgNW electrodes, which were fabricated with the approach developed in Chapter 3, to achieve a highly stretchable ACEL device using ZnS:Cu particles embedded in PDMS as the emission layer. Intrinsic stretchability was achieved in both the electrodes and emission layer, leading to a highly stretchable EL device which could maintain stable emission under stretching strains up to 100%. The highly stretchable ACEL devices could be subjected to repetitively stretching at a large strain of 80%, sustaining 62% of the initial brightness after 1000 stretching–releasing cycles.

With the simple device fabrication of the stretchable ACEL devices, we also demonstrated integration of the ACEL devices with DEAs, leading to an innovative self-deformable EL device which could be dynamically driven to different shapes under electrical biases. The self-deformable EL device could achieve ~55% area expansion under the voltage bias of 5 kV. The developed device and fabrication procedure are believed to have wide applications in highly deformable display and lighting devices, providing new opportunities for soft EL device applications in displays rendering volumetric contents and systems providing interactive user interfaces.

References


Chapter 6

Extremely Stretchable ACEL Devices

By using AgNW networks embedded in PDMS as the transparent and stretchable electrodes, ACEL devices with the stretchability of 100% were demonstrated in the last chapter. With the simple device architecture and unique emission mechanism, the ACEL device can easily achieve significantly improved stretchability with different material designs for the stretchable devices. In this chapter, we will demonstrate that by using ionic conductors as the electrodes and ZnS:Cu particles embedded in Ecoflex as the emission layers, extremely stretchable ACEL devices can be fabricated. The extremely stretchable ACEL device can be elongated to 700% strain with maintained device operation.
6.1 Introduction

Stretchable EL devices with extremely high stretchability (>100% strains) provide the capability to confront more demanding mechanical deformations under flexing, twisting, stretching, folding or conformably wrapping, enabling electronic applications under extremely rigorous mechanical. Stretchable conductor is an important part in realizing deformable EL device. In order to fabricate the stretchable electrodes, two different strategies, with one focuses on stretchable structures and the other focuses on stretchable materials, have been exploited. Due to the daunting material challenges in electronic conductors, almost all the endeavors have been geared toward developing conductors with stretchable structures for deformable EL devices. For example, Kim et al. patterned thin metal films into stretchable structures and used them as electrical interconnects to assemble rigid light-emitting elements on elastic substrates. Conventional technologies could be combined to enable stretchable electronics with the approach. However, large-scale and cost-effective techniques need to be developed to manipulate the stretchable structures and to assemble components with significant mechanical mismatches for durable deformable devices. Furthermore, since the metal films are opaque, these metal films are not suitable for electrodes in the stretchable EL devices which require good transmittance for efficient light extraction. Recently, carbon nanotubes (CNTs) and silver nanowires (AgNWs) have been demonstrated as highly conductive fillers in polymer matrix to achieve transparent and stretchable electrodes with their percolating network structure. Combining with stretchable emissive layers, the transparent and stretchable electrodes could be used to achieve fully stretchable EL devices. Although stretchable devices at high strains can be achieved, it is still quite challenging to improve the stretching strains of these thin and transparent NW networks beyond 100% due to the damage on the network structure under large mechanical deformations.

Compared to the stretchable electronic conducting structures, which need to circumvent difficulties in their stretchability, mechanical stability, and transmittance, the intrinsically stretchable ionic conductors can be easily formed with solid polymer hosts, yielding exceeding mechanical properties and transparency. They have been demonstrated as promising materials for soft actuators, strain sensors, and transistors etc. Here,
we report the first demonstration on extremely stretchable EL devices using ionic conductors as the stretchable, deformable and transparent conducting electrodes. Limited by the stretchability in the precedent transparent electronic conductors, the alternating-current electroluminescent (ACEL) devices could only be strained to 100%.\textsuperscript{10} Our breakthrough device architecture with integrated ionic conductor delivers unique emission behaviors in the ACEL devices under extreme stretching conditions. Stretchability of the ACEL devices reaches a record of 700% for EL devices.

