

Additive Manufacturing and Laser Processing of Conductive Nanomaterial - Fundamentals and Applications

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Yongchao Yu
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ABSTRACT

Printable electronics have been developing rapidly in recent decades. Various printing technologies, such as aerosol jet, inkjet, and screen printing, have been developed, and some of these technologies are already being applied to the industrial fabrication process. Along with the development of printing methods, a number of materials have been studied for more advanced electrode devices and component fabrication, such as sensors, transistors, and radiofrequency devices. However, compared with conventional clean room technologies, such as photolithography and thin film deposition process, printing is still limited in resolution. For today's printing technology, the printing resolution is around 1-10 μm , which is significantly larger than a typical cleanroom fabrication limitation of 0.2 μm . We propose that using a laser as a precise tool is a very attractive method for shrinking this technical gap.

In the dissertation research, we combined both laser processing methods and printing methods to attempt to develop a novel fabrication process for printable electrode devices. In chapter 2, the extrusion printing method and laser sintering processes were applied. A 3D printed Al anode was fabricated for an Al-Air battery. By applying the laser sintering process, the battery performance significantly improved. In chapter 3, a flexible current sensor was fabricated by Aerosol jet printing. Additionally, a CO₂ laser was used to create a structured cutting path during the fabrication process. In chapter 4, a laser with a graphene sensor array was developed for multi-target sensing. An FS laser was used for the laser direct writing process. The sensor system has a nice sensitivity and selectivity for multiple

targets. In chapter 5 and chapter 6, the effects of laser irradiation for 1D nanomaterials were studied, and related applications were developed.

Through these studies, we provide evidence for our hypotheses: proper laser processing can improve the performance of printed electrical devices, especially in reducing contact resistance, changing nanomaterial structure, and improving fabrication precision

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Background and Introduction

Printing technology has rapidly advanced in the past decade, and its scope extends well-beyond printing text on paper. Printed electronics are evolving to enable advanced manufacturing of a broad range of functional devices including sensors [1-4], antennas [5-7], near-field communication systems [8-10], and electrical components [11]. With the inherent advantages of low-cost, non-vacuum processing, low process temperature, and high throughput manufacturing, printed electronics are being explored for functional materials and electronic device development on nonconventional planar and curved substrates, such as polymers, papers, clothes, or even on food. To meet the demands of emerging electronic applications, such as portable and wearable electronics, various printing techniques have been designed and created for both academic research and industrial application. Although various printing techniques offer unique printing capabilities and many of them may be only suitable for one particular application, the general features of printing, such as facile manufacturing and low-cost, are attractive compared to traditional microelectronic fabrication processes. However, compared to conventional cleanroom technology, such as photolithography and Complementary Metal-Oxide-Semiconductor (CMOS) technology, printing methods still have huge technical limitations for practical applications. These limitations include film thickness control, available materials, material purity, multi-material integration, and surface roughness, etc. However, the interest in printed

electronics has surged in the past decade as the advances in printed electronics will open new paradigms for flexible, environmentally friendly, and low-cost electronics. For further development of printed electronics, the improvement of printing technologies is important. Combining printing technologies with other advanced fabrication processes could be very attractive. A laser is a high precision machine instrument which can be an ideal tool to compensate for some of the shortages that printing technology has, such as fabrication resolution. Therefore, state-of-the-art fabrication processes that combine both laser processing and printing methods will be mainly investigated in this dissertation and reviewed in this chapter

1.2 Conventional Electronics Fabrication Process for Thin Film Deposition

Conventional electronic fabrications or cleanroom technologies have been developed for a couple of decades. A typical electronics fabrication process based on CMOS process includes cleaning, photolithography, etching, deposition, polishing, et al. In here, we are mainly focus on material deposition processes.

1.2.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a vacuum deposition method for depositing solid material from vapor by a chemical reaction occurring on or in the vicinity of a heated substrate surface [12]. The occurrence of a chemical reaction is an essential characteristic of the CVD method. This process is extensively applied to a thin film, power deposition, and for single crystal growth. Especially in thin-film applications, CVD and related processes process show an excellent ability

to produce coatings of uniform thickness and properties with a low porosity even on substrates of complicated shape. Applications of this process include dielectrics, conductors, passivation layers, oxidation barriers, conductive oxides, and resistant coating, etc. The experimental conditions which need to be controlled typically include substrate temperature, material, and composition of the reaction gas mixture, presser gas flows, etc. [12]. During the deposition process, substrates are usually heated to 600-900°C, and for some applications, the temperature requires over 1300°C [13]. Depending on the application, several CVD processes are available. One example is moderate-temperature or metal-organic CVD (MTCVD/MOCVD), which is achieved by using meta-organic precursors to start the chemical reaction at relatively low temperatures (500-600oC). Another classification is a plasma-assisted/enforced CVD process (PACVD or PECVD), which uses a plasma to active a chemical reaction in the vapor phase. Similarly, in the laser CVD (LCVD) process, the laser is used as a trigger for chemical reactions [14]. More details and classifications of the CVD process are shown in Table 1.1.

Table 1.1 Classification of CVD Method

CVD classification		Conditions	
Substrate Temperature	Hot wall CVD	Wall temperature close to substrate temperature	[14]
	Cold wall CVD	Wall temperature close to room temperature	[14]
Operation Condition	Atmospheric pressure CVD	Atmospheric pressure	[15]
	Low-pressure CVD	About 50 Pa (~0.1-0.3 Tor)	[16]
	Ultrahigh vacuum CVD	Below 10^{-3} ~ 10^{-6} Pa	[17]
Physical Characteristics of Vapor	Aerosol assisted CVD	Precursors are transported to the substrate by means of a liquid/gas aerosol	[18]
	Direct liquid injection CVD	Precursors are in liquid form	
Patriciate Media	Plasma CVD	Plasma enhanced/assisted	[19]
	Laser CVD	Laser density 1×10^8 - 1.5×10^{11} W/m ² based on material	[14, 20, 21]
	Photo-initiated CVD	UV assisted	[22]
	Thermally activated CVD (TACVD)	Infrared radiation, inductive heating, electrical resistivity	[23]

1.2.2 Physical Vapor Deposition

Physical vapor deposition (PVD) of hard coatings such as titanium nitride has been used in industries since the beginning of the 1980s. Two PVD processes, low voltage electron beam and cathodic arc deposition, were responsible for the early commercial success of hard coatings on high-speed steel tooling. The PVD method is a vacuum deposition technique very similar to the CVD process. The main difference from CVD is that for PVD, it used various physical methods to vaporize a solid material in a vacuum environment and deposit it on substrates as a pure material or alloy composition coating. It uses low voltage and high current arc discharge technology. The target material is vaporized and ionized by gas discharge. Additionally, this process allows transferring the coating material as a single atom or on the molecular level, which can provide an extremely pure and high-performance coating on a substrate [24].

Generally, PVD could be classified as four types: vacuum evaporation, sputter deposition, arc vapor deposition, and ion plating. Vacuum evaporation is a PVD process that deposits material without collision with gas molecules in the space between the source and substrate by thermal vaporization. For this process, the equilibrium vapor pressure is an essential factor of the material to be thermally vaporized. Depending on the materials, a vapor pressure of 10^{-2} Torr is typically applied to provide a useful deposition[25]. Another widely used PVD process is the sputter deposition process. For sputter deposition, materials are vaporized and physically sputtered onto a substrate, which is a nonthermal vaporization process. The surface atoms are physically ejected by momentum transfer from an atomic-

sized energetic bombarding particle. Usually, plasma or an ion gun is used for gaseous ion acceleration. Once the surface atom that has been struck attains enough energy, it will shake, and this “shake” can transfer to the near-surface region and develops a “Collision cascade” [25]. One of the most straightforward sputter deposition configurations is “DC diode sputtering.” A high negative DC voltage is applied to a conductive surface in gas and forms plasma, and positive ions are accelerated to the surface. Advantages of DC diode sputtering include large sputtering area and a stable long-time operation. Disadvantages include slow sputtering rate and surface heating due to the accelerated electrodes. Also, this method is only suitable for coating on an electrically conductive surface [25]. Another category of PVD is called “Arc vapor deposition.” In arc vapor deposition, the vapor created by a high-current low-voltage DC current is deposited from an anode or a cathode to the substrate [25]. Comparing both cathode and anode methods, the cathode arc vapor deposition process has a more straightforward configuration and has lower radiant heat loads. But in this method, some of the material is ejected as molten globules called “macros.” During the deposition process, these macros could deposit onto the substrate and create pinholes, which will significantly affect the thin film quality [25]. Lastly, in the 1960s, people discovered that controlled concurrent energetic bombardment of the depositing material could be used to modify and tailor the properties of the deposited film material [25]. Based on this discovery, the ion plating method was developed to control or modify the thin film property by utilizing periodic energetic bombardment of film material during deposition. Along with the history of PVD development, a lot

of methods have been developed for high-quality film deposition. However, compared with the CVD process, the uniformity of film thickness still needs to be improved.

It is undisputed that both CVD and PVD deposition processes are well developed for high-quality thin film deposition. Tables 1.1- & 1.2 show typical processing parameters for various PVD and CVD methods. Obviously, most of the conventional fabrication techniques require a vacuum and high temperature (> 500 °C) conditions, and for some of the processes, substrate electronic conductivity is needed. This requirement significantly limits the variety of substrates. Most of the polymer, paper, and low-temperature materials are not suitable for this process. Therefore, for a long time, it was challenging to fabricate electrodes on a flexible substrate. In addition, to create patterns and specific designs, premade masks become necessary, which leads to an increase in the design cost, and the whole fabrication process becomes a very time-consuming process. Therefore, a mask free electrode fabrication process with low operating temperature is urgently needed, and printable electronics have become a topical technology.

Table 1.2 PVD Classifications and Properties [25]

	Advantage	Disadvantage
Vacuum Evaporation	*High film purity *Source vaporized material can be solid in any form and purity *Can use shutter and masks *Low cost and easy to monitor	*Difficult to deposit many alloy composition and compounds *poor film thickness uniformity over a large area * poor source material utilization
Sputtering deposition	*Can deposit elements, alloy, and compounds *Long-lived vaporization with a stable geometry *sputtering source can be defined shapes, such as line or a rod	*Low sputtering rate *Expensive *Nonuniform of deposition flux distribution * energy incident on the target turns into heat
Arc vapor deposition	Anodic arc: *A high vaporization rates *No macros are formed	Anodic arc: *High radiant heat loads *Molten material limits the positioning of the source
	Cathodic arc: *Low radiant heat loads *Alloy materials can be vaporized readily * sources can be placed in any position	Cathodic arc: * formation of “macros.”
Ion plating	*Increase surface coverage *Modify film properties, such as adhesion, density, residual stress, optical properties, etc.	* Difficult to obtain uniform ion bombardment over the entire substrate * Gas from bombarding may be incorporated into film growing *May generate residual compressive stress

1.3 Printable Electronics

1.3.1 Printing Methods 2D to 4D

1.3.1.1 *Aerosol Jet*

Aerosol jet printing is a mask-free direct writing system using a concentrated aerosol beam. The Optomec company developed the first aerosol jet system under the Defense Advanced Research Project Agency (DARPA) Mesoscopic Integrated Conformal Electronics (MICE) program. Currently, the commercial Aerosol system is able to create a design trace from as small as 10 micrometers (mm) to 5 mm, depending on the different jet nozzle and ink properties. Usually, liquid ink viscosities between 0.5 and 2500 cP are employed [26]. The printing process starts with an atomization process. Figure 1-1 shows the basic schematic of an aerosol jet printer. The atomization process transfers liquid ink into 1-5 μm diameter droplets [26]. The carrier gas transports these droplets by flowing to an inject nozzle, where the carrier gas will be combined with the sheath gas. The ink deposition speed and trace quality are mostly dependent on the gas pressures of the carrier gas and the sheath gas. Carrier gas pressure has the greatest influence on ink delivery speed, while the sheath gas pressure mainly controls the printed shape and line quality. Both parameters need to be adjusted for individual ink to perform a high-quality print. For a pneumatic atomizer, a virtual impactor will be placed immediately in front of the deposition nozzle, which plays a role in removing excess gas flow and decreases the polydispersity of the aerosol by removing small particles [26]. Furthermore, a 1-5 mm nozzle-to-substrate distance is ideal for

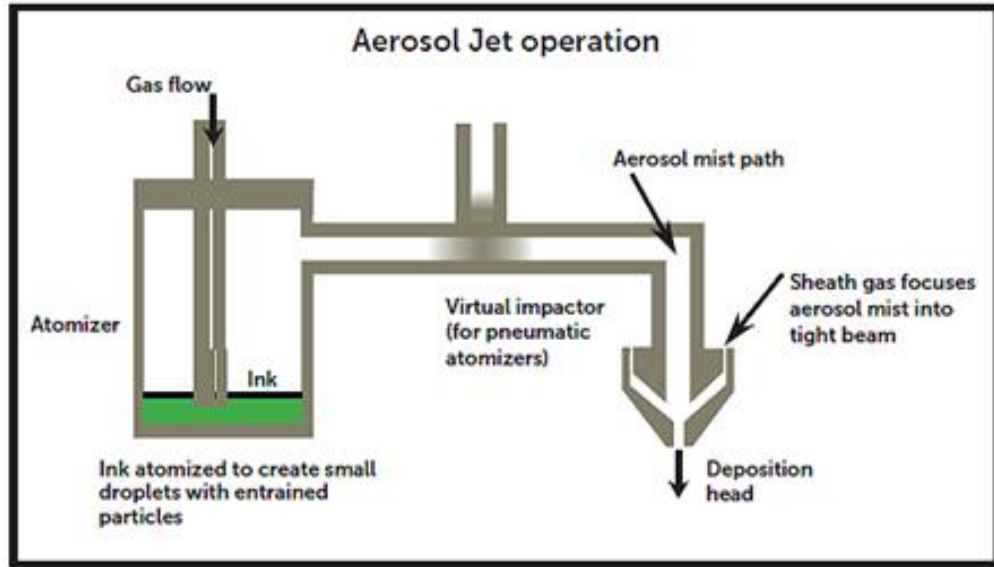


Figure 1-1 Schematic of Aerosol Jet (Source: OPTOMECH)

aerosol printing. This distance range allows the aerosol system to print on a variety of surfaces.

1.3.1.2 Inkjet Printing

Inkjet printing technology has been one of the most widely used printing technologies since the nineteenth century. The inkjet printing is a maskless technology that works by depositing ink drops directly to the desired position on the surface. This method is simple and effective in material cost. High resolution is one of the advantages of inkjet printing, which can easily reach from 300 dpi up to 1200 dpi [27]. However, one of the disadvantages of inkjet printing is the printing speed. The ink drying speed has become a limitation of printing. The dry thickness for inkjet printing is given by

$$d = N_d V_d \frac{C}{\rho} \quad (1-1)$$

where d is the dry thickness, N_d is the number of drops delivered per area (cm^{-2}), V_d is the volume of each drop (cm^{-3}), C is the concentration of the solid material in the drop (g/cm^{-3}), and ρ is the density of the material in the final film [28].

In general, inkjet printing can be divided into two different methods, continuous inkjet (CIJ) and drop-to-drop (DOD) methods [28]. Figure 1-2 shows the schematics of two different inkjet printing methods. In the CIJ process, ink drops pass through a charged electric field. Depending on the angle and intensity of the electric field, drops will have different charged levels. Then drops will pass through deflector plates, which regulate the deflection of charged drops through the electrical field. The drops will be separated by their charged intensity. The less charged drops will be delivered to the surface while more charged drops will be collected in an ink catcher and recycled. By controlling the charge of each drop, the CIJ printing method implements non-continuous pattern printing. On the other hand, for a DOD technique, an electrical-pulse (data pulses) controlled pressure transducer allows the drops to be delivered only when they are needed. The DOD method has less material waste than the CIJ method, even though the CIJ method collects some ink to be recycled. Because it does not require recycling and has less material waste, the DOD method is more advantageous for printing when using some functional materials, such as graphene or carbon nanotubes, and some expensive materials, like gold and silver.

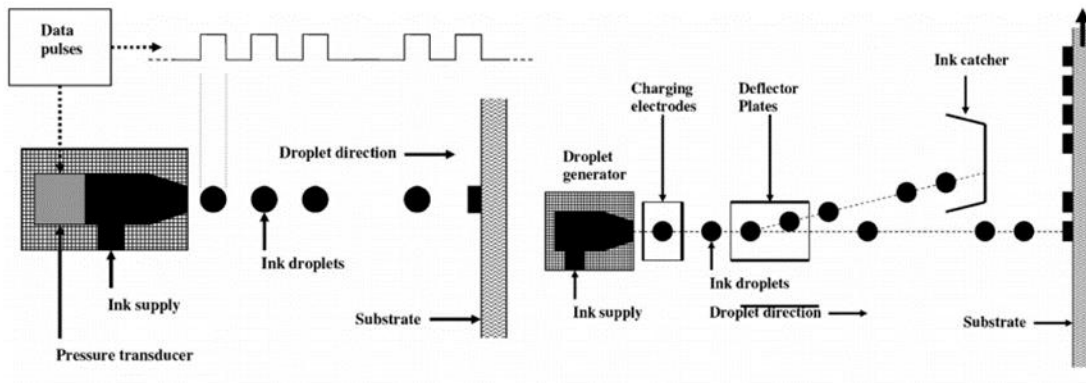


Figure 1-2 Schematics of inkjet printing methods [28]

1.3.1.3 Extrusion and Screen Printing

Extruding printing is a process designed for high viscosity ink. Usually, during the printing process, ink is extruded through a nozzle by physical force. Because of high ink viscosity, this method usually is applied for creating 3D structures [29, 30]. In order to print smoothly, inks are usually a combination of functional materials, such as metal nanoparticle, graphene, and carbon nanotube, with polymer binder materials, such as polyvinylpyrrolidone(PVP), polyvinylidene difluoride (PVDF) and Polydimethylsiloxane (PDMS) [31, 32].

The screen-printing method requires a mask to transfer the ink to the substrate by a blocking stencil. Usually, a blade or squeegee is moved across the screen to fill the open gaps and squeeze the ink into a predesigned mesh. This technology has a very long history. Today, it is also being applied to various printable electronic applications [33, 34]. In general, the quality of the screen printing is dependent on several factors including printer setting, screen options, substrate preparation, and ink quality [35]. Compared with other printing methods,

screen printing is more advanced for large-size and large-scale printing (Table 1.3). However, this method requires pre-designed masks; therefore, it has increased costs during the structure design process.

1.3.1.4 3D Printing and 4D Printing

Since 1980, the concept of three-dimensional printing has shown unprecedented development from both the academic community and industry. Up until now, a number of printing methods have been investigated and commercialized. Commonly, these printing methods are grouped into five groups [30]: material jetting (e.g., inkjet printing), extrusion (e.g., direct ink writing), photopolymerization, powder-bed fusion, and lamination. Table 1-3 presents examples of standard printing methods and their properties. Herein, I will only discuss the most commonly used methods for additive 3D printing applied in printable electronics, which are material jetting and extrusion.

Material jetting and extrusion printing are the two most prevalent strategies for 3D printing of electrodes material printing. Both methods are straightforward procedures with high cost-effectiveness, flexible choice of materials, and the ability to construct 3D structures without additional masking requirements. The printing resolution of direct ink writing is normally determined by the size of printing nozzles, ink viscosity, and various substrates that may be used during printing. Figure 1-3 (a) shows a printed 3D hemispherical antenna on a hemispherical glass substrate. Along with printing on a pre-designed 3D structured substrate, by depositing high viscosity ink, it allows printing a free-stand 3D structured electrode device. Figure 1-3 (b) demonstrates a fully printed 3D Li-battery [36].

Based on the 3D printing concept, the new term of “4D printing” has been given to the printed material that evolves into a predesigned shape, pattern, or structure over time [37]. The main requirement of a 4D printed object is that, after the printing process, the printed object responds to stimuli from either the natural environment or human intervention, which leads to a physical/chemical change of state over time. Acerce et al. showed that the dynamic expansion and contraction of electrode films prepared by restacking exfoliated metallic MoS₂ nanosheets could produce considerable mechanical forces by applying an external voltage (Figure 1-3) [38]. Several critical factors, including printed pattern structure, swelling ratios, and elastic moduli can be used to tailor the final structural properties of 4D-printed products. The 4D printing with shape-morphing features has been considered a dominant paradigm for designing and fabricating multifunctional structures. The 4D printing of nanomaterials remains an underexplored avenue for the fabrication of multifunctional, programmable, and smart structures/devices [39].

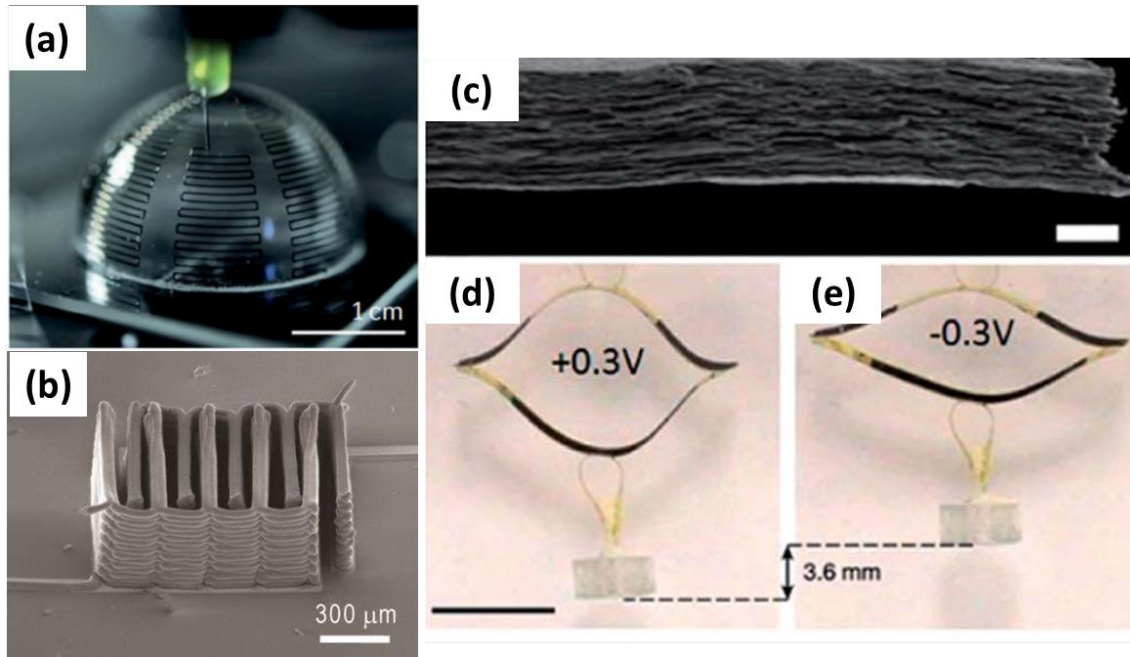


Figure 1-3 (a) Photo of a printed antenna on a hemispherical surface[40], (b) SEM images of printed 3D structured Li-battery [36], and (c–e) image dynamic expansion and contraction of a MoS₂ electrode . Scale bars of (c) and (d) is 2 mm and 1 cm, respectively[38]

Table 1.3 Examples of Standard Printing Methods and Their Properties

Printing method	Dimension	Features	Ink viscosity (mPa s)
Screen Printing	2D	High particle load High viscosity	1000-10000
Aerosol jet	2D/3D	High resolution Large material variety	1-1000
Inkjet	2D/3D/4D	Good uniformity Large application variety	1-50
Extrusion	2D/3D/4D	Low cost Easy to operation	30-10 ⁷

1.3.2 Printable Material

Although numerous printing methods have been developed, covering a wide printing size range, such as meter to micron size, the remaining technical barriers are what can be printed, and whether printed components can be directly applied on different materials. These barriers will determine if the printing is a viable method for manufacturing. In this section, different nanomaterials that have been involved in printable electronic applications are mainly discussed.

1.3.2.1 Conductors

Conductive materials are one of the most important components for printable electronic devices because they not only become a significant functional complement but also allow for a connection between various components of the device. The development of printable conductors allows printing to become a desirable method, which avoids the need for photolithography and leads to cost reductions [41]. Additionally, conductive ink is a simple solution to reduce the use of toxic materials, which is more environmentally friendly. So far, many kinds of conductive materials have been developed and studied. Low processing temperature, high conductivity, flexibility, and stretchable ability are typical properties of conductive materials. Nanoparticles, nanowires, and nanotubes are products created using conductive materials. For conductive materials, Al, Au, Ag, and Cu are desired candidates due to low curing temperature and good conductivity [42, 43]. In addition to their desirable electrical properties, the mechanical properties of conductive inks also attract attention for their flexible and stretchable applications [44]. Recently developed nanowires are highly flexible and

robust, and therefore conductive nanowires are promising materials for pressure and strain sensors [45-47]. Gond et al. reported a highly sensitive pressure sensor with gold nanowire. These gold nanowires-based pressure sensors can be operated at a battery voltage of 1.5 V with low energy consumption ($<30 \mu\text{W}$), and are able to detect pressing forces as low as 13 Pa with fast response time ($<17 \text{ ms}$), high sensitivity ($>1.14 \text{ kPa}^{-1}$) and high stability ($>50,000$ loading-unloading cycles) [45].

Applications of nanowires in highly flexible string sensors include health monitoring, motion detection, human-machine interface, as well as others [48-53]. Other than string sensors, it is also very easy to fabricate various sensors for environmental applications, such as temperature and humidity sensors by changing the structure and using material properties [54-56]. Furthermore, studies on silver-nanowire-based stretchable and flexible devices have been reported. Silver nanowires are considered strong candidates to overcome the limitations of indium tin oxide (ITO) as transparent electrodes [57]. Electrical and mechanical properties of conducting materials have significantly improved for printable electronics, and they have been inspiring other printable materials (semiconductors and/or insulators) to develop combined future applications.

1.3.2.2 Metal- oxide Semiconductors

Metal-oxide-based semiconductors have been widely used in various applications, such as sensors, field-effect transistors (FETs), catalysts, solar cells, and energy harvesting. More importantly, in printable electronics applications, it is well known that metal-oxide semiconductors are desirable materials for use in

sensors [58]. The sensing mechanism of metal oxide is very complicated. However, the most commonly accepted mechanism is described as a trapping of electrons by adsorbed molecules, inducing band bending that is responsible for changes in conductivity [59, 60]. Metal-oxides can be divided into two groups: transition-metal oxides and non-transition-metal oxides. Fe_2O_3 , TiO_2 , V_2O_5 , and WO_3 are representative transition-metal oxides, which are used as photoanodes, catalysts, and chemical detectors. Unlike transition-metal oxides, non-transition-metal oxides such as ZnO , SnO_2 , In_2O_3 , and Ga_2O_3 show good conductivity and high sensitivity [61, 62]. These materials can form the channel layer for transistors and are useful for multifunction sensors [60].

1.3.2.3 1-D nanostructured Semiconductors

Nanowires have gained a massive interest since the 1990s and became one of the most active research materials due to unique their one-dimensionality [63]. At the same time, the one-dimensionality of nanowires provides some promising solutions for many critical problems that have plagued the thin-film community, such as the reduction of lattice mismatch. The integration of optically active semiconductors onto silicon is critical for the next generation of computing tools. However, the conventional thin-film technology has run into interfacial lattice mismatch issues, which result in highly defective optical materials [64]. Nanowire growth provides a natural mechanism for relaxing the lattice strain at the interface and enables dislocation-free semiconductor growth on lattice-mismatched substrates, for example, GaAs on silicon and germanium [65, 66]. Additionally, nanowires also show unique physical properties. It has been reported that the yield

strength of gold nanowires is 100 times that of bulk materials [67]. The Young's modulus of nanowires is size-dependent due to surface stress effects, and it is significantly higher than that of the larger ones whose modulus tends to that of bulk materials [68, 69].