6.2 Experiment Methods

6.2.1 Extremely stretchable ACEL device fabrication

Similar to the fabrication of highly stretchable ACEL device in Chapter 3, ZnS:Cu embedded in polymer matrix is exploited as the stretchable emission layer. Ecoflex 00-50 which possesses high stretchability of 980% is used as the host polymer for the ZnS:Cu particles. Instead of using spray-coated AgNWs networks as the transparent electrodes, ionic conductors are prepared by dissolving Lithium percolate in PC. The ionic conductors are blended with PMMA in acetonitrile to achieve gel-like solution for the stretchable and transparent electrode deposition. Detail fabrication procedure of the extremely stretchable ACEL device can be found in Chapter 3, Section 3.4.6.

6.2.2 Characterization

The transmittance spectra were measured by a Shimadzu spectrometer (UV-2501pc). Capacitance and resistance of the ionic conductors were measured by an Agilent E4980A precision LCR meter. Stretching test of the sample was performed on a home-made motorized linear translation stage in room temperature. A functional generator (Yokogawa FG 300) connected with a power amplifier (Trek PZD 2000) were used to applied alternating voltage for the highly stretchable ACEL devices. Emission from the device was collected by an optical fiber connected to an Acton SP-2300 monochromator. Emission spectra from the devices were measured by a Princeton Pixis 100B spectroscopy CCD detector on the monochromator. Luminance of the devices was measured by a Konica CS-200 spectroradiometer.
6.3 Result and Discussion

Figure 6.1a shows a schematic of the extremely stretchable ACEL device. The device composed of the bottom and top ionic conductors with sandwiched Zn:Cu/Ecoflex emission layer. The alternating current was capacitively coupled to the device through three capacitors connected in series, as shown in the equivalent circuit in Figure 6.1a (right). Capacitors $C_1$ and $C_3$ were formed by the electrical double layers at the ionic conductor/external electrode interfaces on each side of the device. The emissive Zn:Cu/Ecoflex composite constituted the capacitor $C_2$. Electrochemical stability is a key consideration when the ionic conductors are applied in devices which operate under high voltage. Especially, the ACEL devices generally require 100-1000 V for light emission. Depending on the electrode materials, the electrochemical stability window for the lithium-based polycarbonate electrolyte is around 3 V.\textsuperscript{20} In the electrical double-layer, due to the small charge separation (in the range of a few nm), they have large capacitance on the order of $\sim 10^{-1}$ F/m\textsuperscript{2}. On the contrary, the dielectric capacitor in the emissive layers of ACEL devices with polymer binders have significantly larger charge separation (around 200 µm), leading to much smaller capacitance on the order of $\sim 10^{-7}$ F/m\textsuperscript{2}.\textsuperscript{11} Compared to $C_1$ or $C_3$, $C_2$ is quite small ($C_2/C_1$ or $C_2/C_3 = \sim 10^{-6}$, depending on the area of the capacitors). With all the capacitors connected in series, one can obtain $C_1V_1=C_2V_2=C_3V_3$ as the charges stored in each capacitor are the same. Thus, it can be derived that most of the voltage will drop across the emissive layer with small voltage distributed on the double layer interfaces ($\sim 10^{-3}$ V for ACEL device operate at 1000 V) due to their much larger capacitances. As shown in Figures 6.1b and c, bright emission could be achieved in the ACEL devices using ionic conductor as the highly stretchable electrodes. The device could be stretched uniaxially, elongated diagonally, twisted or subjected to other mechanical deformations. The ionic conductors and emission layers can be easily deposited with solution-processible methods. They can be patterned into different device geometrics. As shown in Figure 6.1c, the stretchable ACEL device was patterned. Emission properties of the patterned device could maintain even under highly stretched states.
Ionic conductors are interesting for their extremely high transmittance and stretchability compared to conventional electronic conductors. As illustrated in Figure 6.2a, the prepared ionic conductors in a 40 ml bottle shows excellent transparency. A thin layer of ionic conductor (∼200 µm in thickness) was coated on a glass slide, Figure 6.2a (right). Transparency of the ionic conductor was measured with another glass slide as reference. As presented in Figure 6.2b, transmittance of the ionic conductor almost reaches 100% (beyond the photometric accuracy, ±0.3%, of the Shimadzu UV-2500pc spectrometer) in the wavelength range of 350-850 nm. To study the electrical properties and stretchability of the ionic conductor, a 200 µm-thick ionic conductor was coated on a 3M VHB tape with two graphite electrodes used as external connections, as illustrated in Figure 6.2c inset. The ionic conductor was tested under stretching strains up to 700%, as shown in Figure 6.2c. Resistance of the conductor increases as the stretching strains increase with $R/R_0$ in proportion to $\lambda^2$ (where $R$ and $R_0$ are the resistance of the ionic conductor under deformed
and undeformed states, $\lambda$ is the stretch ratio). As well known, resistance of a conductor can be given by $R_0 = \rho L_0 / A_0$, where $\rho$ is the resistivity of the ionic conductor ($\rho = 1780 \ \Omega \cdot \text{cm}$), $L_0$ and $A_0$ are the length and cross-section area of the conductor. Under the stretch ratio of $\lambda$, $L/A$ of the elastomer is proportional to $\lambda^2 L_0 / A_0$. It is obvious from Figure 6.2c that the measured resistance closely matches the $R/R_0 = \alpha \lambda^2$ curve ($\alpha$ is a constant), indicating that change of the resistance is only attributed to the geometric change of the ionic conductor and the resistivity is independent of the mechanical deformations. The stretchability and mechanical stability of the ionic conductors significantly exceed the transparent electronic electrodes. For example, resistance of the stretchable and transparent AgNWs embedded in elastomers increased 20-35 times at the strains of 100%. Resistance in CNT film embedded in elastomer changed more than 8 times at the strains of 120%. In addition, the significantly deteriorated conductivity under repeated deformations is another critical problem in these electrodes. On the contrary, the ionic gel can easily accommodate the mechanical deformations and maintain constant conductivity after recovered from the stretch. Resistance of the ionic conductor rarely changed after repetitively stretched to 700% for 1000 cycles, as shown in Figure 6.2d. Though conductivity of the ionic conductors is still lower compared to the electronic conductors (around $10^2$ lower), they are suitable for electronic components such as the ACEL devices in which the conductivity requirement can be easily met.
Figure 6.2 (a) Photographs of the as-prepared ionic conductor in a glass bottle (left) and ionic conductor coated on a glass slide with a thickness of ~200 µm (right). (b) Transmittance spectrum of the ionic conductor on glass slide. Another similar glass slide was used as reference. (c) Resistance of the ionic conductor measured as a function of the stretching strains. Inset shows a schematic image of the ionic conductor under stretching test. (d) Electrical resistance of the ionic conductor at the relaxed state after stretched to 700% with different cycling numbers.\textsuperscript{21} Reproduced with permission from reference [21].