1.3.2.4 2-D Nanostructure Semiconductors

Graphene has attracted tremendous attention since 2004, with researchers attempting to understand its properties and potential applications [70]. One of the most important properties of graphene is that it provides long-range ballistic transport, which allows electrons to move without scattering over large distances [71]. The mass-less ultrahigh mobility of charge carriers could be as high as $10^5 \text{ cm}^2/\text{Vs}$ [72]. In addition, the mechanical hardness of graphene is higher than that of diamond, which is also considered a robust material for flexible devices [73]. High crystalline quality graphene can be grown using thermally intensive processes, such as chemical vapor deposition and thermal decomposition of silicon carbide. However, the high temperature process limits the types of substrate that can be used for the direct growth of graphene. Therefore, in order to use graphene on a substrate that cannot withstand high temperatures, such as polymer substrate, a transport process is needed. Therefore, rational design and scalable processing of graphene materials capable of functioning at low temperatures on a variety of substrate platforms has attracted significant interest recently.

Several methods have been developed for high quality, low cost, and large-scale graphene fabrication. One of the most popular methods is Hummer's

method, which is a chemical preparation method [74]. Hummers' method typically relies on the oxidation of bulk graphite powders, which causes natural dispersion of graphene oxide (GO) sheets with surface polarity and hydrophilicity. This method provides a scalable and low-cost process, but the end product is graphene oxide, with very low conductivity. To recover the electronic conductivity, a wide variety of reduction methods, including chemical [75, 76], thermal [77, 78], and solvothermal [79, 80] approaches have been developed. These reduction methods focus on reducing the GO to produce rGO. Additional deposition and patterning protocols are needed in order to fabricate on-substrate graphene electrodes. Therefore, it is crucial to develop a strategy that involves simultaneous reduction, exfoliation, and printing of 3D graphene electrodes into desired patterns on relevant substrates or many potential applications.

1.4 Laser Processing

Although printable electronics technology shows rapid developments in recent years, compared with the COMS technology, it still has a substantial technical gap, especially when it comes to mechanical accuracy and resolution. Today's COMS technology allows fabrication of nanoscale electrodes, while printing technology only allows a fabrication precision of around 1-10 μm . In order to shrink this gap, laser precise machine technologies can play an important role.

1.4.1 Continuous Wave, Pulsed and Ultrafast Pulsed Lasers

The laser can be differentiated into three groups: continuous wave (CW), pulsed laser, and ultrafast pulsed laser. CW laser output is essentially constant

over time and with an uninterrupted beam. CW lasers can run at a power level as low as a few milli-watts and up to 100 kW [81, 82]. A typical laser setup usually contains a laser amplifying medium (active medium), an energy pump, and a laser optical cavity (Figure 1-4). Research shows that under certain external excitation conditions, many materials can become active media and generate a laser. These materials can be gas, solid, liquid, and semiconductor. The wavelength of a laser is determined by the characteristics of the laser medium. Therefore, choosing a proper laser medium is very important. For example, the active medium of a ruby laser is made of the host of sapphire (Al_2O_3), which is doped with small amounts of chromium ions (Cr^{3+}). And for a CO_2 laser, the active gas phase material is generally comprised of carbon dioxide, nitrogen, hydrogen, and helium. Another important component of a laser is the pump, which is the energy source for the active medium and generates photons. If the amplifying medium is a solid, pumping is usually achieved by irradiating it with intense light. This energy is absorbed by atoms or ions within the medium which raises them into higher energy states to generate light. Again, a proper pumping method needs to be selected based on different materials. Usually, for solid materials, pulsed Xenon lamps and iodine tungsten lamps are used. For gas mediums, laser mediums are usually activated by a high electrical power discharge. Alternatively, an additional laser also can be used as a pumping method. The amplification of stimulated radiation is not very strong for most of the materials, and photons that are excited from amplification can be consumed by many factors such as observation by impurities and by scattering. Therefore, an optical cavity is used as a component to amplify

the laser intensity and provide a directional laser beam. The simplest cavity is defined by two mirrors facing each other (a total reflector and a partial reflector) whose reflectance can vary between 30% and close to 100%. Light bounces back and forth between these mirrors, gaining intensity with each pass through the gain medium. Photons that are spontaneously emitted in directions other than the axis are simply lost and do not contribute to the laser operation. As laser light is amplified, some of the light escapes the cavity, through the partial reflector. The output of the laser is the part of the beam that is transmitted by the output coupler. In an ideal laser, all the photons in the output beam are identical, resulting in perfect directionality and monochromaticity. In order to sustain gain as light travels back and forth between the mirrors, the waves must remain in phase and “reproduce” their wave pattern, which means that the cavity round-trip distance must be an exact multiple of the wavelength

$$N\lambda = 2 \times \text{Cavity Length}$$

where λ is the laser wavelength, and N is an integer called the mode number. This mode number is usually a huge integer, since the wavelength of the light is much smaller than a typical cavity length.

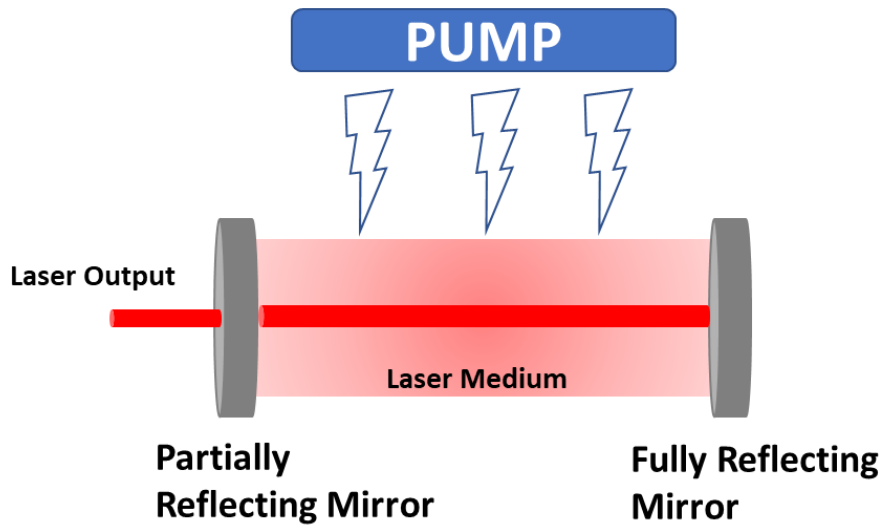


Figure 1-4 A schematic of the laser working principle

Some of the laser medium material, such as ArF and XeC, only lasts for several nanoseconds [81, 82]. These materials are not suitable to be used in a CW laser. Due to the short-lasting time, people define these laser devices as “pulsed” lasers, which typically produce pulses of 0.5-500 ns. The working principle of a pulsed laser is different from operating a CW laser. Due to the short laser reaction time, the simple two-mirror cavity structure cannot produce energetic pulses. The key factor in producing these energetic pulses is to control the laser gain and the amplification process. The energy will be stored and released when it reaches its maximum. This process results in an extremely high laser gain, which is called Q-switched operation, and can be conceptualized as a two-mirror cavity with an optical gate located between one of the mirrors and the laser medium (Figure 1-5). When the gate is closed, and the laser medium is pumped, photons cannot circulate in the cavity, and the excitation of the atoms builds up. As soon as the

gate is opened, photons start to build up via stimulated emission with a substantial gain at each round trip. A fraction of them (~20% to 40%) get coupled by the partly transmissive mirror. The result is a pulse with a very sharp raising time and a slower falling time, with a typical duration of 1 to 200 ns. The pulse duration depends on several parameters including: the type of gain medium, the amount of energy it can store, the cavity length, the repetition rate of the pulses, and the pump energy.

Pulsed laser produces a series of short pulses at a specific width and frequency. Usually, pulsed lasers produce lower average power than CW lasers. However, a pulsed laser can produce a peak power that is greater than its average power because energy is stored up in gain medium before it is released. This is the most critical characteristic of a nanosecond-pulsed laser: the capability to “store” and release energy very rapidly [82]. For example, a 25 W pulsed Nd: YAG laser can produce peak powers up to 5 kW for a few milliseconds. This regime is often applied for time-resolved scientific experiments, manufacturing processes related to ablation, and some other types of nonthermal materials modification.

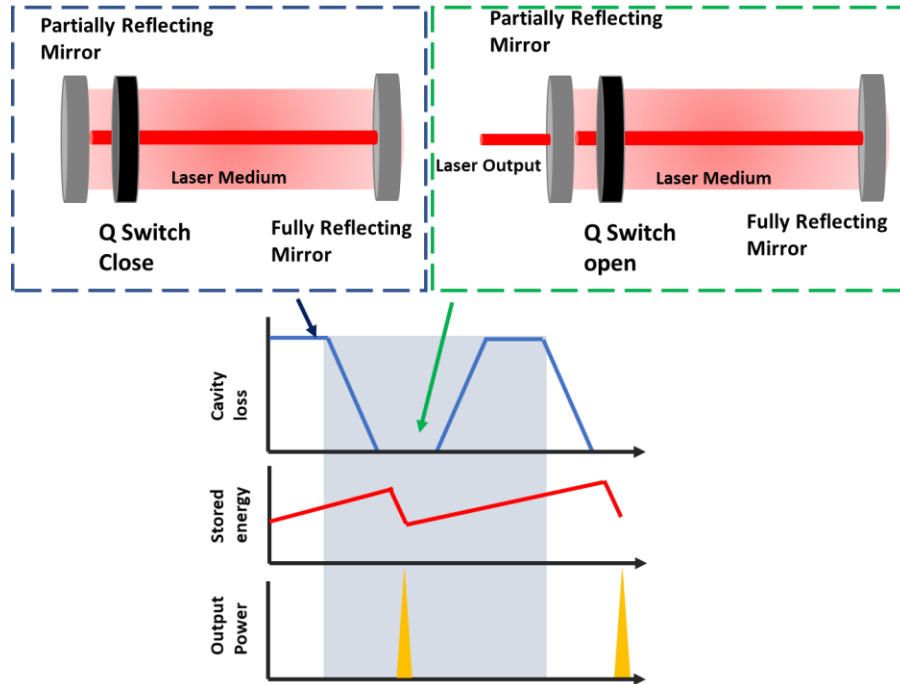


Figure 1-5 Operating principle of a Q switch pulsed laser.

Pulsed lasers that produce pulses in the time range of 5 femtoseconds to 100 picoseconds are defined as an ultrafast laser. Ultrafast lasers for material processes were first reported in 1987 by Srinivasan et al.[83, 84]. Ultrashort pulses are generated when light waves with a large number of modes, or integer multiples of half the light's wavelength (λ), are coherently emitted through their in-phase superposition, also known as mode-locking (Figure 1-6). With this technique, the modes are locked in phase (mode-locking regime), and their coherent interference causes the intracavity optical field to collapse into a single pulse traveling back and forth in the laser cavity. Every time the pulse reaches the output mirror, part of it is coupled out and available.

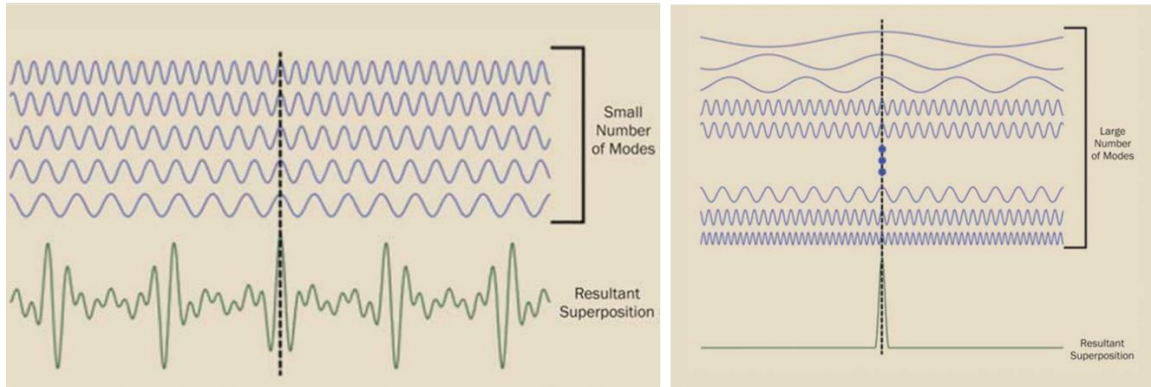


Figure 1-6 Working principle of the mode-locking regime in ultra-fast laser [81].

In our study, a semiconductor laser and a fiber laser were mainly used. The semiconductor laser is a laser based on semiconductor gain media [85]. A semiconductor laser is usually fabricated by growing a P-doped layer on top of an N-doped semiconductor substrate. Light is generated by flowing the forward current to a p-n junction. In forward bias operation, the p-type laser and the n-type laser are connected to the positive terminal and negative terminal respectively. Electrons enter from the n-type layer through holes in the p-type layer. When the two meets at the junction, an electron drops into a hole and light is emitted at that time[85]. This mechanism of light emission in a semiconductor laser is the same as a light-emitting diode (LED). Therefore, in some semiconductor lasers, diodes are used as light emission sources [86]. A fiber laser is a laser where the active medium is an optical fiber with rare earth elements doping; typically, erbium, ytterbium, neodymium, thulium, praseodymium, holmium or dysprosium [87]. Usually, compared with a gas medium laser, a fiber laser has an advantage in light quality, energy conversion efficiency, lifecycle, and stability.

The study demonstrated that by using a femtosecond ultraviolet excimer laser, polymethyl methacrylate was ablated without the formation of a heat-affect zone. Compared to the nanosecond laser ablation, the ablation threshold was reduced significantly. Limited heating diffusion on the surrounding region of the processed area is one of the essential features of ultrafast laser processing [88, 89]. Figure 1-7 shows the schematic of the thermally affected zone by different laser irradiations. As the length of the laser pulse reduces, the heat-affect zone will be reduced, and the material ablation will be enlarged. This feature encourages high precision microfabrication for various materials, such as biological tissues, semiconductors, and insulators [90]. For an ultrafast interaction, the absorption of photons stimulates the carriers within a hundred femtoseconds (fs), which is too short for disturbing lattices. The efficient energy transfer from the electrons to the lattice was via electron-lattice scattering after the end of the laser pulse [91, 92]. Depending on the electron-phonon coupling strength of different materials, the thermal coupling between free electrons and lattices typically occurs in the range of 1-100 ps. The typical electron-phonon coupling time of a hundred fs is much shorter than the heat transfer period by thermal conduction. Therefore, the thermal diffusion to the laser-irradiated surrounding area is minimal [93]. This is very attractive for the high-resolution processing of ultrafast laser. In an ideal case, ultrafast excitation only occurs within the focal spot.

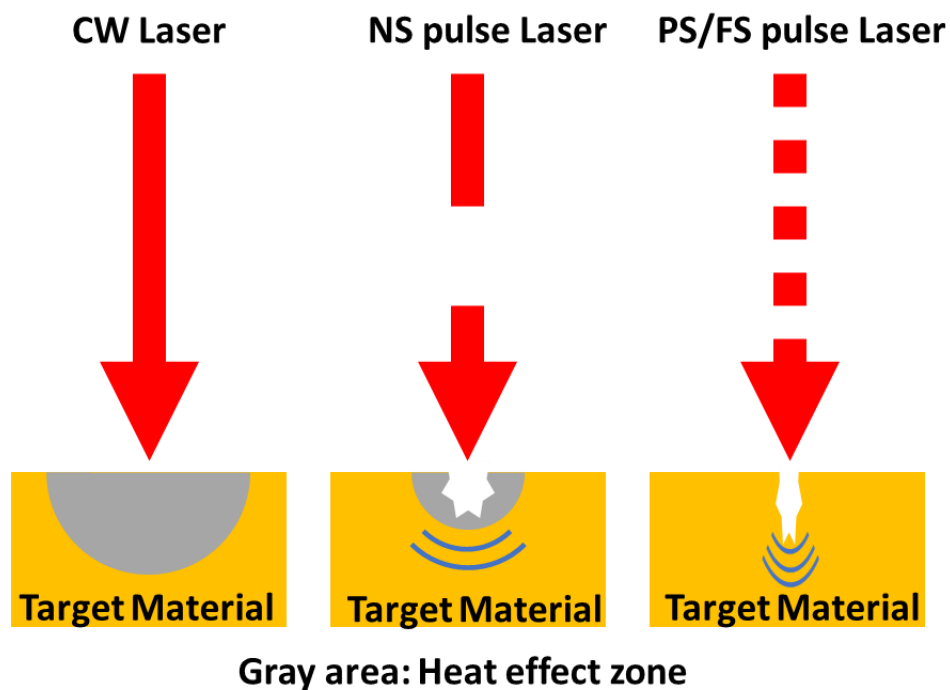


Figure 1-7 Schematic of laser thermal affected zone by different laser irradiation

1.4.2 Laser Reduction

Taking advantage of high energy and high heat intensity, laser reduction has been applied in many fields, including metals and 2D materials. In 2012, Kaner et al. reported a laser direct writing approach for reducing GO films using a DVD laser burner [94, 95]. The laser scribing technique allowed for the controllable fabrication of 3D architectures from 2D stacked GO layers. The intensity and power of a 788nm wavelength IR laser can be controlled by a light scribe program. The maximum power output of 5 mW laser beam is pulsed through an objective lens to focus on the substrate surface, as shown in Figure 1-8(a). This technique is based on producing photothermal effects (the temperature may range from 300 to 500°C)

through an IR laser beam to volatilize the functional groups (epoxy, hydroxyl, and carboxyl [96]) on the GO surface and produce conductive reduced GO. This maskless process allows an elective reduction of GO to create any pre-programmed pattern, which has led to the fabrication of many graphene-based electronics and energy storage devices [97, 98]. Figure 1-8 (b) shows an image of fabricated micro-devices on Kapton tape. This approach shows significant promise as a solid-state approach for scalable fabrication of graphene-based devices from GO films in a single processing step [94]. Distinctively, the Tour group pioneered the fabrication of graphitic carbon from commercial polyimide through CO₂ laser irradiation and extended this concept to a variety of natural and synthetic carbon precursors [99, 100]. Extremely high localized temperatures are produced by laser beams, resulting in violent lattice vibration due to the energy from laser irradiation, which can easily break the C-O, C=O, and N-C bonds and lead to their rearrangement to form their pre-determined structures. Since the laser converts the carbon precursors into a graphitic material, this technique is referred to as laser-induced graphene (LIG). As of today, laser reduction graphene shows enormous potential and has already become one of the core techniques in flexible micro-device fabrication. Table 1-4 shows laser technologies that have been used to produce graphene architectures from various carbon sources.

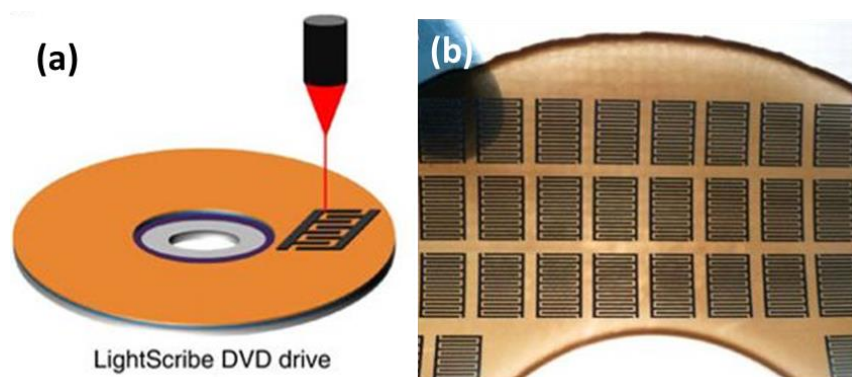


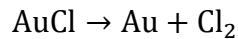
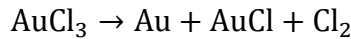
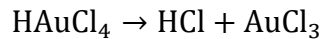
Figure 1-8 (a) Schematic diagram showing the fabrication process for an LSG micro-supercapacitor and (b) image of micro-devices fabricated by LSG process[94].

Table 1.4 A Table for Laser Technologies Used to Produce Graphene

Architectures from Various Carbon Sources

Carbon source	Laser type	Laser Power	Application	Reference
Go	LightScribe DVD burner	788m, 5mW	Super capacitor	[94]
Go	LightScribe DVD burner	788m, 5mW	LED	[101]
GO	450 nm	90nW	Strain sensor	[102]
GO	650 nm laser	20mW	Photodetector	[103]
PI	CO ₂ laser	2.4-5.4mW	Supercapacitor	[100]
PI	FS laser	100-400mW	3D supercapacitor	[104]
PI	FS laser	400mW	Sensor	[105, 106]
Lignin	FS laser	450mW	Supercapacitor	[107]
Paper, cloth, food	CO ₂ pulsed laser	3.75W	N/A	[108]
Wood	CO ₂ pulsed laser	7.8W	Electrocatalyst	[109]
CH ₄	532 nm	5W	N/A	[110]

Laser reduced graphene as a mask-free approach has been proven effective in manufacturing in-plane micro-devices. On the other hand, laser reduced metallic material also shows enormous potential for in-plane device fabrication. Li et al. report an in-situ laser reduction of graphene oxide/Au nanoparticle microelectrode for micro-supercapacitors on photo paper. The fabrication process is shown in Figure 1-9. During the laser writing process, a highly focused laser beam leads the decomposition and reduction of AuCl_4^{-1} to form Au nanoparticles[111]. During this reaction, AuCl_4^{-1} is directly reduced by GO that has been mixed in the HAuCl_4 solution. The strong photothermal effect from laser irradiation not only leads to the decomposition of AuCl_4^{-1} but also promotes the reaction through the reduction of GO [112], the whole reduction process is shown as [111]:



Similarly, Zhou et al. developed a $\text{Cu}/\text{Cu}_x\text{O}$ integrated flexible pattern based on laser involved reduction of Cu^{2+} (as shown in Figure 1-9) [113]. In this study, a Cu salt ink is coated on a flexible substrate. A continuous diode laser system is used for creating a designed pattern. During the reaction process, hydroxide from the alcohol solvent and the lactam ring of the PVP contained in solution react first, generating amorphous carbon, methylene gas, methylamine gas, and propionic acid. The propanoic acid is decomposed to formic acid, which then reduces Cu^{2+} to Cu^{1+} and further reduces the Cu^{1+} to Cu [113]. From this reaction, porous

structured highly conductive Cu electrodes are created. Additionally, Zhou et al. demonstrated an approach to rapidly fabricate conductive silver electrodes on transparent flexible substrates based on laser reduction (Figure 1-9 (e)) [114]. A 405 nm CW laser is used for silver nitrate reduction. Ag ion ink is synthesized via an ion-exchange between silver nitrate and sodium citrate (Figure 1-9 (f)). A remarkable bonding strength is observed, and after a test in which it was bent 1500 times, the resistance only increased by 5.2%. These studies show potential for laser involved metal electrode fabrication on flexible substrate, which would significantly benefit in microelectrode device fabrication.

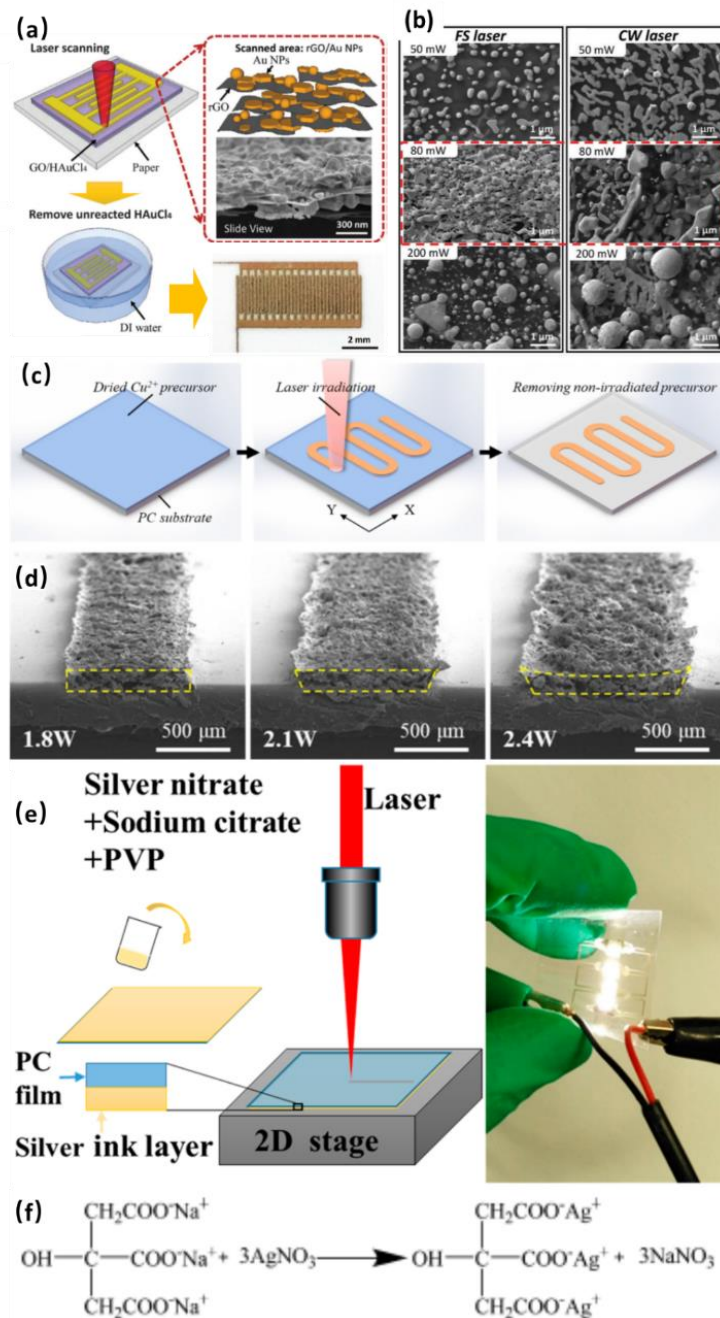


Figure 1-9 (a) Fabrication process for laser reduce Go/Au microelectrode, (b) SEM image of EM images of the FS laser and CW laser written rGO/Au microelectrodes [111], (c) Schematics of the laser direct writing process for laser reduced Cu electrode, (d) Tilted SEM images of the Cu pattern with varied laser power [113], (e) Schematics of laser direct writing silver electrode and fabricated electrodes, and (f) Reaction of AgNO₃ and Sodium Citrate [114].

1.4.3 Laser Sintering

Selective laser sintering (SLS) is one of the most promising methods in additive manufacturing that uses a laser beam to selectively fuse and sinter polymer particles or metal powder by scanning cross-sections on the surface of a powder bed layer-by-layer into an object that has a desired 3-dimensional shape based on a CAD model [115, 116]. After each cross-section is scanned, the powder bed is lowered by one-layer thickness. A new layer of material is deposited on top and the laser scans for the next layer. This process is repeated until the object is completed. SLS can produce parts from a relatively wide range of powder materials, including wax, polymers, polymer/glass composites, polymer/metal powders, metals, and ceramics [117, 118]. The schematic of the SLS process is shown in Figure 1-10. The primary binding mechanisms of SLS include solid-state sintering, and partial melting of material powder, as well as chemically induced binding and liquid phase sintering [119]. Unlike some other AM processes, SLS does not need printing support structures, and the non-sintered row material powder provides a natural support for holding the 3D structure during the printing process. The laser sintering process also has been applied in the sintering of extrusion printed 3D structure, which will be discussed in Chapter 2.

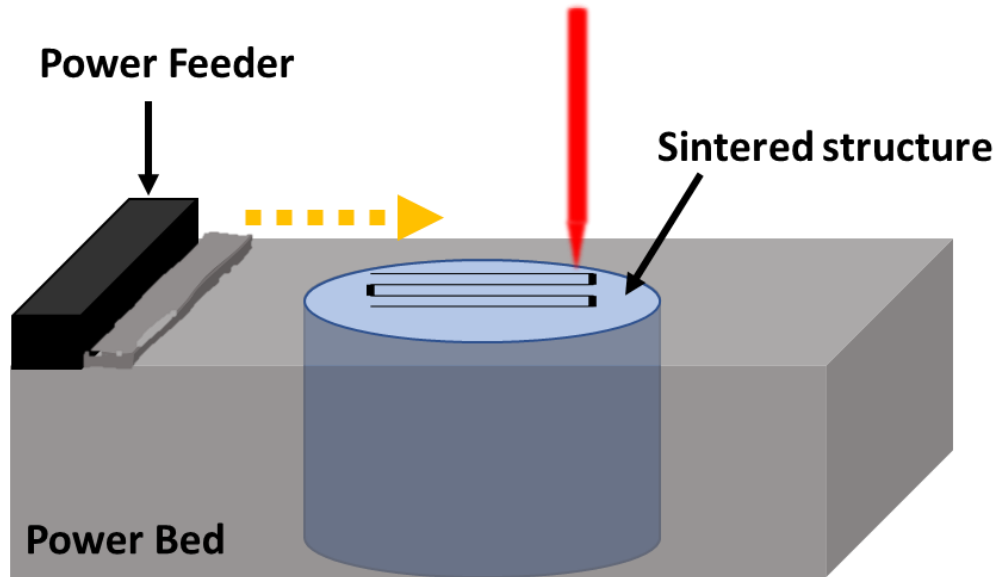


Figure 1-10 Schematic of the selective laser sintering process

1.4.4 Laser Nano Joining

With the exceptions of sintering and reduction, which are relatively large size or large-scale processes, as a precision matching tool, the laser shows promise for nanoscale matching. With the extensive ongoing research of nanoelectrode devices and nanoelectromechanical systems, an inevitable next step is studying nanoscale interconnections. Naturally, nano-component (nanowire, nanotube, nanoparticles, etc.) joining becomes an essential step for high-quality nanodevice fabrication, which provides not only mechanical support and integration but also has significant contribution to electrical connection and optical coupling of an object [120, 121]. For a nanoscale joining, various methods have been proposed and applied to join NWs, such as cold-welding [122-124], Joule heating [125-128], thermal annealing [129] and mechanical pressure [130].

A laser is a powerful tool for precision tool with important role in micro- nano-size machining and joining in recent years [131, 132]. Peng et al. found that that end to end joints of nanowires can be readily obtained by selective activation on single-crystal nanowire surfaces due to lattice matching at the ends of the nanowire [123]. However, the formation of Y- or T-shaped end-to-side joints between metal nanowires, especially when they are not initially in contact, are desired for nanocircuits. Similarly, Lin et al. report their recent research about FS laser joining of silver nanowires with end to side joints in Y and T shape joining. After FS laser irradiation, melting and deformation occur in and near the gap between components. As Li describes, the ultra-short pulse laser provides direct energy into the components in the vicinity of the gap, producing a strong localized heating effect and partially melting the nanowires, causing a flow of metal into the gap, forming a bond. Under these conditions, the cross-sectional area of one nanowire component can become smaller as silver metal is drawn into the gap in response to electrical forces[132]. Figure 1-11 shows experimental results for silver nanowires joining and FEM simulation results. Additionally, Dai et al. shows their result of using CW laser in Cu nanowire spot welding [133]. As opposed to a FS laser, the high thermal effect from a CW laser totally melts the end of Cu nanowire and reshapes it to a sphere structure, as shows in Figure 1-11 (e). With the development of research about laser nanojoining, people have a decent understanding about joining based on identical metal material, such as silver-silver joining and copper-copper joining. However, joining between different metal materials or metal-polymer joining still needs to be investigated.

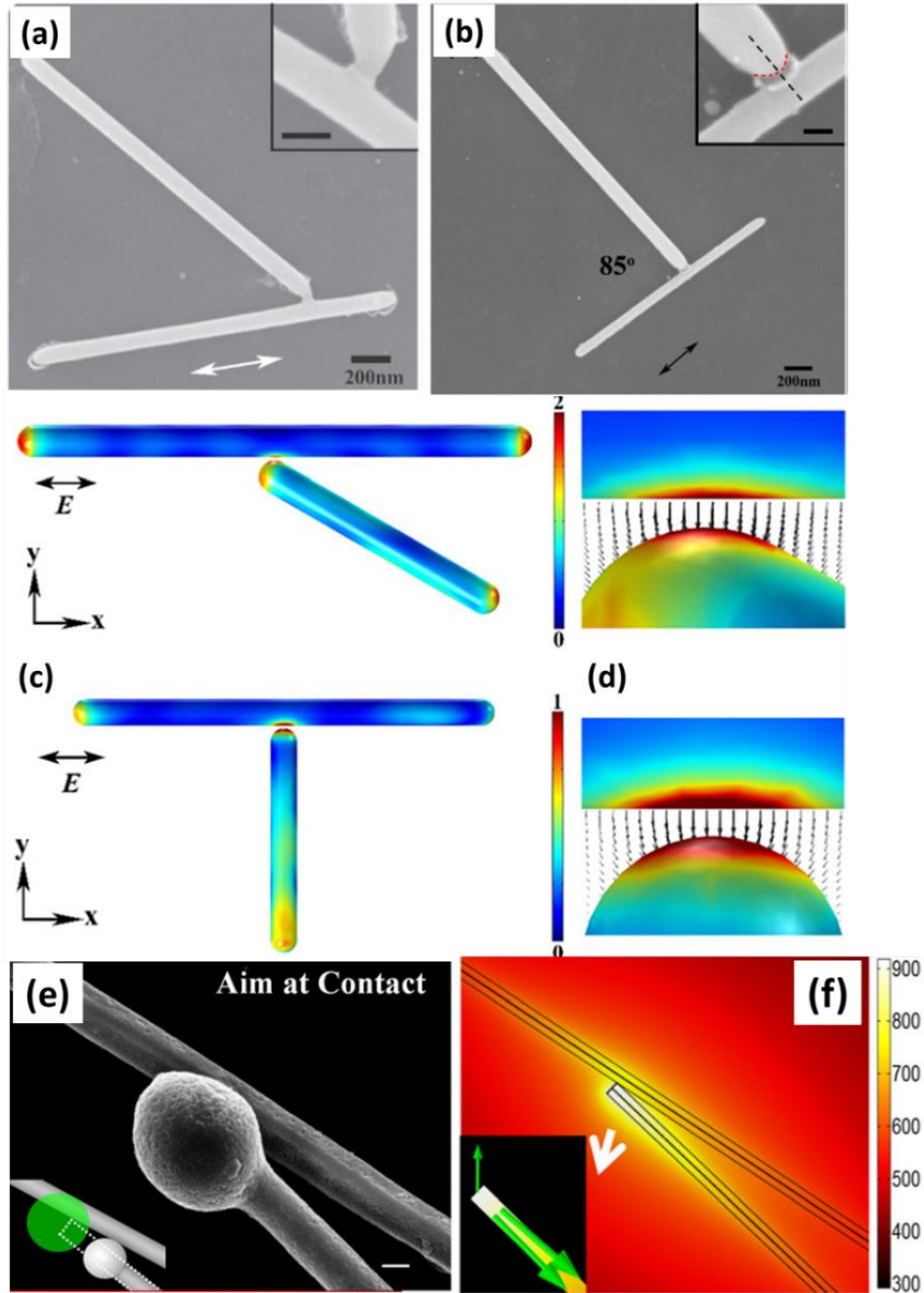


Figure 1-11 (a-b) Different types of joined branched silver nanowire structures after FS laser irradiation and (c-d) FEM simulation of the normalized electric field intensity near silver nanowire structures irradiated with a polarized plane wave.[132]. (e-f) SEM image of Selective nano welding of Cu nanowires and simulated results of corresponding temperature profiles [133].

1.4. 5 Laser-Processed Micro- and Nanodevices

1.4.5.1 Energy Storage Devices

As development of micro-electrical devices grows, wearable and compact energy storage devices are urgently needed. While researchers are developing high-performance batteries, laser processing attracts huge attention and shows potential impacts on the battery industry. Laser processes for cutting, annealing, structuring, and printing of battery materials have great potential to minimize the fabrication costs and to increase the electrochemical performance and operational lifetime of a battery [134]. The concepts of laser cutting and laser annealing of electrodes take advantage of high energy and fast process speed of laser processing to increase fabrication efficiency [135-138]. A different approach to increase battery performance is using lasers for electrode surface processing, such as laser-assisted self-organizing structuring and direct structuring. Both methods use targeted approaches to create 3D structures on electrodes' surface to increase active surface area, which leads to increased areal energy capacities while maintaining high power densities.

Figure 1-12(a) shows the SEM image of a laser structured 3D pattern on LiCoO₂ thin film on a silicon wafer as a cathode material for Li⁺ battery. The research shows that 3D structured cathodes provide higher capacity than unstructured samples. Also, the capacity of the unstructured films dropped by 37 % after the five-fold increase of charging current from C/20, while the structured films dropped by 22.5 % and 15 %, respectively [139]. Laser induced surface patterning also has been used in thick film applications (shown in Figure 1-12(b)).

As a result, it's been shown that laser-structured cathodes exhibit discharge capacity retention of 68% at a 1C rate, while unstructured cathodes retain only about 45% of their initial capacity at the same discharge rate [140].

As a power source, a battery provides large power capacity, but charge/discharge rates and cycle life are still limited. As an important power source, supercapacitors are being developed as energy devices for microelectronics as they can provide both a high energy density and a long cycle life [141]. At the same time, laser direct writing on polymer substrate is gaining interest as a promising technique for flexible electronic devices, due to the porous structure and high conductive carbon that can be introduced by a laser. This discovery also shows promising results in supercapacitor fabrications. Jung et al. demonstrated a flexible supercapacitor with $\sim 800 \mu\text{F}/\text{cm}^2$ specific capacitance at a 10 mV/s scan rate based on femtosecond laser-induced porous carbon on polyimide substrate [142].

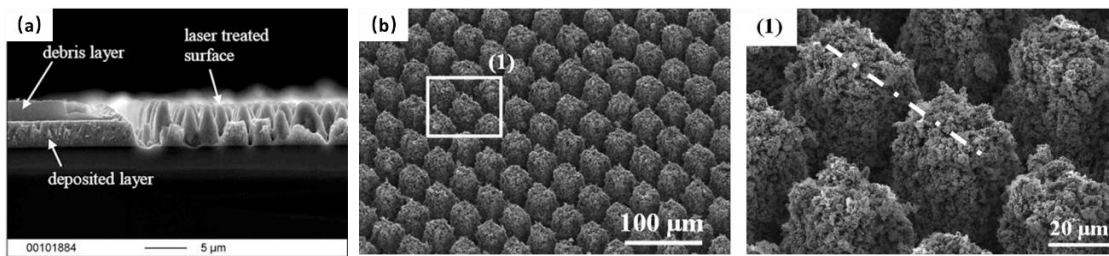


Figure 1-12 (a) SEM image of a cross-section of laser structured LiCoO_2 thin film deposited on a silicon substrate [139] and (b) laser structured LiMn_2O_4 thick films

Li et al. developed a direct laser writing of graphene oxide/Au nanocomposite micro-supercapacitors with an areal capacitance of 0.46 mF/cm^2 at a high scan rate of 100 V/s [111]. Cai et al. utilized a 405 nm semiconductor laser to irradiate the PI sheet to prepare the carbon electrodes of supercapacitors [143]. The obtained supercapacitors exhibited a high performance of approximately 31.9 mF/cm^2 at 0.05 mA/cm^2 current density, which is due to the hierarchical porous structures and thickness of the carbon electrode, which were formed during the laser writing processing. Taking advantage of the limited thermal effect of the FS laser, Wang et al. reported a novel fabrication process in which a laser 3D direct writing technique was introduced to fabricate multi-layer micro-supercapacitors (MSCs) [104]. Multilayer MSCs were fabricated by a bottom-to-top process on a PI substrate. Figure 1-13 shows the SEM image for the cross-section of the 3-layer MSCs. Conductive layers were partially overlapped with a total thickness of around $140 \text{ }\mu\text{m}$ for 3L MSCs for a stable interconnection. For the processing, the femtoseconds laser was focused at a position that was $80 \text{ }\mu\text{m}$ below the surface of the PI sheets by using a $\times 50$ objective lens which induced the carbonization of the bottom layer. Then the second carbonization layer was written by focused laser at $65 \text{ }\mu\text{m}$ below PI sheets surface, which created the middle layer. Finally, the focusing laser was adjusted to the surface of PI sheets to produce the surface carbonization. Due to its 3D structure, the 3-layer stacked MSC shows a specific capacitance as high as 42.6 mF/cm^2 at 0.1 mA/cm^2 current density.

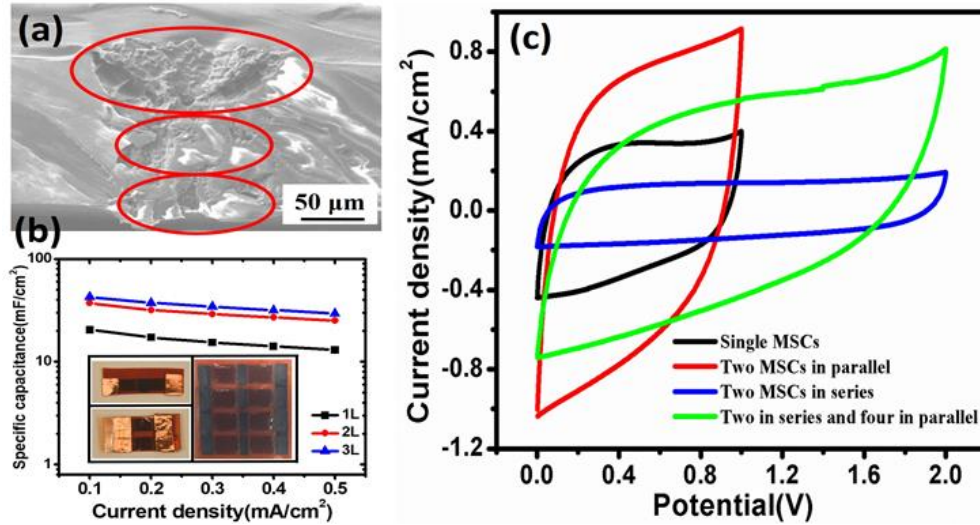


Figure 1-13 (a) Cross-section of three layers electrode. (b) The specific capacitances of MSCs calculated from GCD curves as a function of current density CV curves of 1L, 2L and 3L MSCs obtained at scan rates of 10 mVs-1 and inserted is the photos of fabricated carbon electrodes of different connections (c) GCD curves of four kinds of connections of MSCs at current density of 0.1 mA/cm².

1.4.5.2 Sensors

The laser as a tool for precision machining has made a considerable contribution to sensor fabrication. It has been previously stated that the LIG, a typical representative for sensor use, provides a large surface ratio with good conductivity. Naturally, LIG is applied as a material for various chemical and biosensors. Cheng et al. published their recent research about a biphenol-A (BPA) sensor on a polyimide substrate [105]. An aptamer-based, highly sensitive and specific sensor for atto-to femtomolar level detection was fabricated by laser direct writing technology (Figure 1-14(a)). Additionally, excellent mechanical properties of LIG expanded the number of applications of LIG based sensors. Rahimi et al. reported a high stretchable and sensitive strain sensor based on LIG [144]. The

sensor can stretch to about 100 % strain, and the gauge factor is up to 20,000, which provides very high sensitivity (Figure 1-14(b)). Tian et al. developed a laser patterned pressure sensor, which showed a sensitivity of 960 %/kPa in a pressure range up to 50 kPa with a low response time as 0.4 ms (Figure 1-14(c)) [145]. In addition to physical parameters (temperature, humidity, force, etc.), LIG also has been applied to the bionics area. Tao et al. reported a LIG-based sound sensor [146]. The sensor can detect weak vibrations from different human activities such as a cough, hum, scream, swallow or nod. By differentiating differences in frequency and intensity, the sensor can detect different sounds (Figure 1-14(d)). These applications take advantage of resistance changes of the graphene layer due to shape changes (pressing, stretching, or vibrating).

In addition to LIG, the laser-induced forward transfer (LIFT) technique has become an important method for high resolution and direct printing of a wide range of materials, especially for high-resolution electrodes fabrication. The principle of LIFT is to transfer a small part of the material from a thin donor layer onto a receiving substrate by a focused laser beam [147]. It has been shown that LIFT can achieve submicron resolution for the printing of metals by using a femtosecond laser [148]. A LIFT printed humidity sensor has been demonstrated by Fernández-Pradas et al. [149]. Silver electrodes were transferred and printed on paper with approximately 100 μm resolution. Besides metals, LIFT is also able to

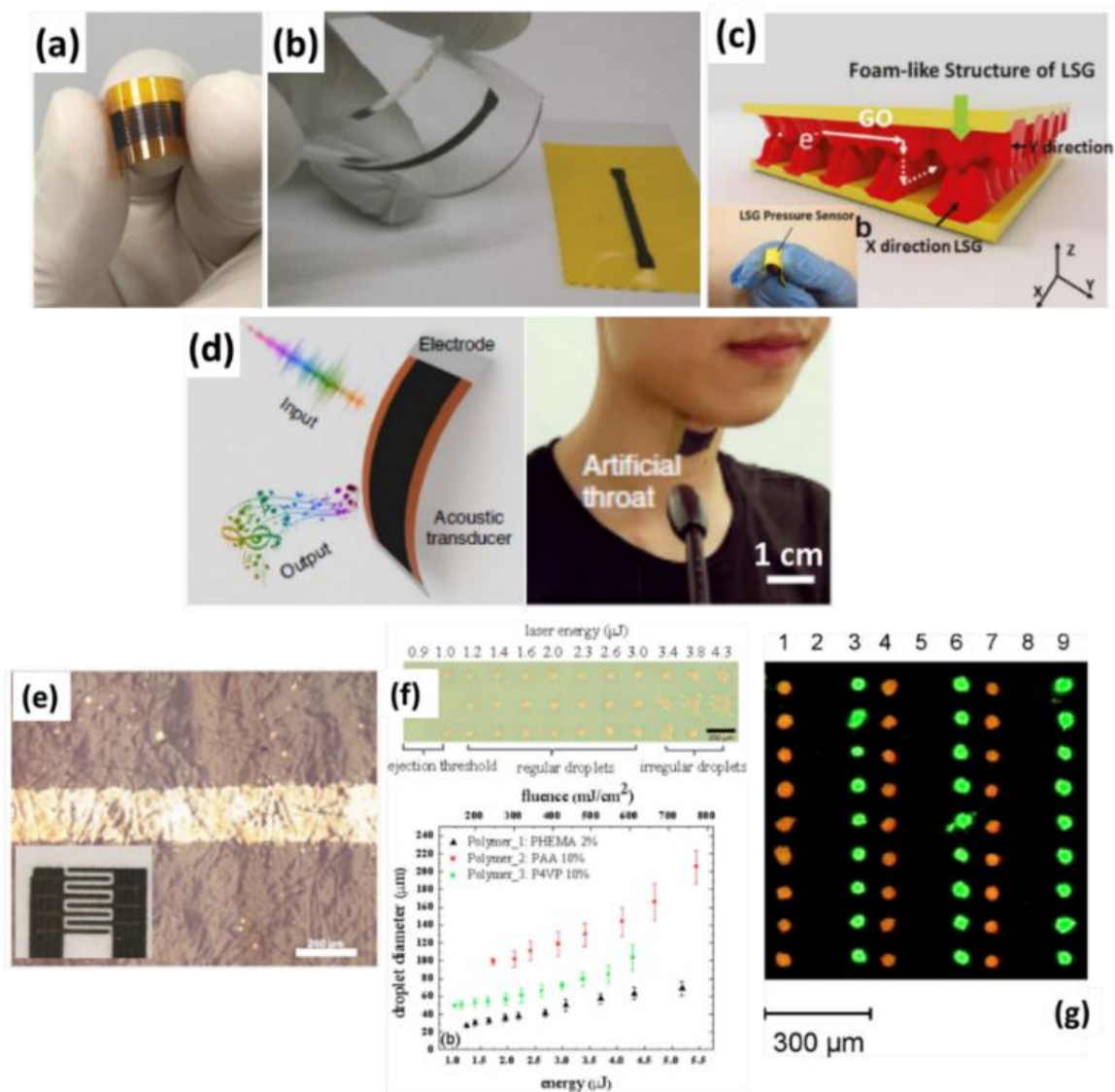


Figure 1-14 (a) Image of LIG BPA sensor[105], (b) image of LIG strain sensor [144], (c)schematic of LIG pressure sensor working principle [145], (d) LIG sound sensor [146], (e) image of LIFT printed Ag line (inset: fabricated humidity sensor), (f) LIFT printed polymer drops [150] and (g) fluorescence image obtained DNA drops transferred by LIFT[151].

print/ transfer polymer materials. Boutopoulos et al. demonstrated using LIFT to transfer different polymer materials [150]. In this research, poly (2-hydroxyethyl methacrylate), polyacrylic acid, and poly (4-vinyl pyridine) were successfully transferred to a silicon substrate and it was shown that the optimum sensitivity of the sensors could be achieved by varying the polymers' drop size. In 2004, Serra demonstrated a functional DNA microarray was prepared through the LIFT [151]. The transfer process allowed decreasing the spot diameter to around 40 μm . This work significantly extends the potential of LIFT in biosensing applications.

1.4.5.3 Semiconductor Nanowire Field Effect Transistor (FET) and Memristor

The combination of nanotechnology and integrated circuits results in a field-effect transistor: an electronic device which uses an electric field to control the flow of current. Field-effect transistors have various applications that have been reported such as flat-panel displays (transparent flat transistor TFT), computers, smartphones, video game systems and personal digital assistants [152]. Novel transistor applications demand some basic features such as high mobility, compatible fabrication processes, suitable substrates, and excellent transparency or flexibility in some special situations. However, due to the material properties and fabrication processes, traditional FETs based on amorphous or polycrystalline silicon have a hard time meeting the requirements of the rapid expansion of functional microelectronics, especially for the transparent and flexible electronics.

Compared to silicon-based channel materials, low-dimension conductive and semiconductive materials with excellent electrical and optical properties have attracted intensive attention in recent years [153-155]. By eliminating the

limitations of poor material properties occurring with organic semiconductors and amorphous oxide thin films, such as low carrier mobility and material stability, low dimensional materials present potential applications in high-performance electronic devices [156]. Among various low dimensional materials, metal oxide nanowires with controllable size and electrical properties are especially attractive as 1D semi-conductive material for FET. These high-quality semiconducting metal oxide nanowires can be synthesized easily by vapor or solution methods, which have attracted great interest in transparent flat transistor (TFT) applications. Additionally, the beneficial properties of metal-oxide nanowire, such as one-dimensional geometry, sub-micron size, usually large band-gap, and excellent properties mentioned above make metal oxide nanowires excellent candidates in high-performance TFTs with characteristics like flexibility, high transparency, high carrier mobilities, high on-off ratios, low threshold voltages, and steep subthreshold slopes.

Si and Ge nanowire have been studied as a semiconductive transistor material since the late 1990s [157], and Si-based transistors exhibit properties comparable to bulk single-crystalline devices [158]. Because of the high electron and hole mobilities, Ge nanowire devices also have been studied. Compared to Si nanowire FETs, Ge nanowire devices are expected to have smaller contact resistance effects because the smaller Ge bandgap will yield a lower Schottky barrier at the metal/NW interface [159]. Field-effect transistors prepared from vapor-liquid-solid (VLS) growth Ge nanowires exhibited on currents and transconductances up to 850 $\mu\text{A}/\mu\text{m}$ and 4.9 $\mu\text{A}/\text{V}$, respectively, with device yields

of >85% has been reported [160]. Additionally, Ge/Si core/shell nanowire has been reported to reduce the Schottky barriers effect [161]. As one of the most prominent materials in the metal oxide family, ZnO has been intensively studied for its versatile physical properties and potential applications in electronics, optoelectronics, and piezo electronics [162, 163]. ZnO is a direct bandgap (3.37 eV at room temperature) semiconductor, with a stable wurtzite crystal structure and polar surfaces. It is well known that ZnO nanowires have a large number of surface defects, mainly oxygen vacancies, that will adsorb gas species and act as scattering and trapping centers [164]. These defects and chemical species have important influences on the performance of ZnO NW-FETs.

Another novel application of metal oxide nanowire is memristor or resistive switching random access memory (ReRAM) devices, which are gaining wide attention for the application of non-volatile memory devices [165, 166], logic circuits [167, 168], and neuromorphic computing [169, 170] due to the advantages of simple structure, fast switching speed, high density, and low power consumption, etc [171-173]. The memristor device was originally proposed as the fourth elemental circuit unit theoretically by Chua in the 1970s. In 2008, Strukov et al. established the first resistive switching devices based on TiO_2 . Since then, the concept of resistive switching devices has been widely noticed. The working principle of a memristor is unique. As a resistive switch, a memristor material has

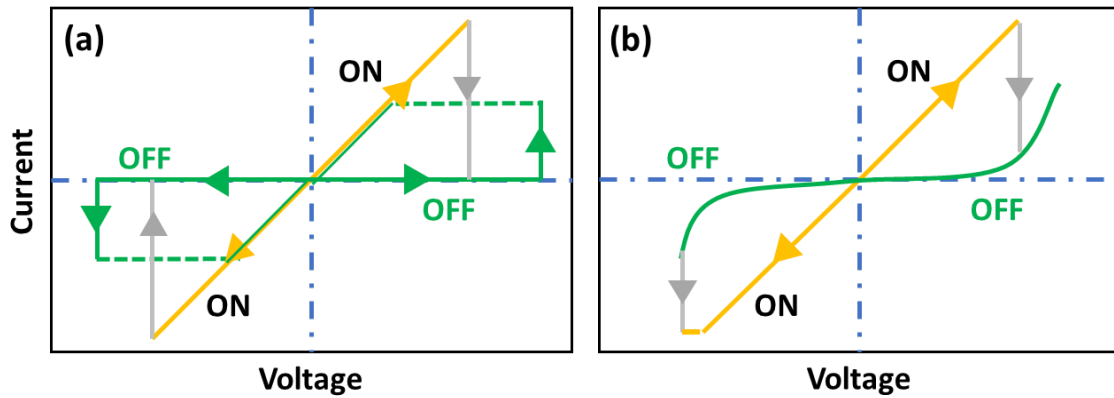


Figure 1-15 Sketches for Current-Voltage characteristic of resistive switching, (a) unipolar switching, and (b) bipolar switching.

at least two states: a high resistance state (HRS) and a low resistance state (LRS). These two states can be switched regarding applied voltage or current. Figure 1-15 shows a typical current-voltage curve for unipolar switching and bipolar switching. The switching mechanism of the memristor is divided into thermal, electrical and ion-migration induced resistive switching. And Ion migration mechanism could be further divided into cation-migration cells and anion-migration cells. The former is based on the electrochemical growth and dissolution of metallic filament, and the latter is based on the formation of electronically conducting paths and remove local reduce processes [174].

Although the ReRAM concept has been widely accepted since 2008, in the past decade, it has shown a rapid development. The materials that have been developed for ReRAM devices can be classified into five types: binary transition metal oxides (TiO_2 , VO_2 , CuOx , FeOx , WO_3 , Ta_2O_5 , NiO , etc.), Perovskite-type complex transition metal oxides ($(\text{Ba}, \text{Sr})\text{TiO}_3$, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, BiFeO_3), Large

bandgap high-k dielectrics (Al_2O_3 , SiO_2 , and Gd_2O_3), Carbon-based materials (graphene oxide, amorphous carbon materials), and emerging organic and bio-materials [172]. The applications of memristive devices include multilevel memory for data storage [175-177], logic calculation[178-180], and neuromorphic computing [181-183].

In summary, all the FET and memristor applications that have been discussed in this chapter are based on the standard CMOS fabrication process, which required a cleanroom environment and high processing temperature. In order to produce a low-temperature fabrication process, especially when using a polymer or a paper as a flexible substrate for flexible electronics development, printing technology becomes a critical process. Additionally, laser processing can be applied as auxiliary processing for printing technology. This processing for FET or memristor devices has not been reported yet.