Stretchable ACEL devices have been demonstrated with AgNWs film embedded in PDMS as the stretchable transparent conductors with limited stretchability at 100%.\textsuperscript{10} Utilizing the extremely stretchable and transparent ionic conductor, we demonstrate that the stretchability of the ACEL devices can be significantly improved. As shown in Figure 6.3a, the ACEL devices could be elongated up to 700% with maintained device operation. Figure 6.3b shows the emission performance of the extremely stretchable ACEL devices before stretch. Luminance of the ACEL device was plotted against the electrical field under the frequency of 2 kHz. As discussed in the last chapter, emission brightness and the applied
voltage on the ACEL devices follow the relation of $L = L_0 e^{\beta/\sqrt{V}}$, where $L$ is the luminance, $V$ is the applied voltage, $L_0$ and $\beta$ are the constants determined by the devices.\textsuperscript{26} The experiment data fits well with the relation (Figure 6.3b), which was preserved under different strains (Figure 6.3c) with varied $L_0$ and $\beta$. The relation between the emission brightness and applied voltage leads to unique behavior of the device under stretching strains. The emission performance was examined when the device was stretched to different states under constant bias. As shown in Figure 6.3d, emission intensity of the stretchable EL device first increased with the stretching strains and reached the maximum values at 280% ($I_{280}/I_0 = 282\%$, $I_{280}$ and $I_0$ are the emission intensity at 280% and 0% strains respectively). The emission intensity began to decrease after the strains exceeded 280%. Emission intensity at 700% strains still maintained at about 70% of the emission intensity at 0% strain (original unstrained state). Emission spectra of the device remained unchanged under strains, as shown in Figure 6.3e. Variation of the emission intensity of the stretchable EL device under different strains can be understood by the brightness-voltage relation with the effects of reduced emissive layer thickness and increased device area under increased strains. Reducing the film thickness leads to increase in the electrical field in the emissive layer (contribute to increase device brightness) while increasing the device area leads to declining phosphor density in the polymer matrix (contribute to reduce device brightness). Relation between the emission film thickness and phosphor density in the emissive layer was discussed in detail in the last chapter. Different from the stretchable ACEL device using AgNW films as the transparent electrodes, which showed slightly increase in the emission intensity before the strains of 30% with subsequent decrease in the intensity under larger strains, the intensity was observed to increase until the strains reached at 280% in the ACEL devices using ionic conductors as the transparent and stretchable electrodes. It is believed that the varied network structure and resistance in the AgNW films contribute to suppress the emission intensity under larger stretching strains. With the network structure, light transmittance takes place through the open regions. In return, the electrical field will be focused around the nanowires with decreased field intensity in the open regions away from the nanowires. Under increased strains, the area of the open zones will increase with further decreased electrical field in these regions, resulting in the emission intensity loss in the devices. Compared to the AgNW network, ionic conductors can fully
cover the surface of the emission layer with much stable resistance under different strains. Consequently, with less affect from the electrodes, intensity was only observed to decrease after the strains had exceeded 280% where the reduced phosphor density and electrode conductivity began to dominate.
Figure 6.3 (a) Photographs of the EL device stretched to different strains. (b) Luminance-electrical field characteristic of the stretchable ACEL device under 0% strain. (c) Luminance-electrical field characteristics of the ACEL device under different strains. (d) Emission intensity of the EL device under different stretching strains. (e) Electroluminescent spectrum of the elastic EL device at the stretching strains of 0%, 200%, 500% and 700%. Reprinted with permission from reference [21].
Cycling stability of the stretchable EL device was also investigated. The highly stretchable ACEL device was stretched between 40-400%. As it requires a relatively long time (a couple of hours) for the highly strained device to fully recover to the initial state, the device was only allowed to relax at 40% to reduce the testing time. Figure 6.4a shows the stretching test of the device in 25 cycles. $B_{400}/B_{40}$ varied from 1.66 to 2.01, where $B_{400}$ and $B_{40}$ are the brightness of the device under stretching strains of 400% and 40% respectively. The variation might be contributed to the change in the strained states due to the mechanical hysteresis in the highly strained polymer. Figure 4b shows that performance of the device is quite stable under the cycling test compared to previously reported full-stretchable EL devices.\textsuperscript{9,10} Emission intensity of the device maintained at ~85% after stretched to 400% for 1000 cycles. The emission fluctuation in the initial stretch-relaxation cycles was attributed to the contact problem with the graphite electrodes during the initial measurement. The excellent mechanical compliance in the ACEL device exceeds all the demonstrated EL devices with fully stretchable device structures.\textsuperscript{6,9,10,22,27,28}

![Figure 6.4](image)

Figure 6.4 (a) Cycling stability of the device in 50 cycles. (b) Mechanical stability test of the device with 1000 cycles.\textsuperscript{21} Reproduced with permission from reference [21].