1.5 Research Objectives and Hypotheses

The core object of my Ph.D. research is to develop a novel fabrication process for high-quality electronic devices on a flexible substrate, combining printable electrode technology and laser technology. Compared to metal and polymer material, semiconductive material based printed devices are very attractive but less established. The physics, microstructure, and properties controlling the joining of semiconductors to metal are complicated. When a semiconductor and metal contact each other and intermixing occurs, their electronic structures will be changed at the interface due to the fact that the

bonding configurations differ from those in the bulk materials [184]. This situation is even worse at a micro and nanoscale.

This situation is even worse at a micro and nanoscale.

Two typical connections exist between semiconductive nanowires and electrodes. A Schottky barrier usually occurs due to differences in work function of the metal and the semiconductor, which is defined as the minimum energy needed to remove an electron from the solid to a point in the vacuum immediately outside the solid surface. This leads to a quadratic increase in the magnitude of electrostatic potential, and the resulting potential barrier will be parabolic in shape. Moreover, the so-called diffusion potential V_{do} is given as:

$$V_{do} = \phi_m - \phi_s \quad (1-2)$$

Where ϕ_m and ϕ_s represent the working function of the metal and the semiconductor, respectively. If $\phi_m > \phi_s$, V_{do} is positive, and the bands are bent upwards; for the case of an n-type semiconductor, this produces a barrier which the electrons have to surmount in order to pass from the semiconductor into the metal, which, as we will see, leads to rectifying properties. On the other hand, for a p-type semiconductor, the band-bending causes no impediment to the motion of holes, and no rectification takes place, thus giving 'ohmic' contact [185]. Controlling the barrier height is a challenging task in transistor fabrication. It greatly depends on the material characteristic and semiconductor crystallization [186].

Lasers are a powerful energy source, able to deliver high energy to a material within a very short period. The laser-induced energy can be precisely localized in space and time, enabling excellent control over the manipulation of

materials[187]. In this dissertation, I will discuss laser processing for different types of material, including polymer, Al nanoparticles, and Cu nanowires. The laser processes include ablation, carbonization, sintering, and partially melting and recrystallization. Researches have shown that laser interaction can lead to changes in crystal growth, resistive switching, magnetization dynamics, structural distortion, and structural transformation for semiconductive material [188-191]. Therefore, there are good reasons to hypothesize that laser processing has a significant impact on printed semiconductive devices.

In this research project, I hypothesize that laser welding could reduce the contact resistance between nanowires and electrodes, which will lead to performance improvement in printed memristor devices. Also, high energy density and rapid local temperature change will lead to the recrystallization of semiconductive nanowires, and device performance could be finely tuned by appropriate laser irradiation. In some cases, organic residues from nanowire synthesis processes could create an additional junction between metal and semiconductor, which may create potential barriers and may create rectifying properties for a semiconductive nanowire device. During the laser welding process, organic residues will be removed by local heat and provide direct contacts between metal and semiconductor nanowires. This will decrease the impurity interference during the measurement and improve the device performance.

The first step will be testing and comparing the electrical characteristics of Tellurium Nanowires (TeNWs) before and after laser irradiation. A Current-Voltage measurement will be performed to detect contact resistance changed. And relative

memristor characterization will be studied, such as frequency dependence, active time.

This dissertation will be organized as follows. After the literature review of printing methods and laser processes in Chapter 1, in Chapter 2, I will discuss laser sintered Al nanoparticles for the Al-Air battery application. The thermal effect induced by a nanosecond pulse laser was used to selectively sinter the printed 3D structure. After sintering, microstructure and conductivity of sintered electrodes were investigated. The experiments showed that the conductivity increase of the Al anode could result in the enhancement of battery performance. In Chapter 3, I will mainly discuss the direct-write printed current sensor for load monitoring applications. This work presented an aerosol jet printing process, and CO₂ laser cutting was applied for further processing to create a sensor. This application shows the feasibility of combining both laser processing and aerosol printing technology for device fabrication. In chapter 4, ultrafast laser-induced graphene-based flexible sensing array for multi-elements detection was discussed. A pattern recognition process was applied for multi-flavor detection and prediction. In chapter 5, a single Cu nanowire welding by a femtosecond laser was accomplished for glucose sensing application and will be discussed. This study showed clear evidence of the nonthermal welding phenomenon induced by an ultrafast pulse laser. In chapter 6, based on the knowledge from the previous chapter, laser induced tellurium nanotube welding for memristor applications will be discussed. Lastly, conclusions and outlook will be discussed in chapter 7.

2. LASER SINTERING OF PRINTED AL NANOPARTICLE ANODES FOR AL-AIR BATTERIES

Disclosure

This chapter is based on a publication originally published by Yongchao Yu, Min Chen, Shutong Wang, Curtis Hill, Pooran Joshi, Teja Kuruganti, and Anming Hu in 2018.

[192] Yu, Yongchao, Min Chen, Shutong Wang, Curtis Hill, Pooran Joshi, Teja Kuruganti, and Anming Hu. "Laser sintering of printed anodes for al-air batteries." Journal of The Electrochemical Society 165, no. 3 (2018): A584-A592.

Yongchao contributions in the article: Fabricated Al-Air batty cell, including Anode and cathode printing, laser sintering, battery performance measurement. Co-authors' contributions are listed as follows: Shutong Wang helped in battery performance measurement, Curtis Hill helped for Al ink fabrication. Dr. Pooran Joshi and Dr. Teja Kuruganti constructed in article revision. Dr. Anming Hu was the PI on the research, assisted in data analysis and experiment design and revised the article.

2.1 Motivation and Background

With the development of portable electrical devices and electric vehicles, high energy density storage devices show unique features as a power source. To date, lithium-ion batteries, as one of the popular compact power sources, are well-developed and have shown significant progress in the past 20 years. Due to their outstanding energy and power capabilities, Li batteries govern current worldwide rechargeable battery markets [193-195]. However, the large-scale demand for Li results in a steadily growing price of Li because of the low abundance of Li in the Earth's crust. Based on calculations, the current Li resource can only be sustained for a couple of decades, if considering a 5% growth of consumption per year [196]. Therefore, there is an urgent need to explore new, cost-effective battery systems as successors for Lithium-ion batteries. Metal-air batteries, containing metal anodes and oxygen cathodes, have been considered as one of promising energy storage devices due to their high theoretical energy density. Many active materials, such as Al, Zn, Ni, Mg, and Fe, have been reported as potential anode material for metal-air batteries [197, 198]. Among the materials of interest, Al has attracted extensive attention as a potential battery anode because of its high theoretical voltage and specific energy density. As reported, the theoretical cell voltage of an Al-air battery is 2.7V with 1.2-1.6V operating voltage. A theoretical energy density can reach 8140 Wh/kg, although the actual energy density of 300–500Wh/Kg is reported so far [199, 200]. Additionally, the low atomic weight (28.98 g/mol) coupled with trivalent oxidation of Al, yielding a low equivalent weight per voltage, offers a huge advantage as an anode material in melt-air batteries [201-203].

In this chapter, we are reporting a laser processed 3D-printed Al anode for Al-air battery. Laser sintering was applied to remove the organic solvent in the slurry and increase the conductivity of the printed anode. A Pt/C coated hydrophobic carbon paper was used for the air cathode, and a gel-style KOH was introduced as the electrolyte and waterways for the electrochemical reactions. The benefits of 3D nanostructured anodes include high mass loading of electrode materials and large battery capacity. Besides, the laser sintering provided a fast and controllable process for printed 3D structures. By combining 3D printing and laser sintering methods, this study displays the possibility of the novel fabrication process for printed batteries.

2.2 Fabrication Process

2.2.1 Anode

The anode of the Al-air battery was prepared by a lab-made extrusion 3D printer, including a sample moving stage (BECIC MST 300 model) and an extrusion system (Nordson HP3cc). A high viscosity Al nanoparticle slurry was applied as an active material, and a 3D structure was printed on 160 μm thick Al film (McMaster-Carr) as a current collector. The slurry contained Al nanoparticles with a size distribution in the range of 0-200 nm. Figure 2-1(b) shows the Al nanoparticle size distribution based on the statistical measurement of 200 particles, 86% of Al particles are distributed in a range of 20 nm to 80nm. In order to make a printable Al slurry, 25%wt of terpineol and the ethyl-cellulose mixture was used as the carrier to form a high viscosity Al slurry. The mass ratio between

terpineol and ethyl-cellulose was 10:1. The Al nanoparticle slurry was prepared by three-roll mixing of Al nanoparticles and organic carriers. Al anode has a very obvious parasitic corrosion reaction or self-discharge with the parasitic hydrogen evolution in the alkali electrolyte which needs to be suppressed [204]. The formation of an oxide film of Al_2O_3 or $\text{Al}(\text{OH})_3$; the formation of corrosion products, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$; and parasitic hydrogen evolution, which lowers the electrochemical potential are considered as three main processes that occur on the aluminum surface [205-207]. The one approach to improve the anode behavior is to dope aluminum to reduce the self-discharge loss. The most common dopants for suppression of the self-discharge of Al anodes include Ga, In, Sn, Zn, Mg, Ca, Pb, Hg, Mn, and Ti [208, 209]. In the present work, 6%wt of Sn (about 8% of Al particle weight) was mixed into Al slurry as anode material. The randomly deposited Sn on the aluminum anode surface leads to an increase in hydrogen evaluation overpotential and decreases Al reaction areas. Therefore, the addition of Sn increases cathodic polarization, which reduces hydrogen generation at the anode [207].

To prepare the anode electrode, at the first step, a very thin layer of Al slurry with an area of $1\text{ cm} \times 1\text{ cm}$ and approximately $80\text{ }\mu\text{m}$ thickness was printed on Al film to avoid direct contact between current collector and electrolyte. The 3D structure was printed on the top of this Al slurry layer at a 20mm/min printing speed. A computer program controlled the printing speed and printing path. Additionally, laser sintering was applied to each layer after printing

2.2.2 Cathode

The Pt/C mixture was selected as an active cathode material. The mass ratio of Pt micro-sized powder (Sigma-Aldrich) and carbon black powder (Alfa Aesar) was 4:6, and 10% total weight of Polyvinylidene fluoride (PVDF) (Acros Organics) was mixed as a binder material. Pt particles, carbon black, and PVDF were well-mixed in an agate mortar. And N-Methyl-2-pyrrolidone (NMP) (Acros Organics) was used as a solvent. Carbon materials, with excellent reliability and low costs, such as activated carbon, carbon black, graphite, and graphitized materials, have been extensively applied in various catalytic processes [210]. On the other hand, Pt has a high catalytic activity for oxygen reduction reaction, as well as the combination of Pt and carbon is considered to further improve the catalytic activity [211]. The cathode material was applied on conductive carbon fiber paper (Ion Power. GDL 24 AA, 190 μm thickness) with a 1 cm $\times$ 1 cm area, and the active material thickness was 60 μm . The carbon paper was selected as a current collector on the cathode electrode because of its porous physical structure. In a metal-air battery, oxygen molecules will flow into the battery cell and participate in electrochemical reactions [212]. Figure 2-1(c) shows a typical SEM image of carbon paper. The porous structure of the carbon fiber paper offers a large number of passageways for oxygen to accompany active materials, which can lead to a complete chemical reaction in a discharge reaction. Moreover, the contact angle was measured with DI water drops. The angle is 111.5° (Figure 2-1(d)). The hydrophobicity of the carbon paper will limit the water exudation from the battery cell. It provides a relatively watery environment for battery reactions.

Cathode electrodes were placed in a furnace maintained at 60°C to ensure complete drying for 12 hours.

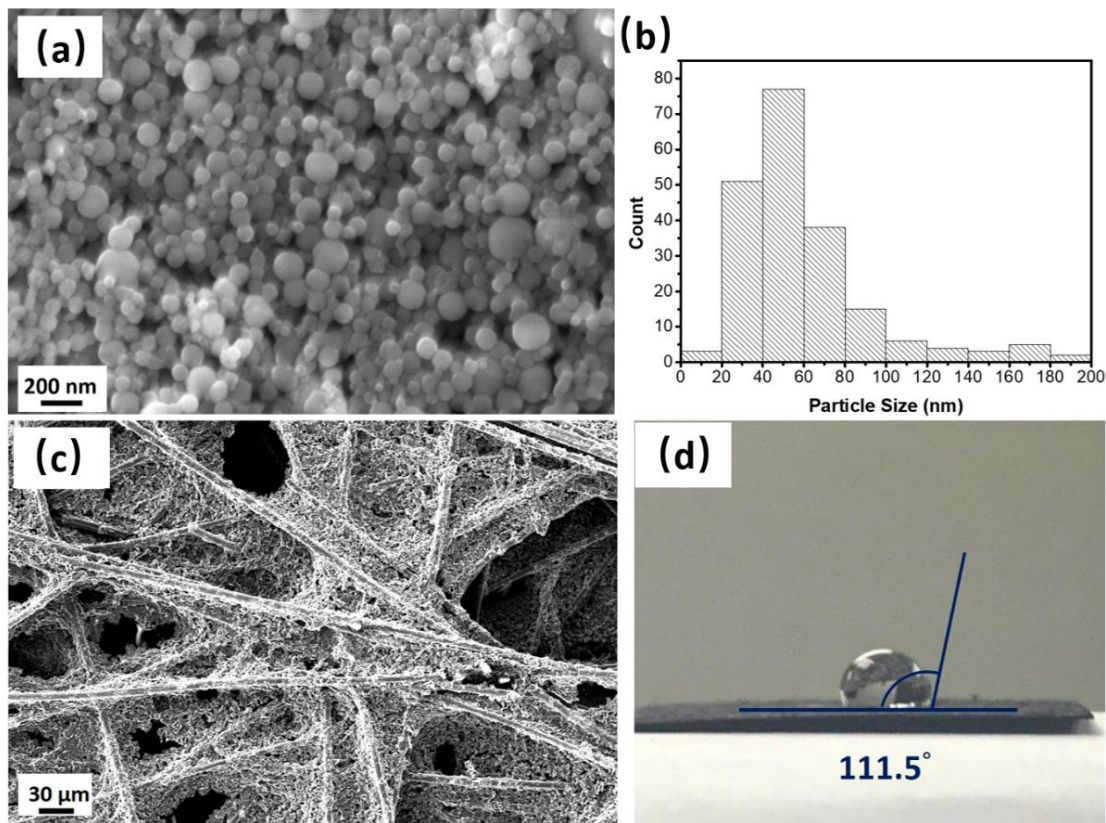


Figure 2-1 (a) Typical SEM image and (b) the statistic Al nanoparticle size distribution in the Al NP slurry, (c) SEM image of the carbon paper and (d) the contact angle of a water drop on carbon paper [192]

2.2.3 Electrolyte

2 M KOH gel electrolyte was applied between the anode and the cathode. The gel electrolyte was prepared by mixing polyvinyl alcohol (PVA) (ACROS Organics)/water solution and KOH solution (Fisher Scientific). 1.5 g PVA was dissolved in 15 mL distilled water maintained at 80 °C with constant stirring for 2 hours. Then the pre-prepared 5 mL 18 M KOH solution was slowly added into the PVA solution. Flocculent precipitate could be observed after the KOH solution was added. The precipitate dissolved in about 15 min. After a clear solution was generated, the solution was cooled down to room temperature and stored in the refrigerator at 4 °C for 4 days. A membrane separator-free battery system could be established by using this gel electrolyte. The schematic of the Al-air battery working principle is shown in Figure 2-2 (a).

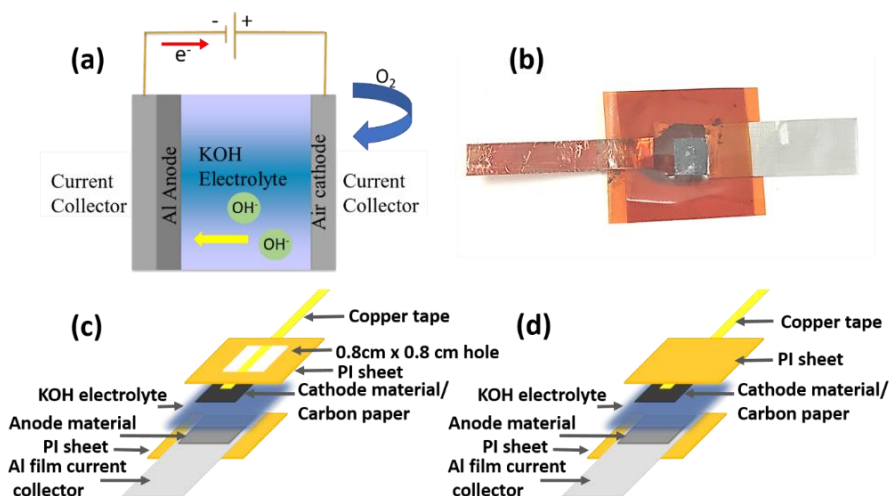


Figure 2-2 (a) Schematic of Al-air battery working principle, (b) image of a packaged battery cell, (c) schematic of an Al-air battery, and (d) schematic of an Al alkaline battery[192]

2.2.4 Battery System

Figure 2 (b) shows a picture of a fully packaged battery. Figure 2-2 (c) shows the schematic of an Al-air battery cell. Anode and cathode are sandwiched between two slices of polyimide sheets (3DXTECH, 50 μm thickness). For better air ventilation, there is a $0.8\text{ cm} \times 0.8\text{ cm}$ hole, which is opened on a polyimide (PI) sheet. Copper tape is drawn from cathode current collector for measurement. In order to distinguish a discharge mechanism between an Al alkaline battery and an Al-air battery, an Al alkaline reference battery system was designed for comparison (Figure 2-2 (d)). The processes for anode, cathode, and electrolyte preparations were the same as for an Al-air battery. The only difference in the design of these two battery systems is that for the Al-alkaline battery system instead of using a PI film with $0.8\text{ cm} \times 0.8\text{ cm}$ hole, a piece of solid PI film is used to cover the cathode electrode to avoid the air flow into the battery cell during the discharge process. The overall thickness of battery cells is about 3.8 mm, including gel electrolyte and shelling film. Its weight is approximately 1g.

2.2.5 Laser Sintering

To prepare a 3D printed structure, a highly- concentrated viscous active material slurry is required [213]. As introduced previously, the anode material was fabricated by mixing active material and the polymer carrier (terpineol and cellulose) to form an appropriate ink. The polymer-carriers used in the slurry are nonconductive materials. Therefore, the polymer binder has a negative contribution to the electrode conductivity and energy storage density. Laser

sintering is hence introduced to remove the polymer binder. Al nanoparticle is a highly reactive material [214] and somehow pyrophoric. To avoid oxidization, a reduced atmosphere or buffer gas is an efficient process for Al nanoparticle sintering [215]. Various sintering techniques are being investigated for anode sintering, including thermal sintering [124, 216], photonic sintering [217, 218], plasma sintering [219], and electrical sintering [220]. However, most of these sintering processes have disadvantages such as time-consuming, or easy to damage the sensitive substrate. For the thermal oven sintering process, it commonly takes a couple of hours to increase the temperature. Although other sintering processes, such as electrical sintering and plasma sintering, could achieve fast sintering, both of them are the local processing methods. A laser sintering process was investigated to sinter a complicated 3D structure with a high throughput [221]. A high repetition rate Q switched fiber laser (CAS LASER Co.) was used to sinter the anode material. The wavelength of laser is 1064 nm and the pulses repetition rate is 50 kHz. The sintering of anode was conducted in a vacuum environment to prevent oxidation of Al nanoparticles.

2.3 Results and Discussion

2.3.1 Laser Sintered Al Anode and Discharge Performances

The electrical properties and microstructures of Al anode were studied after laser sintering. Figure 2-3 shows typical SEM images of Al anodes sintered at different laser powers. As shown in (a), SEM analysis established that the Al nanoparticle sizes were in the range of 20-80 nm. But due to the low conductivity of non-sintered

slurry, it was a challenge to get a high-resolution image of this sample. Figure 2-3 (b, c, d, e) show the effects of the laser sintering at a laser power level of 3 W, 10 W, 15 W, and 20 W, respectively. The laser beam was adjusted to 10 mm in diameter, which is the same as the size of the active material on the current collector. To ensure evenly sintering for Al anode, the stage was slowly spun at a speed of 5 mm/min during the sintering. The sintering time was fixed at 15 s for each laser power. During the laser sintering process, the organic solvent will be removed from the Al slurry. Furthermore, the large surface area of the nanoparticles allows for a lower sintering temperature as compared to bulk material [222, 223]. At a laser power level of 10 W, the sintering of a small number of nanoparticles is evident (Figure 2-3(c)). When the laser power increased to 15 W, more nanoparticles start to sinter together (Figure 2-3(d)). At 20 W, most of the nanoparticles are sintered together and form a dense structure (Figure 2-3(e)). An effective sintering process is critical to fabricate high conductivity anodes [216, 217]. At the same time, nanostructures can improve the initial discharge capacity for battery applications [224, 225]. Therefore, an appropriate sintering level, high conductivity cathode, and keep nanoparticles structure are required for batteries. Also, due to the high self-discharge for pure Al material, some polymer residuals will help in decreasing the corrosion of anode material from alkali electrolyte. However, as the laser power is increased above 15 W, parts of the Al material layer start to ablate or peel-off from the substrate (blue circle in Figure 2-3(d, e)). At 20W, most of the material is ablated, as shown in Figure 2-3(e). Therefore, in

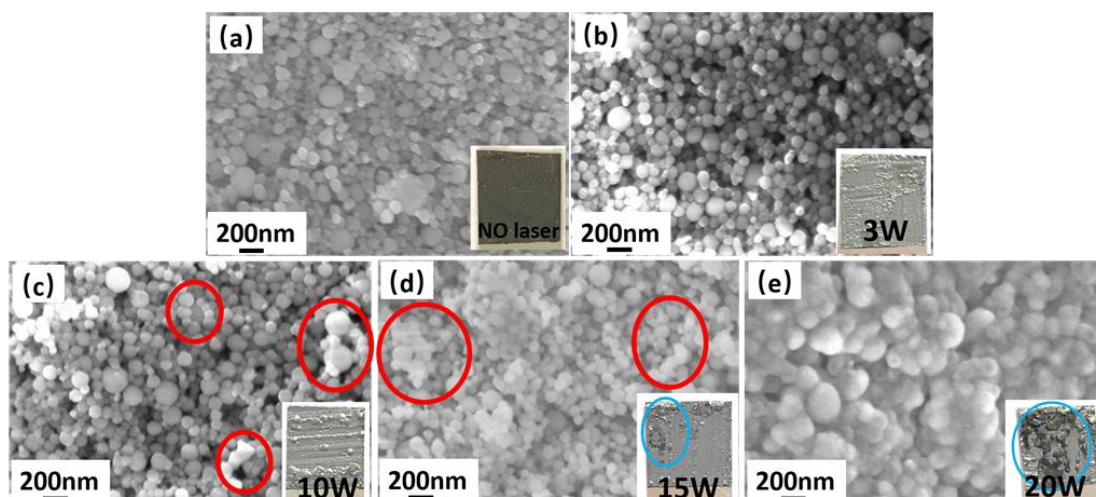


Figure 2-3 SEM images of Al anodes (a) without laser sintering, (b) sintered with 3W laser power, (c) sintered with 10W laser power (red circles: area of nanoparticles are sintered together) and, (d) sintered with 15W laser power (blue circles: exfoliation of material layer due to high laser power, red circles: area of nanoparticles are sintered together) and (e) sintered with 20W laser power. The laser focal point diameter is 10 mm with a 50 kHz pulse repetition rate. The sintering time is 15s for all powers [192].

the present study, 10 W was established to be an appropriate laser power level for effective sintering.

To study the laser sintering effect, one layer 0.2cm x 1cm rectangle anode was printed with a thickness of around 300 μ m and sintered at different laser powers. Current vs. voltage (I-V) curves were measured using an electrochemical working station, and weight losses were measured and calculated by weighting the

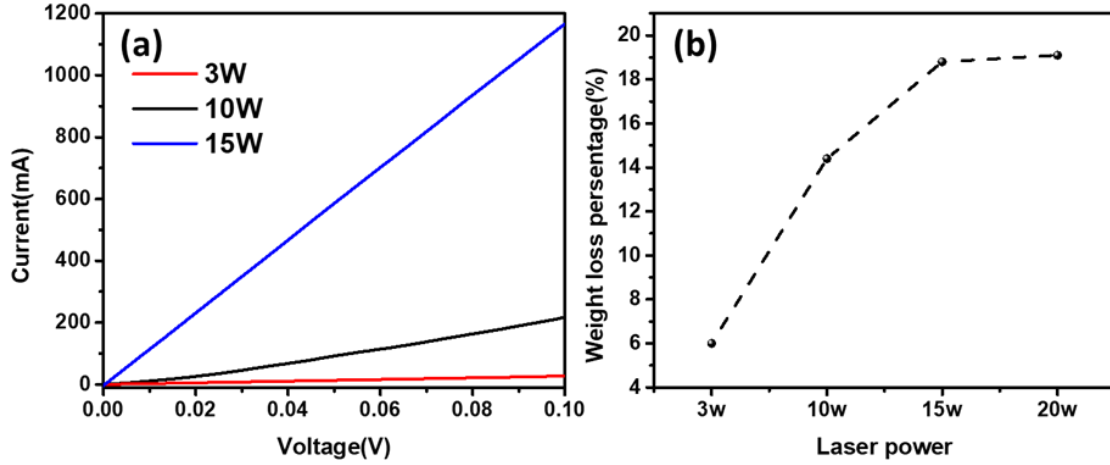


Figure 2-4 (a) I-V curves of Al inks and (b) the weight loss of Al ink after laser sintering [192]

mass change of Al films before and after laser sintering. Figure 2-4(a) shows the I-V curves of Al films. As a result, when the laser power is less than 3 W, the Al ink was still nonconductive. Once laser power increases to 20 W, a significant deformation will produce, and the ablation of the printed Al films will occur (Figure 2-3(e)). Therefore, 3 W, 10 W, and 15 W samples were systematically studied. The resistivity of the sintered Al sample was calculated by the equation:

$$\rho = \frac{RS}{L} \quad 2-1$$

Where R is the resistance (Ω), S is the cross-section area (m^2), and L is the length (m). The resistivity of laser-sintered Al films is approximately $3.0 \times 10^{-4} \Omega\text{m}$, $2.78 \times 10^{-5} \Omega\text{m}$, and $5.12 \times 10^{-6} \Omega\text{m}$ for the laser power of 3 W, 5 W, and 10 W respectively. The resistivity of pure aluminum bulk is $2.65 \times 10^{-8} \Omega\text{m}$. [226] Besides, the mass change percentages were shown as 6%, 14.3%, 18.6%, and 19.2% as

laser power increased from 3 W to 20 W. The key factor of mass change is considered as the consequence of the remove of the nonconductive polymer binder. By comparing Figure 2-4 (a) and (b), it is clear that the bounder material is removed by laser sintering and leads to an increase of conductivity of Al ink.

Figure 2-5 shows discharge capacities for different battery cells with diverse anode sintering levels. The anode was prepared by the extrusion printing method on Al film. The thickness of the active material layer was controlled to be around 80 μm with a 10 mm $\times$ 10 mm surface area, and the mass of active material was approximately 11 mg. The battery performance was measured with a Landt Instruments battery testing system. The density of the discharge current was set at 0.5 mA/cm² (approximately 0.3 C). It is clear that the laser-sintered anodes show significant increases in electrical performance. The black line represents a non-sintered anode sample for Al-air battery, which shows a pretty low discharge capacity of only about 2 mAh/g. The observed low discharge capacity can be attributed to a large amount of non-conductive polymer contained in the Al slurry blocking the electrical contact between Al nanoparticles and the electrolyte, hindering the transport of OH⁻ ions between cathode and anode. Hence, the electrochemical reaction is minimal. On the other hand, after the laser sintering of Al anodes, the battery discharge performances show a significant improvement in the discharge characteristics. The sample processed at 3 W laser power shows a discharge capacity of 121 mAh/g at an operation voltage of 0.75V. As the laser power is further increased to 10W, the battery performance further improves, as shown in Figure 2-5. The sample provides a 239 mAh/g discharge capacity and a

0.95 V operation voltage. It is obvious that laser sintering at an appropriate power level has a dominant influence on battery performance. The higher laser power creates a higher thermal effect to Al anode, which facilitates the removal of binder polymer. At the same time, it sinters Al nanoparticles together (as shown in Figure 2-3 (c)). This leads to an improvement in anode conductivity and decreases in the battery internal resistance. However, an applied power higher than 15 W leads to material ablation. Thus, appropriate laser power at around 10 W leads to effective removal of polymer binder and an increase in the contact surface area between Al nanoparticles and electrolytes, eventually leading to a complete electrochemical reaction, which results in a significant increase in discharge capacity.