6.4 Conclusions

In conclusion, ionic conductors were developed as innovative electrodes to improve the mechanical property of the stretchable ACEL devices in this chapter. The ionic conductors exceeded with their unique features of extremely high stretchability and transmittance
compared to the conventional electronic electrodes. The ionic conductors were prepared with simple blending processes and could be easily deposited onto arbitrary substrates with different methods such as spin-coating, screen printing, inkjet printing, and 3D printing etc. The demonstrated idea expands the research scope of the electrode materials for ACEL devices, benefiting either the traditional rigid and planar devices or the new emerging “soft” devices. With the high stretchability in the ionic conductor, a milestone in highly stretchable ACEL device was reported with a stretchability record of 700%. Unique emission behavior of the stretchable ACEL devices was observed with increased emission intensity at smaller stretching strains below 280% and declined emission intensity at larger tensile strains. At 700% strain, brightness of the device still maintained at 70% of the initial emission intensity at 0% strain. The extremely stretchable ACEL device also exceeded all the preceding works with its excellent mechanical stability which could be repetitively stretched to 400% with fairly stable performance maintained in the device.

References


Chapter 7

Discussion and Future Work

Stretchable devices are essential technologies for the next-generation device applications. Their exceeding mechanical compliance enables applications where rigorous deformations will need to be confronted. As emerging technologies, studies in the stretchable optoelectronic devices are still quite limited, leaving many challenges and hurdles unresolved. In this thesis, innovative structural and material designs have been realized to overcome some of the difficulties, aiming to enable and advance the stretchable optoelectronic devices. Stretchable photodetectors and EL devices with improved mechanical properties were successfully demonstrated. Our insights and suggestions in the future work for the stretchable optoelectronic devices are provided at the end of this chapter.
7.1 Discussion

7.1.1 Highly deformable and transparent photodetectors

With extensive studies being carried out in the NW research community, a number of semiconducting, metallic, inorganic and organic materials have been synthesized in the NW structures. They have been prospected as the promising building blocks for nanoscale devices which will bring revolution to the next-generation electronic applications. In this thesis, functional NWs are firstly studied for stretchable photodetectors with superiority in their intrinsic flexibility, good crystallinity and nanoscale dimension. A spray-coating assembly approach was developed to achieve functional NW network structures, which could be accomplished by a cost-effective and solution-processible method. The process could also be easily scaled up for large-area device fabrications. The network structures composed of ternary oxides NWs (ZGO NWs or ZTO NWs) were demonstrated as promising UV photosensing channels for highly deformable photodetectors. Application of the large bandgap ternary oxides NWs can eliminate the insertion of optical filters, providing miniaturized UV photodetectors which resolve the challenges in the conventional Si photodetectors with low efficiency and high dark current in UV light detection. The AgNW networks assembled with the spray-coating approach could reach the conductivity of 4.5 Ω/sq with the transmittance of 80%. Compared to the prototypical ITO conductors, the AgNW networks exceeded in their good mechanical compliance property and low-temperature processability. With the developed strategy to achieve functional NW network structures for the electrodes and photosensing channels, transparent and highly deformable UV photodetectors were demonstrated. The features of 1D structure, high material purity and good crystallinity of the ZGO NWs contributed to high photosensitivity in the highly deformable UV photodetectors. Photocurrent of the ZGO NW photodetectors reached 3000 times of the dark current.

The NW-NW junctions are important components in the NW network structures which contribute to maintain the electrical interconnections. The NW-NW junctions are also vulnerable parts in the NW networks. The NWs can be easily displaced under large mechanical strains, leading to loss of interconnections between the NWs. The embedding and transferring process is an effective approach to protect the NW networks in stretchable...
polymer matrix. Unfortunately, due to the small bonding strength between the NWs and the PDMS polymer matrix, it is difficult to achieve efficient transfer of the NW networks into PDMS. We demonstrated that with the assistance of Zonyl surfactant, the bonding strength could be improved between the AgNWs and PDMS polymer matrix. Hence, the AgNW networks could be easily transferred into PDMS without affecting the conductivity of the thin film structures. Stretchable and transparent UV photodetector could be successfully fabricated with the developed high efficient transfer method. The photodetector could tolerate tensile strain up to 50% with good photosensing performance maintained in the device. Compared to fully embedded NW structures, the partially embedded photosensing channels achieved improved response and relaxation time, showing the respond time below 0.8 s and the reset time of around 3 s. The elastic and transparent photodetector may find broad applications which can be integrated onto textiles or dermal for wearable and implantable electronic devices.