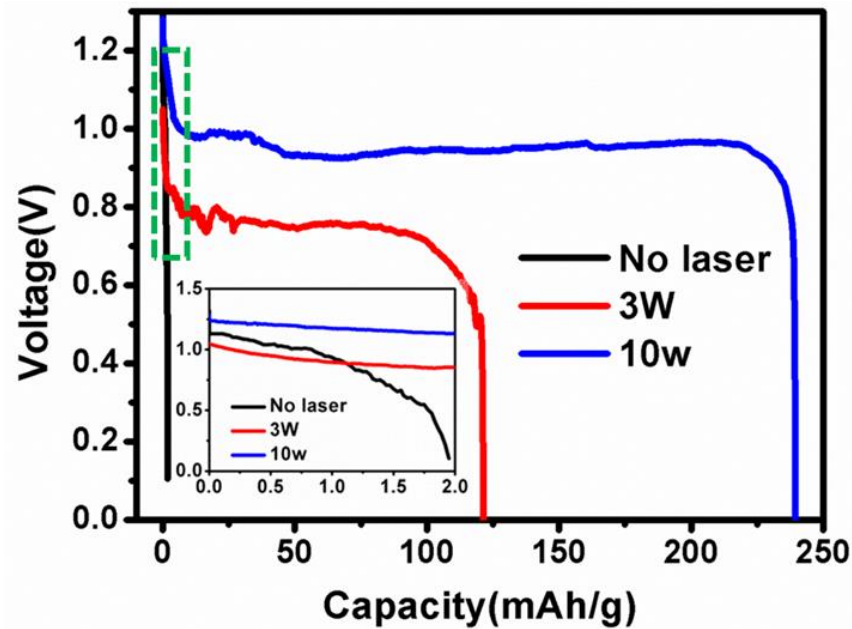


Figure 2-5 The first cycle discharge capacity of Al-air battery with different laser sintering power. Inset: enlarged figure at the 0-2 mAh/g range indicated by the frame of dash lines [192].

For a better understanding of the underlying battery reaction, the electrode microstructure was analyzed in detail by SEM. Figure 2-6 (a-b) shows SEM images for Al anode before and after discharge. After fully discharging, the structure of the active material has changed significantly. Before the reaction, active materials are spherical nanoparticles; after fully discharging, the structure of the active material became an irregular geometry. At the same time, because substance produced by the discharge reaction is $\text{Al}(\text{OH})_3$, which is a nonconductive metallic oxide, therefore, there is some electron charging phenomenon during SEM imaging (Figure 2-6 (b)). To further prove this electrochemical reaction, XRD analyses were accomplished for the anode material before and after discharge. Figure 2-6 (c) identifies the phases of an Al slurry before discharging. The pattern indicates that the material contains both Al and Sn elements. There are no additional peaks that could be observed in the XRD pattern. The organic content is not displayed due to the low scattering cross-section. In Figure 2-6 (d), there are additional $\text{Al}(\text{OH})_3$ peaks. This confirms that $\text{Al}(\text{OH})_3$ was formed during the discharge stage. Therefore, the microstructure change was caused by the formation of $\text{Al}(\text{OH})_3$. During the discharge stage, Al^+ ions receives OH^- ions from the cathode and generate $\text{Al}(\text{OH})_3$.

Figure 2-7(a, b) shows SEM images of the cathode electrodes for Al-air battery before and after discharge. Although no apparent changes could be observed in SEM, XRD analysis has unveiled significant differences. From XRD analysis (Figure 2-7(b, c)), it is obvious that there are additional peaks, which are associated with $\text{Al}(\text{OH})_3$, Sn, and Al elements, in the cathode electrode after the

battery was fully discharged. This is because of the precipitation of anode material during the discharge periods. The active material particle sizes were calculated based on XRD results in Figure 2-7(c,b), using the Scherrer formula ($\tau = 0.9\lambda/(\beta \cos \theta)$), where τ is the mean partial size, λ is the x-ray wavelength, β is the full-width half-maximum, and θ is the Bragg angle. The calculation results show that average crystalline size for carbon (corresponding to 27.1 degrees) before and after discharge is about 23.5 nm and 26.5 nm. The average crystalline size for Pt (corresponding to 39.88 degrees) increased from 5.6 nm to 12.5 nm after discharge reactions. As XRD results show, there are precipitations of anode material on cathode electrodes. These materials absorbed on cathode materials, carbon, and Pt, which may lead to increase particle sizes. Additionally, this phenomenon will block the electrical contact between cathode materials and electrolytes, which will restrain the battery reaction. This is a core problem in high-performance battery development, which must be addressed to realize efficient battery technology.

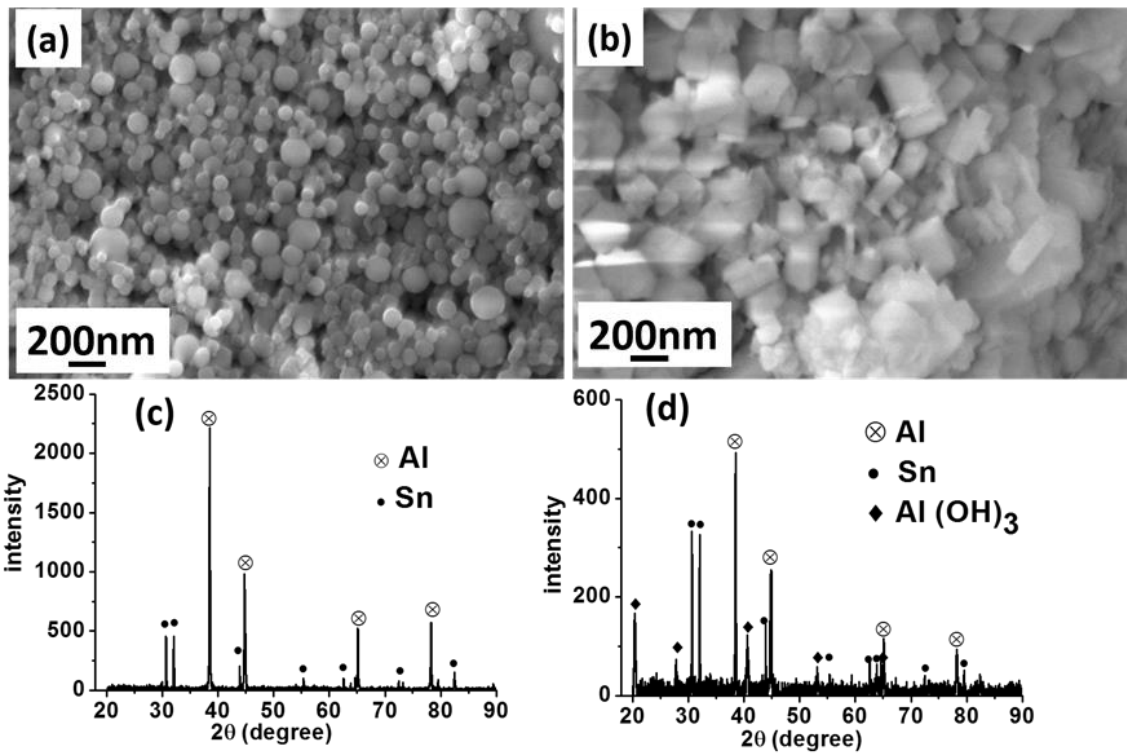


Figure 2-6 SEM images of Al anodes (a) before and (b) after discharge. The local structure is enlarged in the inset figures. XRD patterns of Al anodes (c) before and (d) after discharge [192].

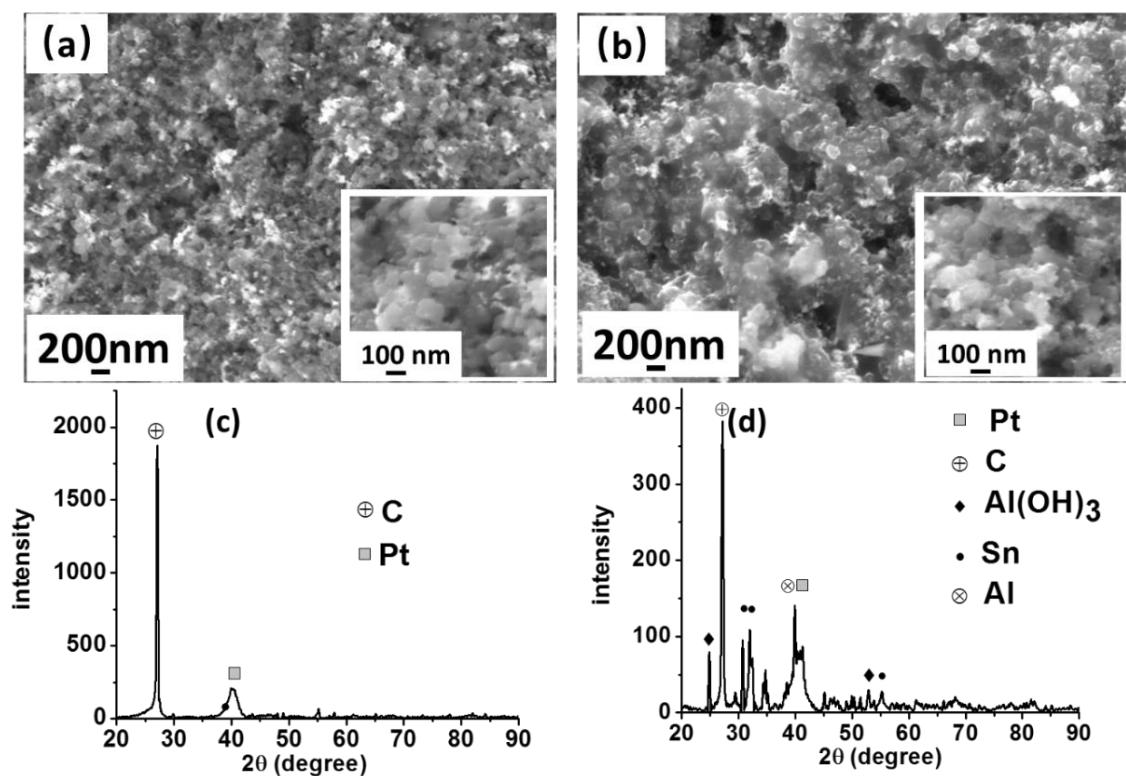
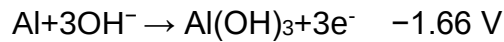


Figure 2-7 SEM image of Pt/C cathode (a) before and (b) after discharge. The local structure is enlarged and shown in the inset. XRD analysis for Pt/C cathode (c) before and (d) after discharge [192].

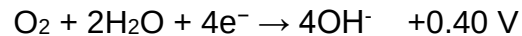
2.3.2 Comparison of Al-Air Batteries to Al-Alkaline Batteries

To distinguish an Al-air battery operation from an Al alkaline battery, a comparison experiment was designed. Two battery systems are designed and prepared. 3 layers 3D printed Al anodes with the same sintering condition were used for both battery systems. The anode Al active material was sintered at a laser power of 10 W for 15 s for both the battery systems. To figure out the differences between the two battery systems, discharge capacity was measured at a discharge current density of 0.5 mA/cm². Figure 8 shows the discharge capacities for both Al alkaline battery and Al-air battery. The figure shows that the discharge capacity of Al-air battery is 50.18 mAh/g with an operating voltage of 1.1 V. But for the Al alkaline battery, the discharge capacity is only 11.2 mAh/g with an operating voltage of 0.56 V. Thus, it is obvious that the participation of oxygen plays a significant role in the metal-air battery discharge reaction, which leads to improvements of operating voltage and discharge capacity. The anode oxidation reaction and the cathode reduction reaction can be expressed as:

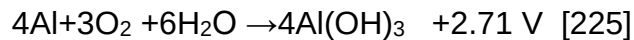
Anode oxidation half-reaction:



Cathode reduction half-reaction:

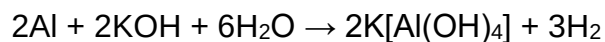


The overall reaction of the cell:



As highlighted in chemical formulas, the oxygen reduction reaction contributes to a theoretical voltage of 0.4 V. Therefore, for an Al alkaline battery,

no oxygen is participated in the reaction. The theoretical voltage would be lower than that of an Al-air battery. On the other hand, the chemical reaction:



would be the part of the discharge reaction for the Al alkaline battery. This reaction not only produces heat but also creates a lot of H_2 gas release, which increases the battery inner pressure and temperature. The current experimental findings are in line with this theory. Also, from the experiments, the oxygen reduction reaction also plays a positive role for active material to have complete chemical reactions. It is reflected in the low discharge capacity of the Al-alkaline battery. From SEM images shown in Figure 6(b) and Figure 8(b), morphologies of anodes are different for two types of battery systems. The Al-air battery system has a more structured crystallizations than the Al-alkaline battery system. Figure 8(c) shows the XRD analysis results of cathode electrodes for both battery systems after discharge. From the results, $\text{Al}(\text{OH})_3$ mainly forms bayerite ($\alpha\text{-Al}(\text{OH})_3$) in the Al-air battery system. However, in the Al alkaline battery system, $\text{Al}(\text{OH})_3$ is existing as both bayerite and gibbsite ($\gamma\text{-Al}(\text{OH})_3$) structures. The crystallization process is dependent on the exact solution conditions. In a basic solution, the low-temperature condition (e.g., $< 40^\circ\text{C}$) mainly leads to the growth of bayerite structure. Meanwhile, at high-temperature conditions ($65\text{--}80^\circ\text{C}$), the predominant $\text{Al}(\text{OH})_3$ crystalline has been found as the more thermodynamically stable gibbsite phase [227-230]. The Gibbsite structure is observed from the Al-alkaline battery system; this demonstrates that during the discharge reaction there was a lot of heat had been produced, and the battery cell inside temperature increases to a

high level, which causes a non-negligible safety issue. Figure 8(d) and (e) show the XRD patterns of cathode after discharge for Al-air battery and Al-alkaline battery system respectively. In Figure 8(d), the black line is the original XRD measurement result. The peak shows a composite structure; therefore, multiple peak fit analysis was applied. As a result, the red line represents a Pt peak at 39.8 degrees with a [1 1 1] orientation. The blue line represents α -Al(OH)₃ peak at 41.59 degrees with a [0 4 0] orientation. The green line is the fitted curve. In Figure 8(e), the red line also represents the Pt peak at 39.8 degrees with a [1 1 1] plane. The blue line shows a little shift compare with Figure 8(c), which represents the α -Al(OH)₃ peak of [1 3 1] plane at 40.65 degrees and the green line is the fitted curve, which is highly overlapped with the red line in Figure 8(e). The Pt particle size was estimated by applying the Scherrer formula to the fitted curve (red line). As a result, for Al-air battery, the average crystalline size of Pt particles is about 12.1 nm, and for Al-Alkaline battery, the crystalline size of Pt particles is about 6.8 nm. As well known that the smaller particle size of catalyst offers a better catalytic effect[231, 232]. As the reaction process, the crystal size of catalyst increases and the redox efficiency decreases. In this battery system, Pt acts as a catalyst. Specially, [1 1 1] orientation of Pt practices provides the active site for the redox reaction [233] also this crystal surface has the most loss atomic arrangement with highest growth rate [234]. Therefore, the crystal will grow along this plane. By comparing the crystal size growth in [1 1 1] orientation for both battery systems before and after discharge. As a result, the Al-air battery has a larger gain in crystal size (approximately, from 5.6 nm to 12.6 nm) than the Al-alkaline system

(approximately, from 5.6 nm to 6.8 nm). To some extent, it represents that the Al-air battery system had more complete redox reactions than the Al-alkaline system in this experiment. At the same time, inhibit the crystal growth and keep the high activity of catalysts during the redox reaction is a challenge and an approach for improving the battery life and performances.

As shown in Figure 2-8 (b), there is some dendritic crystallization occurring in Al alkaline battery after discharge, which was not observed for the Al-air battery system. The unevenly redeposited metal forms a dendritic structure, which leads to inherently unsafe cells with a short lifetime [235]. The factors contributing to dendrite formation usually correlate to high current densities [236], electrolyte salts [237], and electrolyte solvent composition [237]. The water-based gel style KOH electrolyte was used in this battery system; therefore, the contributions of electrolyte salts and electrolyte solvent composition could be very limited. The main factor for forming dendrites could be considered as the current inhomogeneities induced by the passivation layer present on the surface of the anode electrode[235]. As XRD results show, there are mainly two different structures of $\text{Al}(\text{OH})_3$ that exist on the Al-alkaline battery anode, which result in the growth of nonuniform crystals. This could be confirmed by the SEM image in Figure 8(b). The asymmetrical surface structure of anode could cause the increase of local current density and nonuniform current distribution, which could be the factor of inducing the dendritic crystallization in anode electrodes.

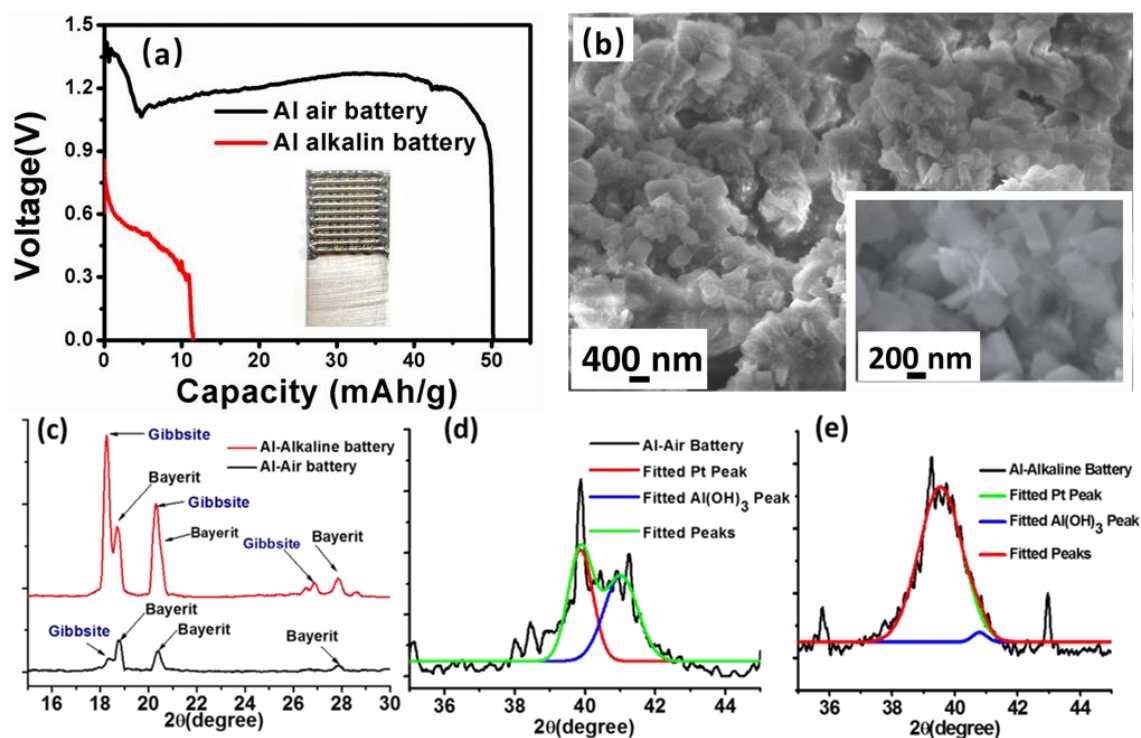


Figure 2-8 (a) Discharge capacity for Al-Alkaline Battery Vs. Al-air Battery. inside: 3D printed 3 layers Al anode, (b) SEM image of anode for Al-alkaline battery after discharge. Inside: enlarged SEM images for Al anodes, (c) XRD analysis for the anode of Al-Alkaline battery and Al-Air battery after discharge, (d) XRD analysis for the cathode of Al-Air battery after discharge and (e) XRD analysis for the cathode of Al-Alkaline battery after discharge[192].

3.3 3D Printed Anodes

A typical thickness of the electrode material for Li-ion battery is around 50-100 μm [238, 239]. Considering the cost of the manufacturing process, a higher mass loading battery electrode is preferred, which will reduce the processing steps and lower the separator cost [240]. However, a thick electrode will significantly increase cell impedance and lose energy efficacy. In order to prepare a thick anode, a 3D printing method was used for anode fabrication. A 3D printed wave-structure was targeted to achieve a larger surface area than a flat surface structure. By increasing the surface area of electrodes, better electrical contact between the electrolyte and electrodes is expected. Also, it enforces the penetration of the electrolyte. From this concept, 3D structured Al anodes were printed by the extrusion printing process. Figure 2-9(a) demonstrates a schematic of the extruding printing process. The Al ink is extruded by a gas pressure driven piston and deposited to substrate through a 23-gauge nozzle. Figure 2-9(b-e) shows the cross-sectional SEM images of 3D printed anodes with different numbers of layers. The layer thicknesses are about 80 μm for 2D printed electrode, and 360 μm , 560 μm , 680 μm for 1 layer, 2 layers and 3 layers 3D printed samples, respectively. The mass loading for these samples is approximately 20 mg, 53 mg, and 62 mg. From the SEM images, it is clear that as the layer number is increased to 3 layers, the 3D structure is deformed. This is mainly caused by the fluidity of the Al slurry, which limits the strength to hold a 3D structure with a large height/width ratio.

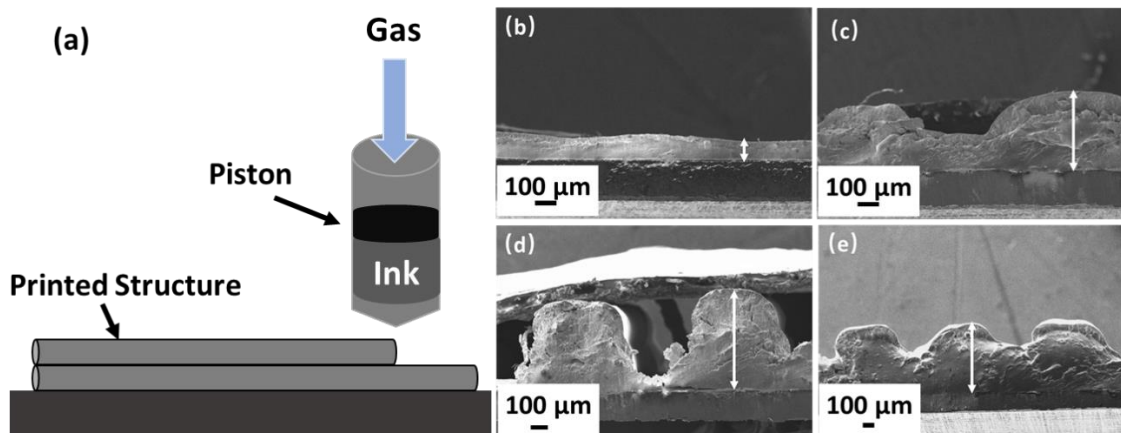


Figure 2-9 (a) Structure of extrusion printing process (b) 2D printed sample with 80 μm thickness, (c) 3D printed 1 layer sample with 360 μm thickness, (d) 3D printed 2 layers sample with 560 μm thickness and (e) 3D printed 3 layers sample with 680 μm thickness[192].

Further discharge capacity measurements were conducted on a batch of battery samples with 3D printed anodes. The discharge current was set at 0.5 mA/cm². The measurement results are shown in Figure 2-10. The discharge capacities are measured to be 1.5 mAh, 2.8 mAh, and 3.23 mAh for 1 layer, 2 layers, and 3 layers, respectively. As the number of layers is increased, the capacity of the battery cell increases monotonously. However, the increase was not found to be linear. The 2-layer sample shows a higher energy density than the 3-layer sample. This may be generated by the deformation of the 3D structure, which leads to a decrease in the surface area. Besides, the relatively large mass loading and high layer thickness can result in a poor electrolyte penetration. From Figure 2-10 (c) and (d), it is very clear that for 3 layers sample, the depth of grooves between each printed line decreased compare with 2 layers sample. During the printing, as the height of the lines increases, part of Al ink flowed down to grooves

and increased the total thickness of the anode electrode. This enlarged distance between the electrode surface and the current collector, which reduces the energy efficiency and lower the battery performance. Also, due to the irregularity of the printed 3D structures, the discharge reaction shows a very complicated phenomenon in the initial period. The potential drop at the initial discharging period could be a consequence of unevenly current distributions in a multi-layer printed sample. In a 3-layer sample, because of the high mass loading of active material and thick material layer, it will reduce the electrolyte permeability and cause uneven contacting between the electrolyte and active material. At the initial stage of the discharge stage, a thin layer of Al(OH)_3 was formed and covered on the material surface, thereby slowing down the electrolyte penetration and resulting in voltage dropping. However, the electrolyte can gradually wet Al(OH)_3 thin layer, and the voltage simultaneously recovers to the original level. For 1 layer and 2 layers samples, which have a thinner material layer, this phenomenon was not observed. This indicates the printed structures need to be further optimized for the battery performance.

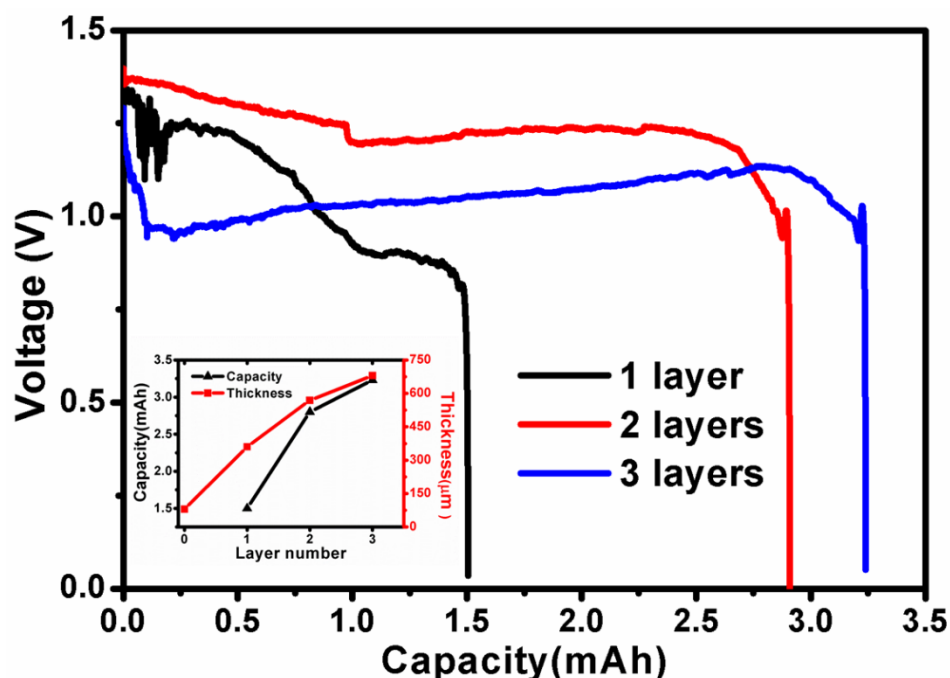


Figure 2-10 Discharge capacity for 3D printed anode and relationship between anode thickness and capacity[192].