7.1.2 Highly stretchable and self-deformable ACEL devices

The EL devices with excellent mechanical compliance are believed to be essential technologies for the next generation lighting and display applications. Emission and mechanical stability of the stretchable EL devices are the important features which are emphasized in our study. We reported that stretchable EL device based on the ACEL devices demonstrated excellent emission stability under stretching strains, which was attributed to the unique emission mechanism of the ACEL devices. Emission intensity of the ACEL devices is mainly governed by the electrical field on the emissive layer with small current through the stretchable electrodes. Resistance variation in the electrodes is generally quite small compared to the resistance of the emission layer and its impact on the device performance is limited. Instead, decrease of the emissive layer thickness (contributes to increase the emission intensity) and decrease of the particle concentration in the emissive layer (contributes to reduce the emission intensity) act as combined effects to achieve stable emission behavior in the stretchable ACEL devices under different strains. A highly stretchable EL device which could maintain stable emission under stretching strains up to 100% were demonstrated. The highly stretchable ACEL devices could be
subjected to repetitive stretching at a large strain of 80%, sustaining 62% of the initial brightness after 1000 stretching–releasing cycles.

A novel idea to fabricate self-deformable ACEL devices was also presented in our study. The DEA is a new type of “smart material” which can generate large mechanical motions under electrical fields. The AgNW networks were fabricated with the developed solution-assembly approach to achieve transparent and stretchable electrodes for the DEAs. Increasing the AgNW amounts for the electrode fabrication helped to increase the actuation performance of the DEAs. With the simple device fabrication, stretchable ACEL devices could be successfully integrated with the DEAs. The integrated self-deformable ACEL device could be driven to dynamic shapes with its emission performance well maintained under different actuation states. The self-deformable EL device could achieve ~55% area expansion under the voltage bias of 5 kV. It is believed that the developed devices will have wide applications in highly deformable display and lighting devices, providing new opportunities for soft EL device applications in displays rendering volumetric contents, systems providing interactive user interfaces, and other unprecedented electronic systems.

### 7.1.3 Extremely stretchable ACEL devices

Stretchable and transparent electrodes are important components to realize deformable devices. Due to limitation in the stretchability of the AgNW network embedded in polymer matrix, stretchability of the ACEL devices was limited at 100% in Chapter 5. It is still challenging to fabricate transparent electronic electrodes with stretchability beyond 100%. On the contrary, stretchable ionic conductors can be easily fabricated with conducting ions in solid polymer hosts. Their stretchability and transparency significantly exceed the electronic conductors.

By using the ionic conductors as the transparent and stretchable electrodes, we demonstrated that stretchability of the ACEL device could be significantly improved to 700%, reaching a new record in the stretchable EL devices. Compared to ACEL devices using AgNW network as the stretchable electrodes, the extremely stretchable ACEL devices with ionic conductors also demonstrated different emission behaviors under
stretching. Studying the emission behavior of the extremely stretchable ACEL device under ultrahigh stretching strains is of considerable interest from both the scientific and technological perspectives. It was found that emission intensity of the ACEL devices continued to increase with the increasing stretching strain until 280%. Intensity of the emission was 2.82 times higher at 280% strain compared to the initial emission intensity at 0% strain. The phenomenon was attributed to the unique emission mechanical in the ACEL devices and the combined effects of reduced film thickness and declined phosphor density in the emissive layer under stretching. The reduced film thickness will contribute to increase the electrical field for charge excitation in the emissive layer, leading to increased device brightness. On the contrary, the declined phosphor density decreases the amount of emission centers in the same area, leading to reduced device brightness. With the excellent mechanical compliance in both the emissive layer and electrodes, the extremely stretchable ACEL device also demonstrated exceeding mechanical stability which can be repetitively strained to 400% with stable performance maintained in the device. It is believed that the demonstrated idea will expand the research scope of the electrode materials for ACEL devices, benefiting either the traditional rigid and planar devices or the new emerging “soft” devices.