2.4 Conclusions

In the present chapter, I have reported on the fabrication and performances of a 3D printed anode for the Al-air battery system. The Al anode was printed using an Al nanoparticle slurry by an extrusion printing technique. Selective laser sintering of printed electrodes significantly increased battery performance. It found that the optimized laser power was 10W with a scanning speed of 5 mm/min with a repetition rate of 50 KHz at a wavelength of 1030 nm. The battery cell could provide a 239 mAh/g discharge capacity at an operation voltage of 0.95V. A comparison experiment for Al-air battery and Al-alkaline battery was accomplished. Furthermore, to increase material loading on the anode and

increase the battery cell capacity, a 3D anode structure was fabricated, and laser sintered. The material thickness partially reached 360 μm , 560 μm , 680 μm for printed 1 layer, 2 layers, and 3 layers, respectively. The battery cell capacities reach 1.5 mAh, 2.8 mAh, and 3.23 mAh for different layer numbers respectively. By combining additive manufacturing technology and laser sintering technology, it gives a possibility to achieve high mass loading battery manufacturing for enhanced battery performance.

3. DIRECT-WRITE PRINTED CURRENT SENSOR FOR LOAD MONITORING APPLICATIONS

Disclosure

This chapter is based on a publication originally published by Yongchao Yu, Aravind K. Mikkilineni, Stephen M. Killough, Teja Kuruganti, Pooran C. Joshi, and Anming Hu in 2018.

[241] Yu, Yongchao, Aravind K. Mikkilineni, Stephen M. Killough, Teja Kuruganti, Pooran C. Joshi, and Anming Hu. "Direct-Write Printed Current Sensor for Load Monitoring Applications." In 2019 IEEE Power & Energy Society Innovative Smart Grid Technologies Conference (ISGT), pp. 1-6. IEEE, 2019.

Yongchao contributions in the article: Fabricated sensor coil and sensor performance measurement.

Co-authors' contributions are listed as follows: Both Dr. Aravind K. Mikkilineni and Dr. Stephen M. Killough were contributed to sensor simulation and circuit design. Dr. Pooran Joshi, Dr. Teja Kuruganti, and Dr. Anming Hu were the PIs on the research, assisted in data analysis and experiment design and revised the article.

3.1 Motivation and Background

In this chapter, I report on a flexible current sensor development employing direct-write printing and additive manufacturing techniques. The integrated current sensor unit incorporates sensing, data processing & storage, and in-field calibration capabilities. A combination of direct-write printing technique and low-temperature curable metallic ink is used to print Ag wires around a 12.5- μm -thick permalloy film. The overall thickness of the polyimide substrate and permalloy sheet remains well-below 500 μm enabling wrap-around sensor functionality. Fused deposition modeling (FDM) additive manufacturing is used to build custom parts for sensor mounting, encapsulation, and an in-field calibration unit using heat and chemical-resistant thermoplastic, which response well to mechanical stress. In the present configuration, the integrated current sensor unit can be powered through USB or 4x AAA batteries to allow data collection and sensor calibration in the field. The flexible current sensor employing a continuous sheet of the permalloy exhibited a well-behaved signal output response at peak current levels exceeding 15A and in the applied ac frequency range of 60 Hz – 10 kHz. Overall, the combination of direct-write printing, thin permalloy material, laser processing, and additive manufacturing technique shows promise for the development of a reconfigurable low-cost current sensor that can be deployed in large numbers at locations of interest to avail the cost and energy-saving opportunities in industrial/commercial and residential applications

New technologies and approaches that are also low-cost are required to successfully exploit the full potential of end-use building loads for energy efficiency and grid services. Advanced sensors and controls can reduce the energy consumption of buildings by 20–40%, representing 0.3–0.4 quad in total energy savings when deployed on existing small and medium-size buildings [1]. Significant portions of building loads are dispatchable, and savings of several billion dollars in energy costs are projected with 10% participation in demand dispatch, enabling transactive energy. With buildings contributing 80% of the load growth through 2040, novel sensors and control technologies for buildings will play a significant role in grid modernization. As highlighted in Figure 3-1, low-cost sensors are required for enhanced control of smart building loads and enable distributed energy resources to be “grid friendly.” These advanced sensor platforms will not only enable monitoring and efficient control of building HVAC electrical loads but also find applications in other market segments such as vehicle systems and distributed energy resources.

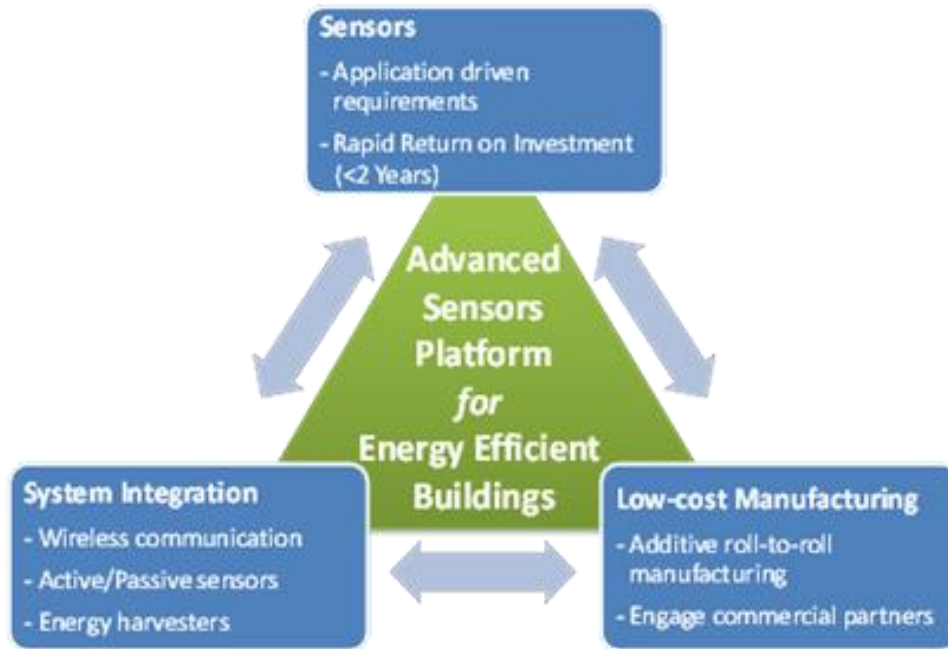


Figure 3-1 Advanced sensor platform elements for grid-interactive smart building [241]

Advanced real-time load and power monitoring techniques are essential to establish a path towards grid-interactive smart buildings. Precise direct current (DC) and alternating current (AC) current measurements are fundamental for efficient power system instrumentation in diverse technology sectors such as automotive, buildings technology, chemical engineering, semiconductor industry, nuclear fusion, renewable energy, and consumer electronics. Techniques based on fundamental principles that lead to inherent electrical isolation, geometrical selectivity, and protection against large voltage/current transients are required for advanced current sensing applications. The basic parameters of any current sensor are linearity, offset, sensitivity, operating bandwidth, offset stability, and

temperature/time sensitivity. Low-cost and high environmental resistance is a must for smart grid and industrial/residential applications. In the present work, we report on the design and development of a low-cost, flexible current sensor and an integrated sensor unit employing a direct-write printing system, thin films of high permeability permalloy, and additive manufacturing techniques. The emerging direct-write printing techniques, as shown in

Figure 3-2, offer large-scale processing and high throughput additive processing of a broad range of functional materials at high resolution to meet the cost, performance, and integration requirements for practical applications.

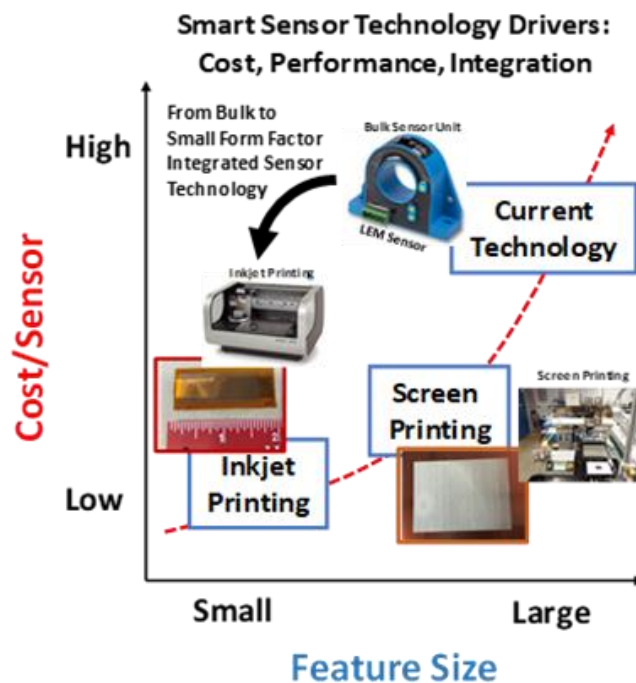


Figure 3-2 Development of a printed current sensor meeting the cost, performance, and manufacturing demands for load-monitoring applications in building and smart grid

3.2 Sensor Fabrication Process and Sensing Mechanism.

3.2.1 Sensing Mechanism

The basic sensing mechanism of this current sensor is based on Faraday's law of electromagnetic induction, with relation of interest for modeling the current sensor is between an excitation current i and its associated magnetic field H along some closed-loop encircling it [242].

$$\oint \mathbf{H} \cdot d\mathbf{l} = i_{enc}, \quad (A)$$

Note that this field is defined as independent of any material properties. The resulting magnetic flux density within some material within the magnetic field is

$$\mathbf{B} = \mu \mathbf{H} = \mu_0 \mu_r \mathbf{H}, \quad (T)$$

In scalar form, at a distance r from the center of the current carrying conductor,

$$H = \frac{i}{2\pi r}, \quad (A/m)$$

$$B = \mu_0 \mu_r H, \quad (T)$$

An annular ring of material (representing the current sensor) centered around the current carrying wire will, therefore, experience a magnetic field

$$H = \frac{i}{2\pi r} = \frac{i}{l} \quad (A/m)$$

where l represents the nominal length of the annular ring of material.

Assume the core material has a permeability $\mu_c = \mu_{c,r} \mu_0$, and contains no gaps, $l_c = l$, then the magnetic flux density within the core is

$$B = \mu_c H = \frac{\mu_c i}{l_c} \quad (T) \quad (7)$$

and the resulting magnetic flux is

$$\Phi = BA_c = \frac{\mu_c A_c i}{l_c} \quad (Wb) \quad (8)$$

where A_c is the cross-sectional area of the core.

The induced open-circuit voltage on the sense loop is given by Faraday's law

$$v_s = \frac{d\Phi}{dt} = \frac{\mu_c A_c n}{l_c} \frac{di}{dt} \quad (V) \quad (9)$$

where n is the number of turns of the sense coil around the core material. This can be rewritten in terms of turn density ρ , turns per unit length, as

$$v_s = \frac{d\Phi}{dt} = \mu_c \rho A_c \frac{di}{dt} \quad (V) \quad (10)$$

Note that the induced voltage increases proportionally with respect to the permeability and cross-sectional area of the core material, as well as the turn density of the sense coil. For a sinusoidal excitation current, the induced voltage also increases in proportion to the excitation frequency.

3.2.1 Printed Current Sensor

3.2.1.1 Silver traces printing

To create the coil, the silver (Ag) trace was printed on one side of a sheet of polyamide substrate. The silver trace was printed using an Optomec AJ200 aerosol jet printing system with CLARIANT Ag nanoparticle ink (figure). AJ200 system offers two methods for fine structure printing, a pneumatic atomizer (PA)

and ultrasonic atomizer (UA). For this work, the ultrasonic atomizer was used since it requires less ink volume than PA. The UA method functions by first atomizing liquid ink into aerosol droplets with diameters of 2-3 μm using high-frequency pressure waves generated by an ultrasonic transducer. The atomized ink droplets are then carried by a transport gas (nitrogen) from the ink vial to a deposition head. At the deposition head, a sheath gas focuses the aerosol and reshapes it into a narrow spray [243]. Typically for fine structure printing, the line width can be adjusted between 10 μm - 100 μm using different combinations of nozzle sizes and sheath gas pressures. In this work, silver coils were printed with 80 μm line width and 35% overlap. After printing, the coils were cured at 250 $^{\circ}\text{C}$ for 30 minutes to improve the overall conductivity of the printed trace. Figure 3-3 shows SEM images of Ag nanoparticles before and after curing at different temperatures. From figure (a), some large ink drop could be observed. And due to the low conductivity of non-cured ink, it is very difficult to get a clear nanoparticle image. Also, it shows very clear that after curing at high temperature, Ag nanoparticles are sintered together and become a bulk structure. However, there are some pinholes still exist, which lead to increase overall resistance. In order to overcome this problem, multi-layer printing is a desirable approach.

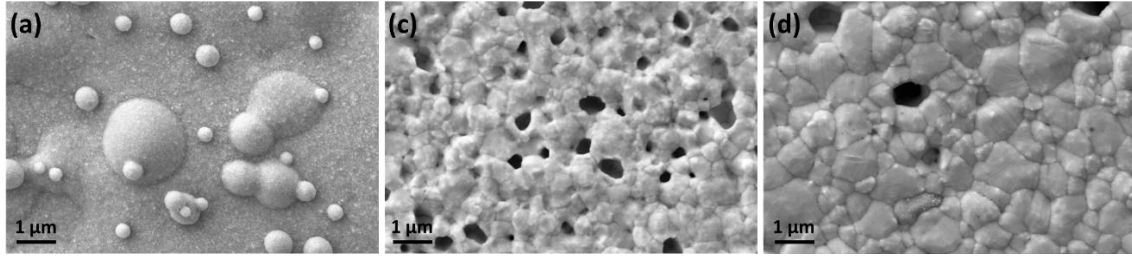


Figure 3-3 SEM image of printed Ag nanoparticle (a) without sintering, (b) sintering at 150 °C for 60min, and (c) 300 °C for 60 min

The sheet resistance and printed film thickness are measured for a comprehensive understanding of the ink characteristic. The figure shows the sheet resistance measurement result for multi-layer printing. As the number of layers increases from 1 to 4, the thickness of the printed silver increases from about 1.5μm to 5.5 μm (Figure 3-4(a)). As the number of layers is increased, the trace resistance drops. As shown in Figure 3-4(b), the sheet resistance drops from 155 milli-ohms to less than 10 m ohms. However, additional layers beyond the third impart minimal conductivity gains. In order to balance the reduction of trace resistance with time and cost of the printing process, the coils were printed using 3 layers of ink. After printing, a layer of polyamide adhesive-backed tape is placed on top of the printed layer as a protective film, avoiding covering the electrical contacts near the ends.

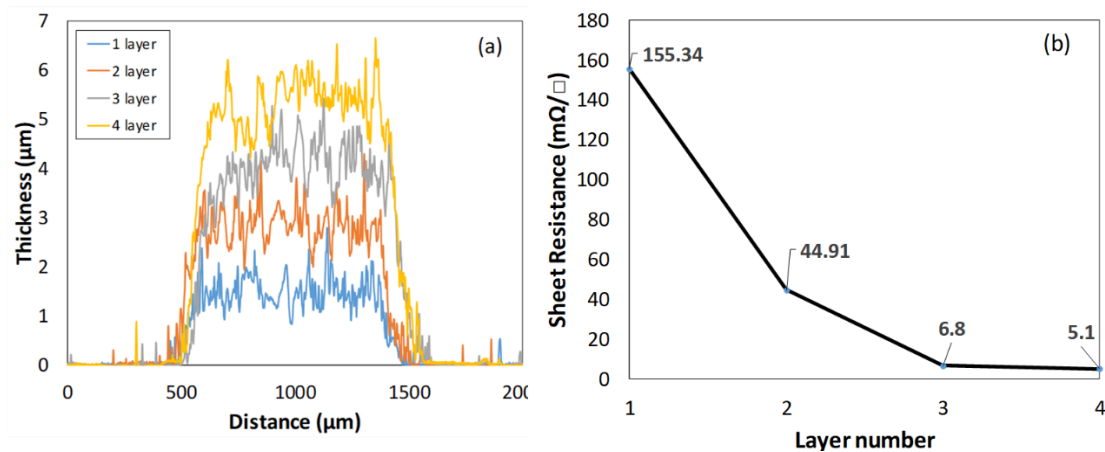


Figure 3-4 Printed Ag film thickness with different layer number and (b) sheet resistance with different layer number

3.2.1.2 Laser Cutting

From design, the silver electrode needs to surround a permalloy sheet as a schematic shown in Figure 3-5(a). In order to create this structure, a laser cutting process is involved in the fabrication process to create cuts. Back lines in Figure 3-5(a) represents laser cutting paths. A 30-watt CO₂ laser is used in this work. The preparation of the cutting process starts with the creation of an alignment guide. A piece of thick cardstock paper that is placed on the print-bed and into which cuts are made using two passes at 100% speed, 6W laser power, and a - 0.19 mm focus adjustment. The laser, in this case, does not cut through the cardstock, but instead only burns the pattern into the top surface. The prepared sense coil is then overlaid on top of the cardstock and is manually aligned such that the cuts lie in their intended location with respect to the printed silver. This is easily achievable with a bright light source given the semi-transparent nature of

the polyamide substrate. After being taped onto the bed in the aligned position, the cardstock is removed, leaving only the uncut sense coil in the aligned position on the bed (Figure 3-5(b)). And the final cutting process is started, this time at 20% speed and 30W laser power, with two passes at a 0.00 mm focus adjustment, followed by another two passes at a -0.19 mm focus adjustment. The cutting process leaves carbonized material along the cutting paths. However, this is easily removed with a dry cloth and compressed air (Figure 3-5(c)). Next, a polyamide encased permalloy strip is woven through the vertical cuts such that the silver trace forms a coil around the strip, as shown in Figure 3-5(d). A tapered leader is attached to one end of the permalloy strip to ease the weaving process. Finally, the permalloy material is trimmed to minimize overlap and copper tape is attached to the electrical contacts using silver epoxy. The additional copper provides reinforcement where the clamping force will be applied when in use Figure 3-5(e). The combination of an improved silver printing process, polyamide protection layer of the silver, and encapsulation of the core material, along with the copper contact reinforcements, make this sense coil robust to handling stresses.

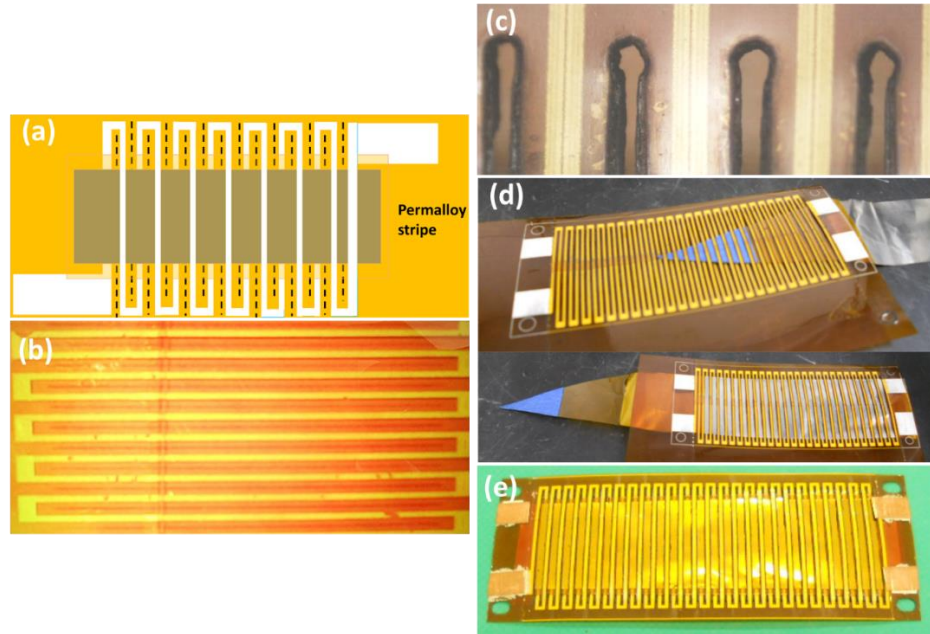


Figure 3-5 (a) Schematic of coil design, (b) images of enlarging printed silver lines, (c) Image of laser cuts, (d) permalloy strip being woven through the cuts, and (e) completed sensing coil.

3.2.2 Simulation and Pretest

Before integrating electrodes components, the printed sensor coil was measured and test in a lab environment. In order to get a clear sensing signal, an AD8421 instrumentation amplifier was used to amplify the voltage from the sense coil by 800 before being fed into an oscilloscope for measurement. Figure 3-6 shows the initial test results of the sensor response for a 1KHz input AC signal. it needs to be mentioned that as input peak-peak amplitude over 50A, saturation shows on current response. At a low current range (1-10A), the sensor shows a very linear response. Figure 3-6(d). The derivations in the previous subsections assume that the magnetic flux within the core material can increase proportionally

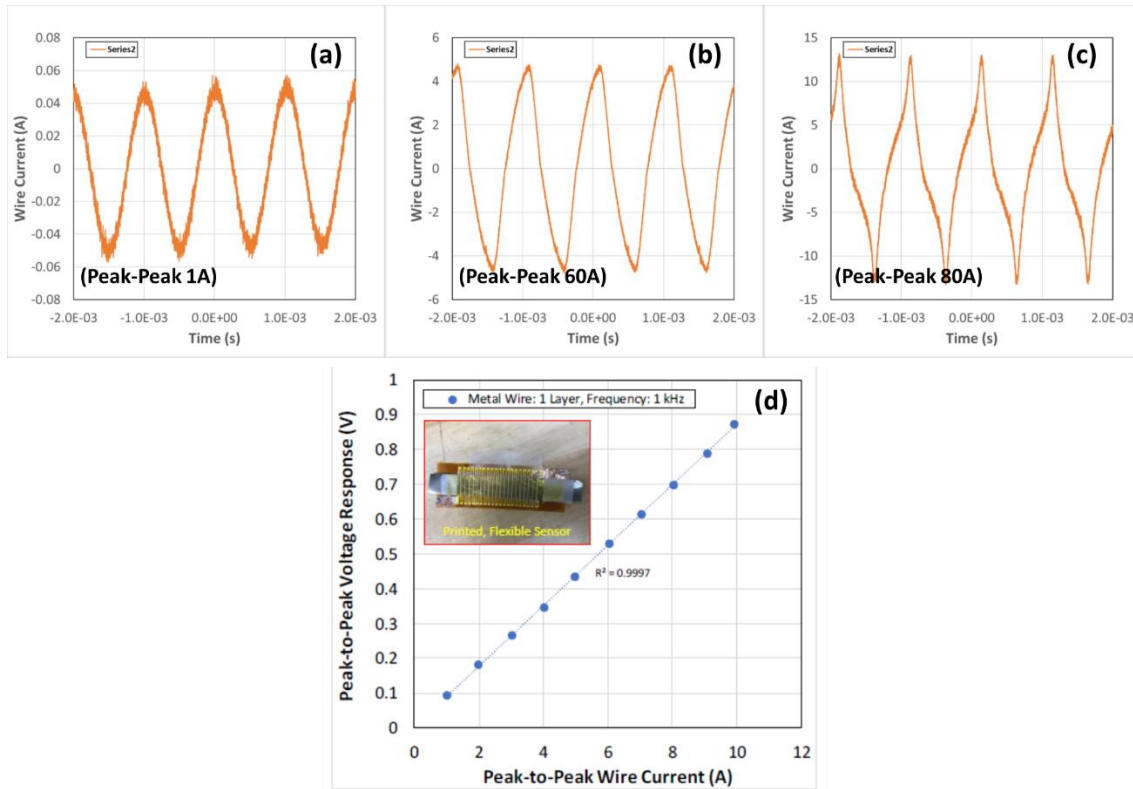


Figure 3-6 Current response of 1KHz AC signal with an amplitude of (a) Peak-Peak 1A, (b) Peak-Peak 60A, (c) Peak-Peak 80A, and sensor voltage response of from 1A to 10A.

with the applied magnetic field without limit. However, most materials will only support a limited flux at which point it is considered to be in saturation.

Electromagnetic modeling of the sense coil was performed to understand better what effect the positioning of the current carrying wire within the sensing loop has with respect to flux density within the core material. The software package Finite Element Method Magnetics (FEMM) was used to simulate an annular ring (core) surrounding a wire carrying a current of 1 A. The dimensions of the simulated setup are kept constant across simulations, with the conductor material selected as copper, and the core material selected as mu-metal, one of the pre-defined core materials available within the software package.

The first simulations were performed for a core with no gap surrounding a current carrying wire. Figure 3-7 (a-b) shows the flux density within the core material with the conductor centered and near the sidewall, respectively. When the conductor is located at the center, the flux density within the core peaks at approximately 600 mT and is relatively uniform along any circumferential path. When the conductor moves close to the sidewall, the Figure 3-7 (c-d) shows the simulated flux density within a core with 1 gap with the conductor centered and next to the gap respectively. beads on the coil design, this case is closer to the real case. In this case, the flux density peaks around 11 mT, which is significantly lower than the no-gap case. The flux density is also seen to no-longer be uniform along the length of the core, instead of being significantly greater opposite the gap. This is especially the case when the conductor is also opposite the gap.

As was observed, flux density can increase significantly (20% in the simulations) within portions of the core material as the conductor moves off-center and closer to the inner wall of the core. It may be possible for that increase in flux to push a portion of the core into saturation. This simulation result conforms to a signal from the sense coil is potentially sensitive to the position of the current carrying conductor within it. To ensure that the conductor is always centered within the sense coil, a two-part coil holder was developed (Figure 3-8).

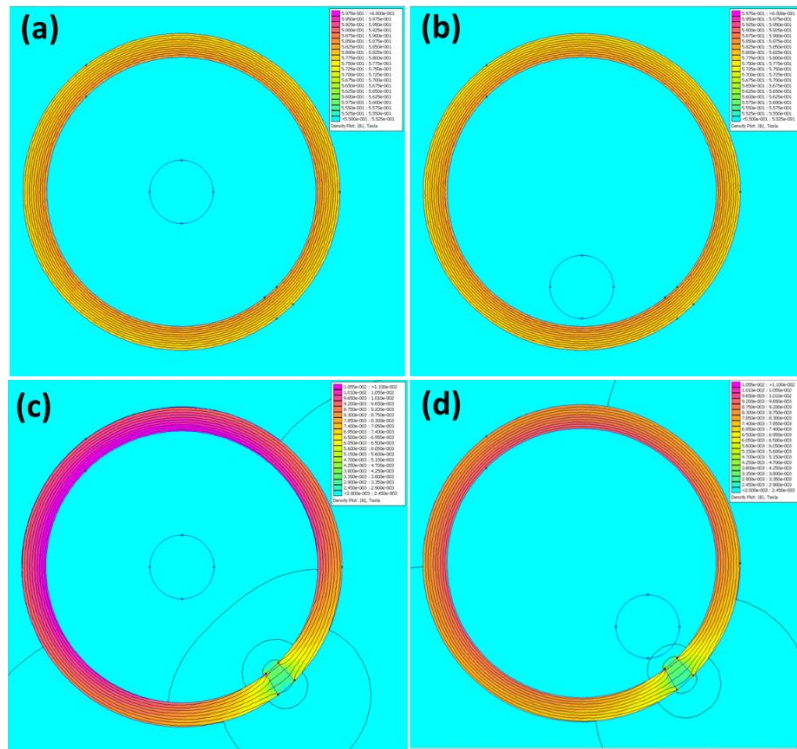


Figure 3-7 (a) Current carrying conductor centered within a mu-metal core, (b) current carrying conductor near an inner wall of a mu-metal core, (c) Current carrying conductor centered within a mu-metal core with gap, and (d) Current carrying conductor near an inner wall near a gap within a mu-metal.