7.2 Future Work

7.2.1 Vertical NW arrays for stretchable photodetectors and EL devices

The NWs possess structural advantages of improved crystallinity and unique waveguide property that are beneficial to increase both the internal and external quantum efficiencies. They are significantly miniaturized photosensing or emissive elements which can be embedded into stretchable polymers to harvest the mechanical conformability in the composite materials. Compared to the thin-film devices, the inorganic NW structures possess inherent advantages for “soft” photodetectors or EL devices with the 1D configuration. For example, NW photodetectors and EL devices have been widely studied for flexible devices, showing advantages over the thin-film counterparts.\(^1-8\). The NW heterostructures are of particular interests with their unique architectures. The \(p-n\) junctions can be fabricated with a core-cell structure or axial heterostructure in a single NW. Each of the NWs can become an independent photodiode or LED. As schematically illustrated
in Figures 7.1a and b, the nanosize functional components can be embedded into elastic polymer matrix to impart stretchability to the device structures. It is believed that with the intrinsically stretchable device configurations, NWs will become important materials in the stretchable photodetectors or LEDs with their great potentials to break the bottlenecks in the thin-film devices which have still encountered difficulties to achieve stretchable and functional layers. The advantages in the NW devices will be fully utilized with effective approaches developed to transfer the NW arrays from high-temperature substrates onto elastic platforms.

![Figure 7.1](image.png)

**Figure 7.1** Schematic images of the stretchable device based on NW structures: (a) Vertical NW arrays embedded in polymer matrix; (b) NW device under mechanical deformations.

### 7.2.2 ACEL devices with reduced operating voltage

The ACEL devices possess great advantage to maintain stable device operation under large mechanical deformation. However, the operating voltage is typical above 100 V in the ACEL devices. The high-voltage operation might become detrimental in applications where high voltages can lead to safety issues, such as wearable and portable electronics. The ACEL devices are currently under intensive study and improvement, showing promising performance and reduced operating voltages (<50 V).\(^9,10\) Many approaches have also been reported to effectively reduce the operating voltage of ACEL devices. For instance, short carbon nanotubes have been demonstrated to increase the electrical field strength in the inorganic powder EL devices and reduce the operating voltage as a result.\(^11\) Similar performance enhancement was also reported from Park’s group. Operating voltage of the organic ACEL devices was reduced to 25 V\(_{pp}\) (peak-to-peak voltage) with high
brightness at 350 cd/m$^2$. The ACEL devices using fluorescent polymer or their hybrids with colloidal quantum dots (QDs) were also reported to achieve extremely bright emission at low operating voltage (~500 cd/m$^2$ at 30 V$_{pp}$, as shown in Figure 7.2a and 7.2b). As shown in Figure 7.2a, the brightness of the ACEL device can be increased with the increased frequency in the low frequency range. However, in the high frequency range, the luminance will begin to decrease with the increased frequency as the current flow decreases and the excited electron will not be provided with sufficient time to recombine before the next excitation cycle occurs. In addition, structure engineering was reported to reduce the operating voltage of ACEL devices. Tandem structure with triple emitting layer stacking in series was observed to achieve six-time brighter emission intensity under the same operating voltage. It is believed that many materials and device architectures can still be explored to effectively reduce the operating voltage of the ACEL devices. And the application of stretchable ACEL devices in wearable and portable devices will not be limited.

![Figure 7.2](image)

**Figure 7.2** (a) The brightness and voltage characteristics of the hybrid ACEL device under different frequencies. (b) Photographs showing high emission brightness from the hybrid ACEL device. Reproduced with permission from reference [13]

**References**


Publication List


# Appendix

Table 1. Materials used in the thesis.

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N.A.: Not applicable.