3.3 Sensor Integration

3.3.1 Sensing Coil Integration

A test fixture is used to attach the coil onto a current carrying conductor as illustrated in Figure 3-8. First, the test fixture is attached to the conductor using an appropriately sized inner cross member as shown in Figure 3-8(a). Next, one end of the sense coil is placed over the two alignment pips on the test fixture (Figure 3-8(b)). The coil is wrapped around the test fixture and is held in place with a coil clamp, which also provides an electrical connection to the coil. Finally, as shown in Figure 3-8(c), the coil and test fixture assembly are enclosed in a clamshell-like outer cover to prevent accidental contact with the exposed contacts (necessary in some high-voltage installations). The other end of the jacketed cable attached to the coil clamp can then be brought away from the potentially unsafe high-voltage area to be plugged into the current measurement electronics. Shielded Cat 5e ethernet cable is currently being used with all but one of the twisted pairs left unconnected (Figure 3-8(d)).

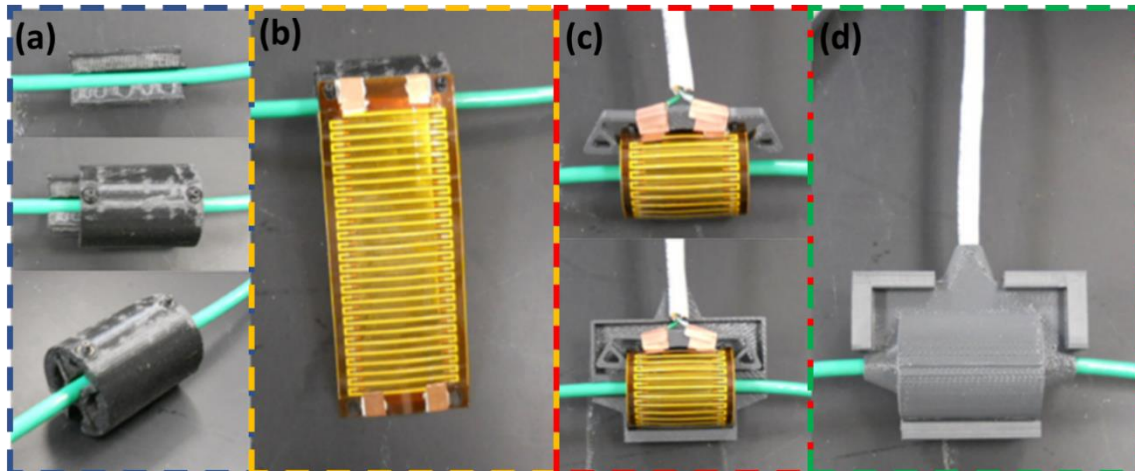


Figure 3-8 Test fixture for installation of the sense coil around a current-carrying wire.

3.3.2 Measurement Electronics

Electronics were designed to allow ease of development and testing of various coil designs and sensing algorithms, as well as to allow data collection in the field. The key components of this system are a low-noise high-gain analog front-end and an arbitrary signal generator for in-field coil calibration. These are centered around an ARM Cortex-M4 microcontroller (Teensy 3.2). A microSD card slot is provided for data collection, and a keypad and display facilitate user interaction while showing real-time measurement data. The unit can be powered externally through USB or internally with 4x AAA batteries and uses a coin-cell battery to maintain its internal real-time clock. The assembled electronics are shown in Figure 3-9, together with a battery holder, which is enclosed in a 3D printed case. On the front of the case are the keypad and display. On the right side from top to bottom is a connector for the sense coil, micro USB connector for power

and data, and a small recessed switch to select between battery or USB power. On the top is a connector for an external current loop for sense coil calibration, and on the left is a microSD card slot. The back has a battery cover underneath, which is a 4x AAA cell holder. The typical response of each current sensor is on the order of $10 \mu\text{V/A}$. In order to be effectively sampled by the ADC available in the selected microcontroller, this signal must be amplified by a factor of 1000 or more to provide a clear signal. The specific implementation for this prototype hardware starts with a low-noise instrumentation amplifier (INA827) with a gain of 1000. The pre-amplified signal is then low-pass filtered using a 4th order Chebyshev filter with 5 kHz cutoff and is finally passed through a programmable-gain amplifier (PGA) to allow an additional gain between 1 and 32.

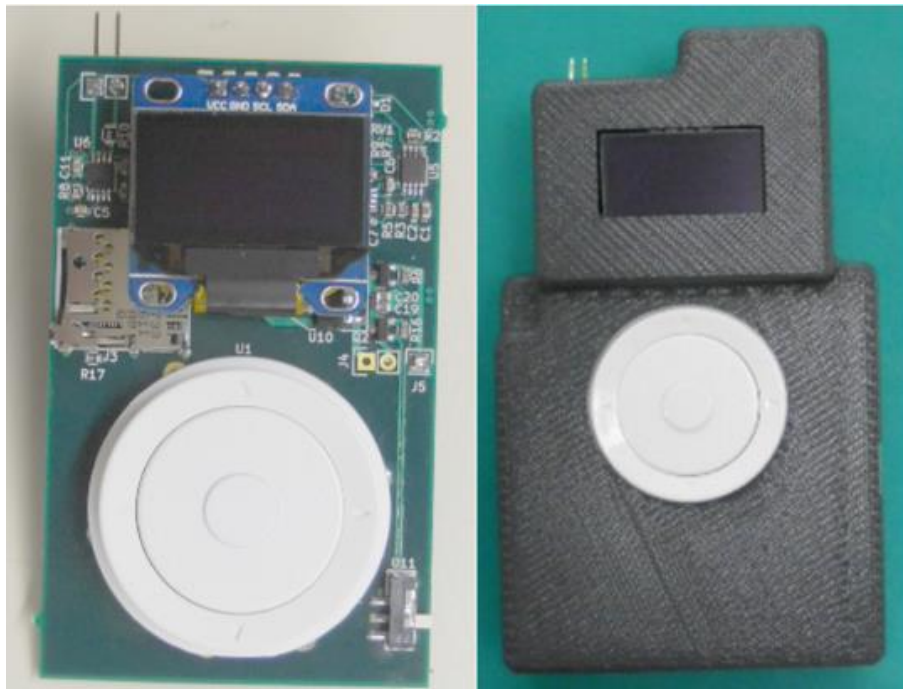


Figure 3-9 Prototype hardware.

The amplified signal is sampled using the microcontroller's built-in 16-bit ADC at 44.1 ksps and low-pass filtered using a 500 Hz cutoff bi-quad filter before being analyzed. The fundamental frequency of the sampled signal is determined using the YIN algorithm [244] which can be implemented relatively efficiently with low-latency. Standard summation methods are used to estimate the RMS and peak amplitudes of the signal.

For in-field calibration and testing of sense coils, a signal generator is used to drive a multi-turn current loop (Figure 3-10), allowing aggregate currents of up to several amps to be generated. The signal itself is generated by the microcontroller, which outputs an analog signal using one of its internal digital-to-analog converters (DACs). The output of the audio amplifier is brought out to a pin header to which an external current loop can connect. The external current loop is designed to allow the sense coil test fixture to mount onto it directly.

This configuration allows any arbitrary signal to be generated, not only sinusoidal ones, which can be useful when characterizing the transient or harmonic response of the sense coils. To ensure that a known current is passing through the current loop, a sense resistor is placed inline with the current loop, and the voltage across it is amplified and sampled by the microcontroller. Knowledge of the actual current allows the signal sent to the DAC to be modified to compensate for changes in power supply voltage or variations between external current loops due to manufacturing tolerances or design changes.

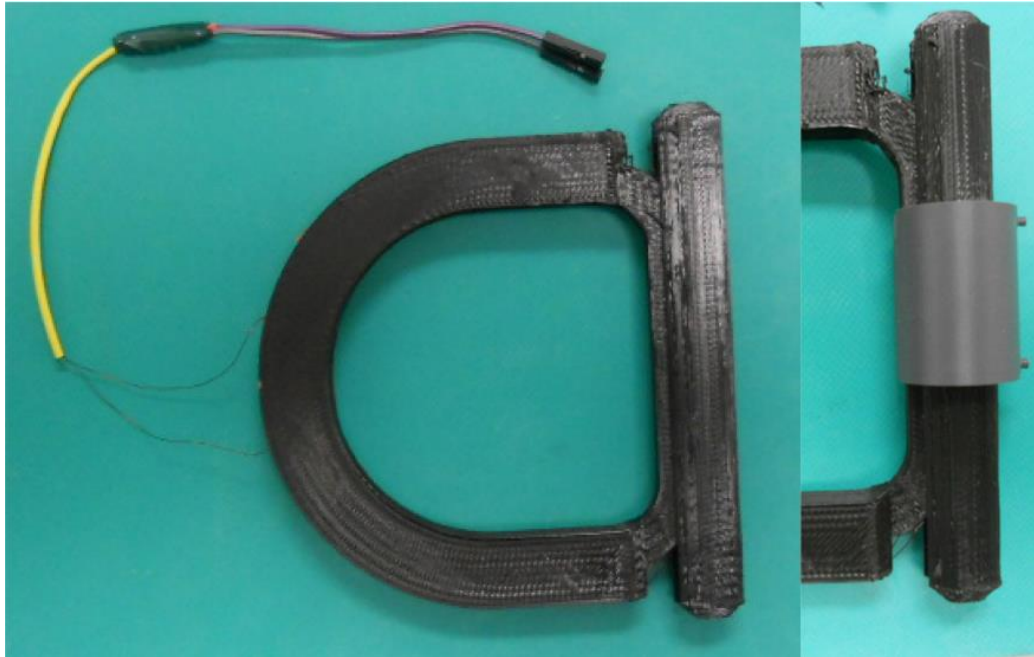


Figure 3-10. Prototype external current loop for in-field coil calibration, consisting of 80 turns of magnet wire wound around a 3D printed form. The sense coil test fixture can slide directly onto the loop for testing.

A microSD card slot is included in the hardware for data storage, including both data collection as well as configuration storage. Each sense coil potentially has a different sensitivity and may each require unique correction curves. While in operation, the measured data can be periodically written to the microSD card allowing stand-alone data collection. The written data includes the estimated frequency, current, amplifier gain setting, as well as a timestamp indicating when the measurement was obtained.

3.4 Results and Discussion

Testing of coil performance used our existing test setup consisting of a sinusoidal oscillator driving a 10-turn current loop. The sense coil shown in Figure

3-8 was attached to the current loop, and its response was measured using the prototype hardware described earlier. A commercial current transformer and oscilloscope were used to obtain ground-truth measurements of the actual current through the loop. The theoretical response of the sense coil assuming a continuous core with no gap can be derived directly from basic electromagnetic field theory, which states that the voltage induced across the coil will be proportional to the time rate of change of magnetic flux, Φ , through the coil. This can be represented as

$$v_s = \frac{d\Phi}{dt} = \mu_c \rho A_c \frac{di}{dt}$$

where v_s is the induced voltage, μ_c is the magnetic permeability of the permalloy (core material), A_c is the cross-sectional area of the permalloy, ρ is the turn density of the printed coil, and i is the current in the conductor being measured. Note that the induced voltage increases proportionally with respect to the permeability and cross-sectional area of the core material, as well as the turn density of the sense coil. For a sinusoidal excitation current, the induced voltage also increases in proportion to the excitation frequency.

In reality, there will always be a non-zero gap between the ends of the permalloy strip leading to the effective response shown below

$$v_s = \frac{d\Phi}{dt} = \mu_c A_c \frac{n}{l + \mu_{c,r} l_g} \frac{di}{dt} = \mu_c A_c \rho^* \frac{di}{dt}$$

where $\mu_c = \mu_{(c,r)} \mu_0$, l is the total length of the coil, and l_g is the length of the gap between the ends of the permalloy strip. The gap causes the effective turn density, ρ^* , to decrease as the gap length increases giving $\rho^* \leq \rho$. Using this model, a coil with a length of 8.5 cm, a density of 3.3 mm/turn, and core

permeability of 60000 with 10 μm gap would have a theoretical sensitivity of approximately 18 $\mu\text{V/A}$.

Another non-ideal behavior exhibited by the sensor is magnetic saturation of the permalloy. This can be modeled as

$$B_{eff} = B_{sat} \left(\coth\left(\frac{H}{a}\right) - \left(\frac{a}{H}\right) \right)$$

Where B_{eff} is the effective flux density, B_{sat} is the saturation point for magnetic flux density in the material, H is the applied magnetic field, and a is a scaling parameter experimentally selected as $B_{sat}/(4\mu_c)$. For simulation, the ideal flux is first found to determine the magnetic field $H = \Phi/\mu_c A_c$, with which the effective flux $\Phi_{eff} = B_{eff} A_c$. The induced voltage then becomes $v_s = d\Phi_{eff}/dt$, which becomes strongly nonlinear as the current, and therefore induced a magnetic field, increases.

Experimental results appear to be in line with the theoretical model. Several coils that have been characterized have shown sensitivities of approximately 10 $\mu\text{V/A}$. Characterization of one of the printed coils was performed using a current loop around which the sense coil was wrapped around using the test fixture described earlier. A commercial current transformer and oscilloscope were used to obtain ground-truth measurements of the actual current through the current loop.

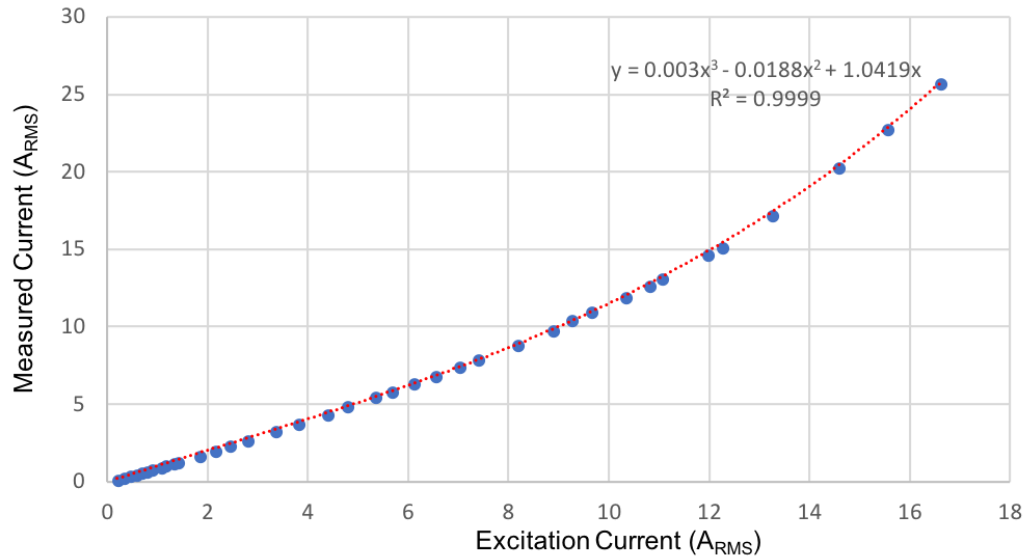


Figure 3-11 Measured Vs. Actual RMS Current

As shown in Figure 3-11 the estimated current using the coil's response appears to be relatively linear for low currents, eventually deviating as the core begins to enter saturation. However, the relationship extending into the early saturation region can be modeled using a 3rd order polynomial as shown by the dashed red line in the figure.

3.5 Conclusions

The design and electrical performance of the direct-write printed flexible current sensor show promise for load monitoring applications in industrial/commercial and residential applications. Key findings of modeling, simulation, and analysis of the integrated current sensor align well with experimental results and are guiding the integration of direct-write printing, additive manufacturing, and sensor electronics concepts to design a low-cost,

reconfigurable field-portable current sensor unit. Future modeling work will focus on extending the current sensing range through design modifications that are compatible with the direct-write printing and additive manufacturing approaches critical to meet the low-cost requirement for widespread deployment in buildings and grid applications.

4. LASER-INDUCED CARBON-BASED SMART FLEXIBLE SENSOR ARRAY FOR MULTI FLAVORS DETECTION

Disclosure

This chapter is based on a publication originally published by Yongchao Yu, Pooran C Joshi, Jayne Wu, Anming Huin 2018.

[106] Yu, Y., Joshi, P. C., Wu, J., & Hu, A. (2018). Laser-Induced Carbon-Based Smart Flexible Sensor Array for Multiflavors Detection. ACS applied materials & interfaces, 10(40), 34005-34012.

Yongchao contributions in the article: Fabricated sensor array, sensor surface functionalization, measurement, and data analysis.

Co-authors' contributions are listed as follows: Dr. Pooran Joshi and Dr. Jayne We constructed in article revision. Dr. Anming Hu was the PI on the research, assisted in data analysis and experiment design and revised the article.

4.1 Motivation and Background

In this chapter, I report a flexible sensor array system that fabricated on a polymer substrate by the laser direct writing process to mimic an electronic tongue for multi-flavors decoction. An electronic tongue is a sensing system that is applied to detect different elements with the same sensor array. By analyzing responses from different measurement units, it enables a cross-sensitivity, namely the ability of the system responding to a range of different analytes in solution without specific functionalization of sensors. In this paper, a six-unit sensing array system was fabricated by a laser direct writing process. Sensing units were introduced on a flexible polyamide surface. A high surface-volume ratio porous carbon structure was created by a laser-induced carbonization process, which provides stable conductive carbon electrodes with high sensitivity. Different surface treatments such as gold plating, reduced-graphene oxide (rGO) coating and polyaniline (PANI) coating were accomplished for different measurement units. By applying principal component analysis (PCA), this sensing system shows a promising result for many flavors detection. The detection limits for each element are about 0.1mM for NaCl and sugar solutions. And it is able to detect 10^4 times diluted commercial table vinegar solution, which originally contains 5% of acetic acid. The detection limit is theoretically lower than the human threshold of 10mM for NaCl and sugar. Besides, the sensing system shows high sensitivity and selectivity for mixed elements. By mapping the data points, the sensor system could detect flavor combinations and provide a reliable prediction of analyte concentration ratios.

A range of bio-nano-sensing technologies has been developed for biomedical diagnostics [245, 246], environment monitoring, or pollution monitoring [105, 247], and monitoring temperature [248], humidity and other physical parameters in daily life [249-252]. The general drawback of these sensors is that these sensors are specifically designed for one certain objective. A sensor sensitive to one physical-chemical parameter can be irresponsive to another parameter. In sharp contrast, sensing by human beings and animals is based on the same sensing system, such as tongues or nose, but can detect a number of objectives. Canonical classification of the senses taken by neurophysiologists embraces five senses. They can be categorized into two groups, physical senses, and chemical sense. For physical senses, it includes sight, hearing, touch, which are adapted to sense physical stimuli; taste and smell are considered as chemical sense, which can perceive changes in the chemical composition of the environment [253]. The concept of the electronic nose was published in 1982 by Oersaud and Dodd. An array of chemical sensors was used to simulate receptors and neural analysis to recognize the pattern of stimulations through pattern recognition methods [254]. The first system for liquid analysis based on the multisensory array was reported by Otto and Thomas in 1985, and the name of “electronic tongue” was presented [255]. Since then, the development of the multi-array sensing system had a rapid increase in the early 2000s [256-259]. Meanwhile, many sensing techniques have been developed for electronic tongue applications, such as optical and enzymatic sensors [260-262], the

electrochemical or voltammetric based sensor is still one of the most widely used sensing techniques[253].

To date, most of the sensor arrays were fabricated by cleanroom technologies, such as lithography and chemical etchings, which are very time consuming and expensive techniques[263-265]. As our knowledge, this is the first electrical tongue sensing system fabricated by the laser direct writing process, which is a fast, low-cost, and environment-friendly fabrication process [266].

As mentioned in chapter 1, the laser ablation of polymer material has been studied since the 1980s [267]. In 2014, Tour et al. of Rice University reported their research progress on laser-induced porous graphene (LIG) films from commercial polyimide. In their research, CO₂ infrared laser was used for the ablation of a polyimide substrate. Recently a high sensitive bio-sensor was fabricated by laser direct writing method using a femtosecond laser [105]. The porous carbon structures with a very high surface-volume ratio were functionalized with an aptamer for specific sensing. For a pristine sensor without aptamer coating, the sensing unit only presents very limited selectivity and is considered as “nonselective”. However, in this work, by integrating responses from a sensor array, different measurement units enable cross-sensitivity, namely the ability of the system to respond to a wide number of different analytes in solution without functionalization with probe molecules [268]. To enhance the selectivity and sensitivity of sensor systems, the large response differences between each measurement units corresponding to the same analyte is considered as an ideal

situation. Different surface treatments on carbon electrodes prepared six different types of sensor units that allow electronic tongue-style sensing.

4.2 Sensor Fabrication and Functionalization

4.2.1 Laser Direct Writing

As the electrode material, the laser-induced porous graphene electrode was induced by laser direct writing (LDW) process. Figure 4-1(a) shows the LDW system for sensor fabrication. A femtosecond laser, with 1030 nm wavelength, was used as the laser source. The laser beam was focused by a 20X 0.4NA objective lenses. The laser power was adjusted by tuning a $2/\lambda$ waveplate and a polarizing beam-splitter. An optical isolator was placed after the shutter to prevent the laser

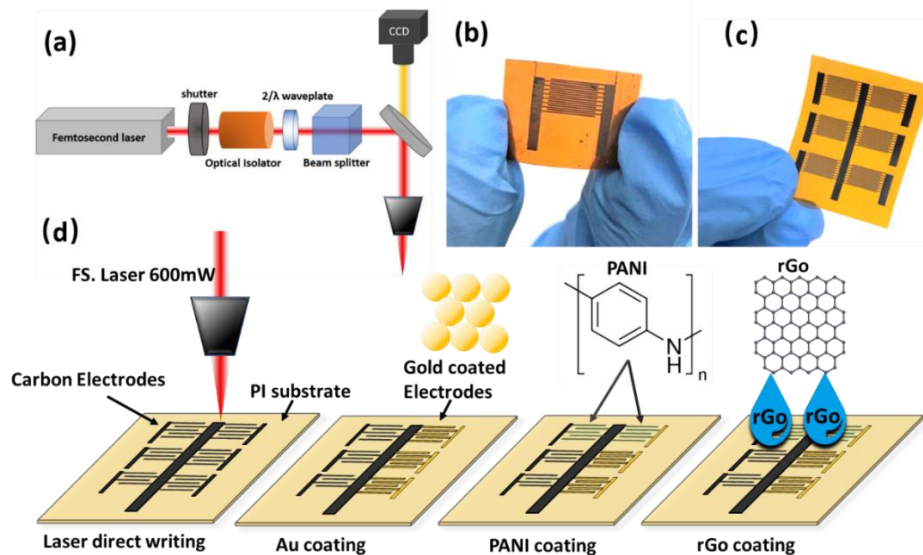


Figure 4-1(a) The setup of the laser direct writing system. Images of (b) a fabricated carbon electrode and (c) a carbon sensor array with six units fabricated on the polymer surface. (d) The schematic of surface sensing process.

beam from reflecting into the femtosecond laser source. A program controllable 3D stage was placed under the object lens to control the movement of the substrate and create different patterns. For this experiment, carbon electrodes were fabricated under 600 mW laser power with 60mm/min writing speed. Figure 4-1(b) shows the image of fabricated carbon electrodes on the polyimide (PI) substrate, which presents as one measurement unit in this study. The working electrode area is 0.5cm x 0.6 cm, with 8 pairs of electrodes in each measurement unit. The line width for each electrode is 100 μ m, with a 100 μ m gap between each electrode. Figure 4-1 (c) displays a sensor array with six sensing units. And Figure 4-1 (b) shows the sensor array fabrication process and the functionalization process.

4.2.2 Sensor Functionalization

For the general functionalization of sensing units, different surface treatments were accomplished on the laser-induced carbon electrode surface. Six different electrodes constitute a sensor array for the measurement, which is carbon electrode (CE), gold plated CE (GCE), rGO drop coated CE (rGO-CE), rGO drop coated gold plated GCE (rGO-GCE), polyaniline deposited CE (PANI-CE), and polyaniline deposited gold plated GCE (PANI-GCE). Figure 4-2(a-f) are typical SEM images of the surface structures for each type of electrode, respectively.

4.2.2.1 Gold Plating

Gold particles were electrically plated onto the carbon surface using a commercial gold plating solution (Carswell) with a 6V DC power for 10 min. A Pt

wire was used as the counter electrode. Figure 4-2(d) shows the surface structure of a gold-plated CE. As shown in the Figure, a thick gold nanoparticle-assembled layer was deposited on the carbon electrode. This process can significantly increase the conductivity of the electrode.

4.2.2.2 rGO Coating

Graphene oxide was prepared by a simplified Hummer's method [74]. In brief, 1.5g graphite powder was added to a mixture of 200 mL $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ with volume ratio 9:1, then 9.0 g KMnO_4 was added slowly. The mixture was stirred at 55 °C for 12 h for a completed reaction. The reaction was cooled to room temperature, and the ice was added into the solution, then about 4 mL of 30% H_2O_2 was added to the solution. After stirring for 12h, the solution was set for sediment and separation. The supernatant was removed, and 250 mL 10 wt% HCl was added and kept stirring for 12 h. Then, the obtained mixture was separated by centrifuging. After the graphene oxide was compounded, the 1M ascorbic acid solution was used for reducing graphene oxide with the GO: ascorbic acid volume ratio of 1000:1. Additionally, the solution was heated to 95°C in an oil bath and held for 6 hours. 20 μL rGO solution was dropped to the electrode's surface and stored at room temperature until completely dry. Figure 4-2(b and e) show images of electrodes after the rGO coating. It could be observed that a thin layer of rGO covered on both carbon and gold-coated electrodes.

4.2.2.3 Polyaniline Coating

Polyaniline (PANI) is one of the most commonly used conductive polymer materials. It has similar electrical properties to inorganic materials such as

semiconductors and metals with various applications[269-271]. An electrolyte solution of 1M H₂SO₄ + 0.05M aniline was used for the electrochemical deposition of PANI onto the carbon electrode [272]. A Pt wire was used as the counter electrode. For electrical deposition, the voltage range was set from -0.2V to 0.8V with a 10mv/s scan speed for 20 cycles. Figure 4-2(c,f) shows the surface structures of PANI coated electrodes. For PANI-CE sample, it is very clear that some polymer structure was introduced on top of carbon layers after PANI deposition and generated the net structure. However, for the PANI-GCE sample, it is very difficult to find PANI from SEM images directly. For better understating of PANI deposition on GCE, Fourier transform infrared spectroscopy (FTIR) analysis was conducted as follows.

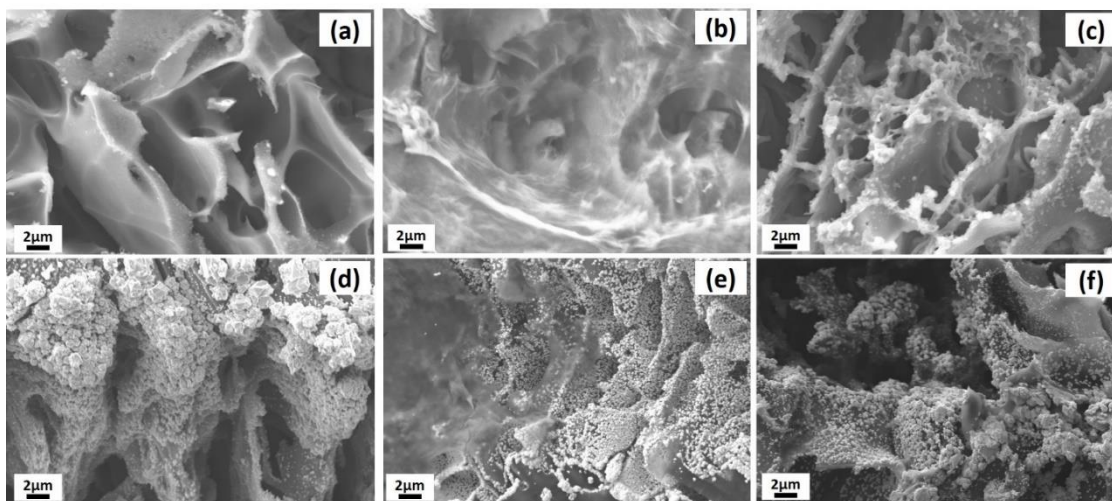


Figure 4-2 SEM images of (a) CE, (b)rGO-CE, (c)PANI-CE, (d) GCE, (e)rGO-GCE and (f)PANI-GCE.

4.2.2.4 FTIR Analysis

Figure 4-3 shows the Fourier transform infrared spectroscopy (FTIR) spectra. From Figure 4-3(a), some additional peaks could be observed from PANI-CE samples. The main bands of the PANI base located at 1585cm^{-1} and 1040cm^{-1} [272, 273]. These peaks prove that aniline was deposited on the surface of the carbon electrode and produced PANI. For rGO deposited samples, Figure 4-3(b) gives the FTIR results for both rGO-GCE and rGO-CE. A strong C-C peak at 1625cm^{-1} was found from both samples. Additionally, C-O (at 1052cm^{-1}) and C-O-C (at 1226cm^{-1}) appear on the spectra results [111, 274]. These peaks are considered as peaks from polyamide substrates and graphene oxide that not reduced completely. Some organic group peaks are obvious in Figure 4-3 (c). Peaks show on 1495cm^{-1} and 1040cm^{-1} are two typical peaks for PANI. Especially, the peak on 1495cm^{-1} represents the benzenoid ring [275]. The C-N bond (1374cm^{-1}) also could be observed from the Figure[273], which is provided by PANI. The FTIR result evidence that PANI and rGO were successfully deposited on electrodes.

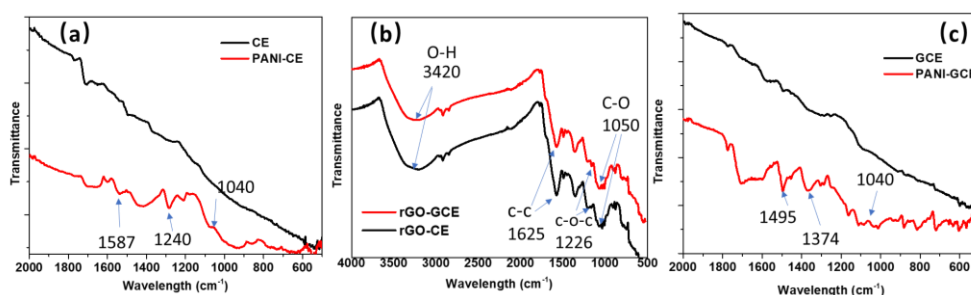


Figure 4-3 FTIR analysis for (a) CE and PANI-CE, (b) rGO-CE and rGO-GCE, and (c) GCE and PANI-GCE.

4.2.3 Data Collections and Sensing Mechanism

Before testing the target substances, the impedance response of the e-tongue sensor system was characterized by distilled water. Figure 4-4(a) shows the sensing system setup for measurements. The testing solution was applied to each sensor unit and signals were collected through six individual channels with an electrochemical working station. Figure 4-4(b) shows impedance responses with different frequencies for each measuring unit. 20 μ L distilled water was dropped to sensors, and impedance data was collected by biologic SP200 Electrochemical working station. The frequency spanned from 1 Hz to 1 M Hz. As shown in Figure 4 (b), GCE based sensor shows a small impedance response than CE based sensor units, which means the GCE sensing unit has a lower resistance. PANI coated sensors show lower impedance responses for both GCE and CE. Non-coated sensors show the largest impedance response for distilled water. Furthermore, all the sensor units provided different responses for the distilled water, which is essential for the principal component analysis (PCA). Typically, the impedance of the measurement unit is dominated by three parts. For the lower frequency range, under 100 Hz, the responses are driven by a double layer effect formed at the electrode/electrolyte interface. In the range of 10^2 and 10^4 Hz, it appears the effect from the coating material over the electrode. And at higher frequencies (>100 kHz), the impedance is mainly governed by the geometric capacitance [263, 276]. The objective of this work is to detect different solutions; therefore, measurement data for the PCA process were grouped and collected from electrical impedance at 100 Hz, which is the frequency that provides more

information about the sample solutions themselves and interfaces between electrodes and sample solutions. Also, as shown in Figure 4-4(b), the impedances for all electrodes are clearly separated.

Salt (NaCl), sugar, and vinegar solution were used as three elements in this experiment to represent three different flavors, salty, sweet and sour. It is well known that NaCl exists in the form of Na^+ and Cl^- ions in water. And the vinegar dissolves in water as H^+ and CH_3COO^- . These ions provide good ionic strength. In addition, vinegar solution presents as a faintly acid solution. However, sugar, as an organic compound, it exists in water with the simple molecule form. Therefore, the impedance responses for each solution will be correlated to the unique properties of each electrolyte.

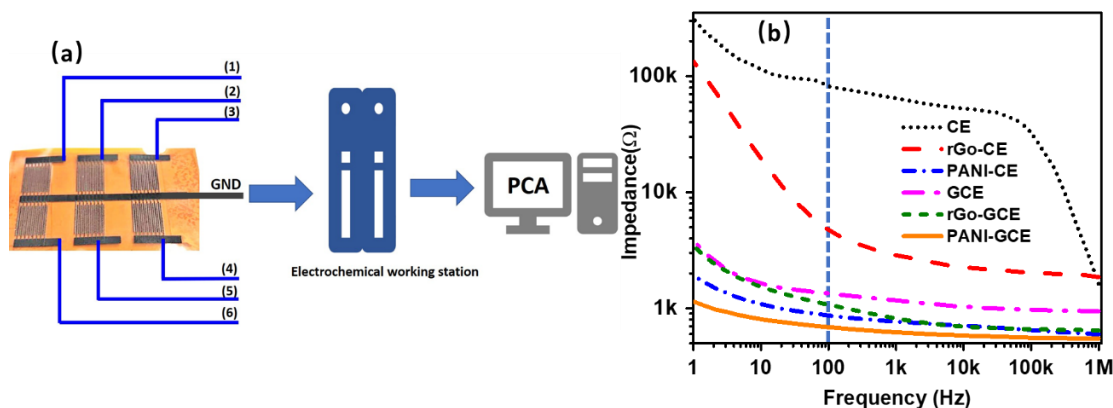


Figure 4-4 (a) The sensing system setup and (b) AC impedance response for distilled water

In order to achieve high sensitivity, the porous structure carbon was used as the electrode material. The porous structure carbon electrode provides a large surface-volume ratio, which will enforce the sensitivity improvement [105]. As well known that the carbon material provides high chemical suitability, none of the three components, salt, sugar and vinegar, that used in this experiment will react with carbon material. Therefore, the porous structure carbon is an ideal material for a voltammetric base sensor. By plating Au nanoparticles, it not only drops the internal resistance of the sensor but also provides enhancements of the local electromagnetic field due to its nanoparticle nature [277]. This makes the gold-plated sensor more sensitive to changes in impedances. Based on these two types of electrodes, the carbon electrode and the Au coated electrode, rGO, and PANI were further coated on both types of electrodes to further distinguish electrochemical properties for different sensing units. Both rGO and PANI are promising materials for electrochemical and bio-sensing [278-283]. The rGO was adopted on electrodes to change the surface properties and the internal resistance of sensing units. Furthermore, a high density of edge-plane-like defect sites, which provides a positive site in electron transfer to chemical and biological species, has been observed for chemically derived graphene [284]. This property may show different responses for Na^+ , Cl^- , H^+ , and CH_3COO^- ions. Additionally, as reported, sucrose molecules will interact with the surface group of the graphene and more functional groups will be created [285]. Therefore, impedance responses from rGO coated sensor units will be easily distinguished for different analytes.

For a similar purpose, the PANI was coated on both carbon and gold particle coated carbon electrodes. The PANI has been reported as a suitable material for pH sensing in aqueous medium recently [286-288]. Take advantage of this property, PANI is an ideal coating material to detect the vinegar solution, which is an acidic solution. The mechanism of pH sensing is basically the function of the ion-selectivity for PANI. This property also shows very promising results for NaCl and sucrose solutions detections[276, 289]. Additionally, PANI has been reported as sugar-sensitive materials for the determination of saccharides[290]. These features of PANI are attractive to improve the selectivity of the sensing system. As a piece of evidence, all sensing units in the sensor array provide different impedance responses for water, as it is shown in Figure 4-4(b).

4.3 Results and Discussion

To fully explore the sensitivity of the sensor system, different concentrations of target samples were applied, from 0.1M/L to 1 μ M/L for NaCl and sugar, which covered five orders difference of analyte concentration. A commercial table vinegar was purchased from a store, which contains 5% acetic acid, and it was used as the initial concentration of the vinegar solution. Then DI water was added to dilute vinegar solution to different concentrations (0.1 to 10^{-6} times diluted). Figure 4-5 shows the PCA results for NaCl, vinegar, and sugar with different concentrations. Black dots, red dots, and blue dots are representing NaCl, vinegar, and sugar respectively. The PCA is a statistical analysis process for identifying the data correlations. The principal components present the maximum variation of the data.

By retaining most of the variation, the dimension of the data set can be reduced. The first principal component (PC1) represents the direction at which the data show the largest variation. The second principal component (PC2) is the direction independent of the PC1 and shows the 2nd largest variation. A typical PCA plot can evaluate the differences and similarities between samples and group the data points with a low-dimensional plot [291]. Different surface treatments were accomplished for different sensing units. Therefore, each sensing unit provides different responses to the individual analyte. Also, along with the concentration changes, the responses from each sensing unit will change accordingly. However, due to different material properties, the changing rates and tendencies that collected from different sensing units may vary for different analytes. By applying PCA, the correlations of data set could be found and used for grouping, identifying and determining the tested analytes. As Figure 4-5 shows, separation and grouping of data sets are observed after the PCA process. Also, linear dependencies are found with changing sample concentrations. The NaCl samples are grouping on the left side. As the concentration of NaCl decreases, the data points move to the right and rise gradually from 0.1M to 0.1mM. However, as concentration decreases to 10uM and 1uM, a large shift occurs. Furthermore, a clear linear dependency also can be observed from sugar samples. Data points for sugar samples grouping on the right side of the plot. As the concentration decreases, the data set moves to the bottom side of the graph. Same as the NaCl mapping result, data points show a significant drop at 10uM and 1uM. This is considered as the detection limit for this sensing system. The vinegar samples

show a very clear linear dependence as samples were diluted from 0.1 to 10^{-4} . Data points are moving from the left side to the right side as the decrease of concentrations. And the result also shows discrepancies for the concentration of 10^{-5} and 10^{-6} . This PCA graph shows that the sensor array system can determine the different targets, NaCl, vinegar and sugar in this case. And the detection limit for this sensing system is 0.1mM, which is much lower than the human threshold that has been reported as 10 mM for both NaCl and sucrose solutions [292]. By grouping data points and by mapping data points on the graph, it can detect components of targets, which means it could be used to differentiate whether the unknown solution is NaCl solution, vinegar, or sugar solution.

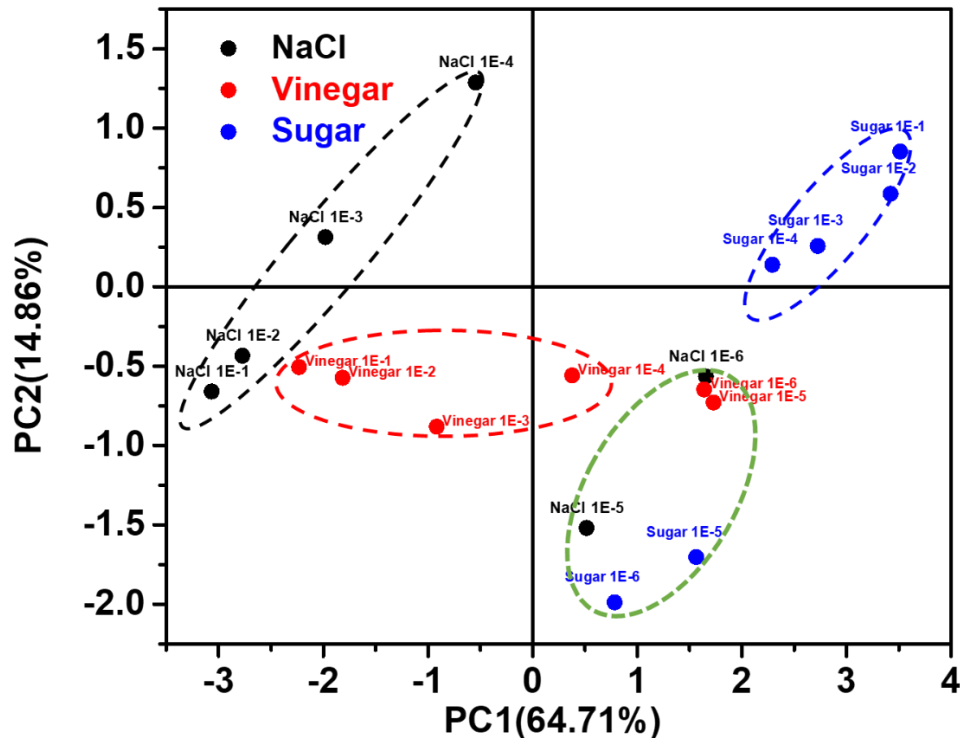


Figure 4-5 Principal component factor scores obtained for target solutions.

For a better understanding of the concentration effects in the mapping position, a series of data fittings were conducted. Data points for PCA were replotted to show the dependency between concentrations and values of PC1 and PC2 for each sample. Figure 4-6 shows fitting results for different analytes. This provides a good base for verifying the concentration values of testing samples. For any concentration data point that can be enforced by the PCA data process for PC1 and PC2 values, there is a specific concentration corresponding to this point. Meanwhile excepting PC2 fitting for vinegar and PC1 fitting for NaCl showing relatively low coefficients of determination value (R^2), 0.62 and 0.83 respectively, R^2 values for other fittings are over 0.9, which represent that over 90% of the data could be explained by fitting models. By combining the PCA result in Figure 4-5 and linear fitting result, the sensor system could easily determine the type of an unknown solution and its approximated concentration. This analysis proves that the sensor system can not only differentiate the type of measuring samples but also provide a quantitative value for the concentration of samples.

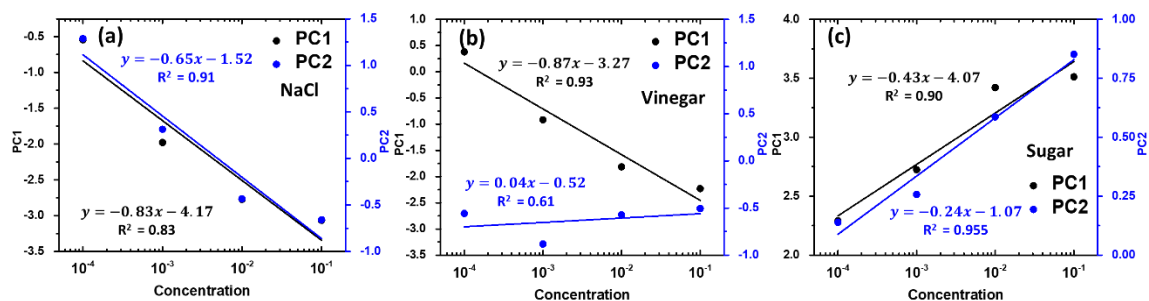


Figure 4-6 Fitting data points for (a) NaCl, (b) vinegar and (c) sugar.

The PCA and fitting process shows a promising result for using the sensor array system to detect and identify the single component and the concentration of the testing sample. Based on this aspect, mixtures of different components with different concentrations were prepared for measuring impedance responses with the sensor system. Figure 4-7 shows the PCA plot for impedance responses of mixed solutions. Three concentrations of the mixture were prepared with two different analytes: 0.1M A + 0.001M B, 0.01M A+ 0.01M B and 0.001M A + 0.1M B, where A and B stand for any two arbitrary analytes chosen from NaCl, sugar and vinegar. 20 μ L mixed solution was applied to each sensing unit for measurements.

As a result, Figure 4-7(b) shows the PCA result for vinegar and sugar mixture. The PCA result shows as green data points on Figure 4-7(a). For the low sugar concentration solutions (0.001M sugar and 0.1M vinegar), the data point for the PCA is close to the 0.1 vinegar range. As the increase of the sugar concentration to 0.1M, the data point moved to the right and get close to 0.1M sugar regime. And data points distribution is very linear. The same phenomena also could be observed for the NaCl/vinegar mixture and the NaCl/sugar mixture, as be shown in Figure 4-7(c) and Figure 4-7(d). Overall, for all the mixture solutions, the PCA results show that the sensing system can detect different element combinations with various concentration ratios. The response of the sensing system can reflect and further be used for deducing element combinations in mixed solutions. This provides a dependable selectivity for the sensing system. Moreover, results show that the sensor has remarkable responses with diluted

elements. Additionally, this response shows a linear relationship with the concentration change. This displays that the sensing system possesses a very promising sensitivity. Besides, the current analysis indicates the possibility of such a sensor array system to measure a complex mixture solution. i.e., a multi-element detection with a single measurement system.

4.4 Conclusions

In this chapter, I discussed a flexible sensor system for multi-flavor detection. A flexible sensor array was fabricated on a PI substrate using a laser direct writing system. The carbon-based sensor units were initially functionalized by different treatments, to offer various impedance responses for sensing NaCl, sugar, and vinegar. The principal component analysis was accomplished for analyzing the experimental data. PCA results show that the sensor array system allows to detect three different flavors, i.e., salty, sweet and sour, and the linear dependence of both PC1 and PC2 could be observed as the concentration changes for each flavor. Additionally, the sensor array was also capable of discriminating mixtures containing two different flavors at different concentrations. This work displayed the potential of laser manufacturing for smart sensing.

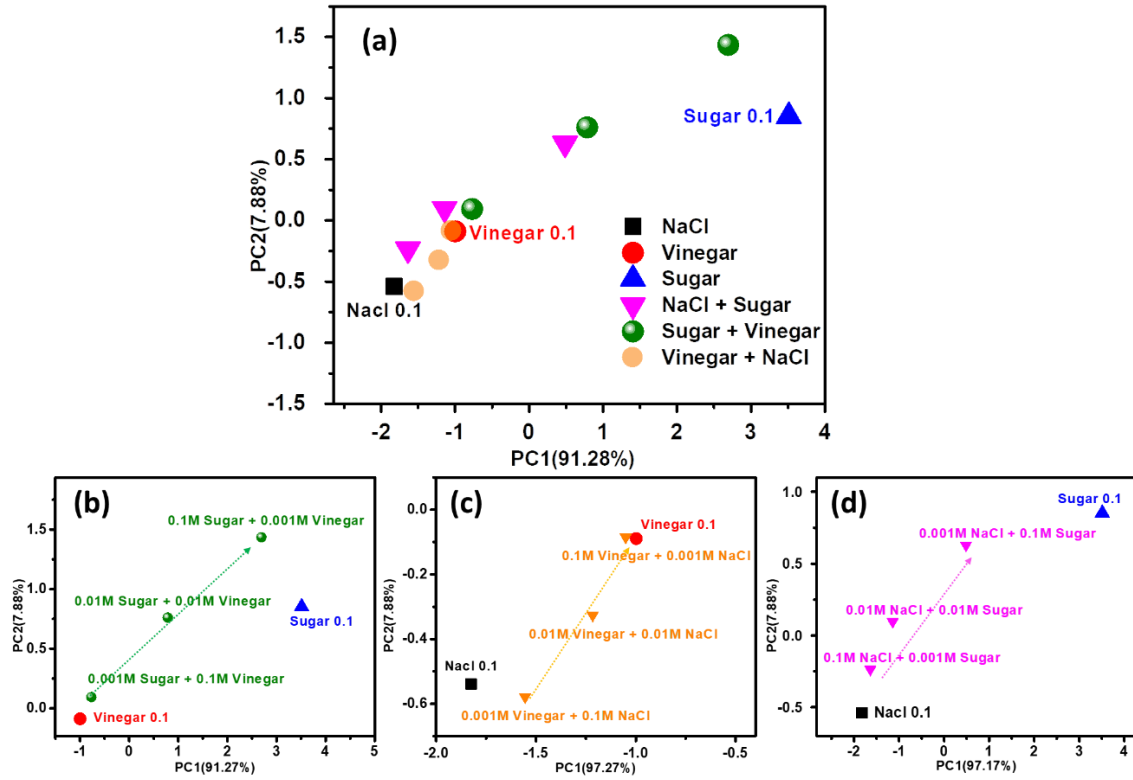


Figure 4-7 (a) The PCA plot for electrical resistance responses of different mixtures, (b) the enlarged figure for vinegar and sugar mixture, (c) the enlarged figure for NaCl and vinegar mixture, and (d) the enlarge figure for NaCl and sugar mixture.

5. LASER-INDUCED WELDING FOR SINGLE COPPER NANOWIRE GLUCOSE SENSOR

Disclosure

This chapter is based on a paper that submitted to Nano-Micro letters by Yongchao Yu, Yangbao Deng , Md Abdullah Al Hasan, Yanfeng Bai, Ruo-Zhou Li, Shuguang Deng, Pooran Joshi, Seungha Shin, and Anming Hu in September. 2019.

Yongchao contributions in the article: Sensor fabrication, Cu nanowire characterization, sensor performance measurement, and laser irradiation study.

Dr. Yangchao Deng and Dr. contributions in this article: Cu nanowire synthesis and characterization, and sensor performance measurement.

Md Abdullah Al Hasan and Dr. Seungha contributions in the article: Computational simulations using 1-D heat diffusion equation and finite difference method

Other Co-author's contributions are listed as follows: Dr. Pooran Joshi and Dr. Shuguang Deng constructed in article revision. Dr. Anming Hu was the PI on the research, assisted in data analysis and experiment design and revised the article.

5.1 Motivation and Background

In this chapter, I investigated a femtosecond (FS) laser-induced nonthermal welling method for the development of a single nanowire sensor. Copper nanowires (CuNWs) are a key building block to facilitate carrier conduction across a broad range of nanodevices. For integration into nanoscale devices, manipulation and welding of these nanowires need to be overcome. Based on high energy density laser processing investigation, we report on innovative welding of single CuNW to the silver film using a tightly focused laser beam combined with manipulation of CuNWs through dielectrophoresis (DEP) method. Two types of laser, femtosecond (FS) and continuous-wave (CW), were employed to analyze, improve, and control Cu-NW melting characteristics under high energy density irradiation. The FS laser welding of CuNWs resulted in a metallic joint with a low contact resistance suitable for functional electronic nanodevices. Computational simulations using 1-D heat diffusion equation and finite difference method (FDM) were performed to gain an insight into metal-laser interactions for high performance welded contact development. Simulation studies on lasers established contrasting melting behavior of metal under laser irradiations. The device feasibility of CuNW based welded contacts was evaluated in terms of the electrical performance of a glucose sensor. It was possible to sense glucose concentration down to 10^{-6} M, demonstrating a path towards integration of CuNW into wearable, flexible nanoelectronics devices.

Nanoelectronics is rapidly evolving towards multi-functional, high reliability, and high integration density systems through 1D-3D integration of materials,

process technology, and packaging. Among the nanotechnology-enabled materials, metallic and semiconducting nanowires have been pursued as key building blocks to manufacture a broad range of nanodevices, e.g., single photon detector[293], transparent and flexible electrodes [294-296], organic electronic and heat-sensitive functional devices [297], electrical and thermal conduction devices[298], foldable capacitive touch pads[299], stretchable and wearable electronics[300-302], and sensors[106, 303, 304]. Specifically, single-nanowire devices with unique nanostructures and properties, become attractive and promising for diverse applications. However, to realize large-scale, reliable manufacture of single nanowire devices, the following two technical barriers must be overcome: nano-manipulation and nano welding.

Nano-manipulation to enable controlled assembly of nanoscale building blocks is essential for nanomanufacturing. To fabricate single nanowire devices, several methods have been established for manipulating NWs, including electric field-assisted alignment[305-308], flow-assisted alignment[309], blow bubble method[310], contact printing[311], direct growth of NW devices[312], Langmuir-Blodgett technique[313], optical tweezer[314, 315], optoelectrical tweezer[316] and micro-robot [317, 318]. Comparing with other methods, the electric field-assisted alignment[319] has been widely applied to control different types of NWs, such as semiconductors, metals, and carbon, normally by a dielectrophoresis (DEP) force. DEP exerts forces on dielectric NWs through induced dipoles when NWs are subjected to a non-uniform electric field. NWs are polarized and aligned with a minimum energy configuration within an applied electric field, which are

along the electric field lines. The electric field-assisted alignment is affected by many factors including the suspending medium, the relative dielectric constant (defined as the ratio of the permittivity of a substance to that of free space) and the geometry of NWs [320].

Welding of NWs can provide an opportunity and potential to form lots of functional nanoelectronics[321], including nanocircuits[322], light-gated nanowire transistors[323], nano waveguides and nanophotonic circuits for quantum computation[324, 325], and nanoplasmonic devices[326]. To realize a nanoscale joining, various methods have been proposed and applied to join NWs, such as cold-welding[122-124], Joule heating[125-128], thermal annealing[129], mechanical pressure[130], and laser (laser-induced plasmonic) joining[133, 327-332]. Solid-state diffusion driven by surface energy has enabled welding of two bare Au NWs in vacuum at room temperature[122] and joining of two silver NWs after removal of the surface-capping polymer at an ambient atmosphere[123, 124]. However, this self-diffusion is difficult to achieve a head-to-side joining (T-shape) since the capping layer is not uniform and the polymer at the sidewall is thicker than the layer at the wire head[123]. Although the Joule heating was suggested to join NWs[125, 126], it is limited to conductive NWs. A nanoscopic mechanical pressing with nanoindentation was developed to join the wire to the substrate[130]. Unfortunately, this press will significantly deform the wire head. The substrate can be damaged seriously by Joule heating, mechanical pressure and thermal annealing unless the processing parameters, e.g., current, pressure, and temperature, are accurately controlled. Compared with other joining methods,

photonic sintering was conducted for joining metal NWs, which can provide non-contact processing and good thermal controllability with minimum thermal damage to the substrate. Due to self-localized plasmonic excitation[327], this plasmonic heat can lead to perfect joining at cross-overlapped NWs[299]. A continuous-wave laser was employed to melt part of NWs for brazing the crossed NWs[133, 333]. This laser nano brazing is similar to autogenous laser brazing developed for metal microjoining [334] . Currently, laser joined metal NWs display a polycrystalline nature with lots of defects at the joined regions[132, 330, 331]. This is quite different from a self-oriented joining with solid-state diffusion where a clear lattice matching is founded. Femtosecond laser joining and a laser-healing of cutting wires show epitaxial recrystallization or enhanced grain orientation[132, 331, 335]. Therefore, the nanojoining quality can be feasibly improved after precise control of laser parameters based on the understanding of the interaction of laser and NWs. In this chapter, for a better understanding of the local melting of a CuNW using a focused laser beam, a comparative study is accomplished with 1030 nm FS laser and 532 nm continuous-wave (CW) laser at different power and atmosphere conditions. To support the experimental observation and explain the difference between two types of laser irradiation, we conducted computational modeling of the temperature distribution of CuNW. For the simulation, we model CuNW as a circular rod with a length of 30 μm and a diameter of 200 nm and assume that laser is irradiated at the tip of a modeled NW, and the temperature is distributed only along the length (defined as x direction) as shown in Figure 5-5. Therefore, a one-dimensional (1-D) heat diffusion model and the finite difference method are

employed for the thermal analysis of both types of laser irradiation. In the case of CW laser, assuming a steady heat supply, the single-temperature model is used to calculate the temperature distribution and its evolution. In contrast, simulations of FS laser irradiation consider the electron and lattice temperatures (T_e and T_l), separately, (i.e., the two-temperature model) due to the time-dependent heat flow from electrons to lattice. This time dependence is because the electron excitation by laser (interaction time: ~a few fs[336]) is much faster than the electron-phonon interaction (~1 ps) and the pulse duration (300 fs) is too short for electrons to excite any ions thermally[91, 337].

As an application, a single copper nanowire (CuNW) device has been fabricated at room temperature with a regular air environment with a 1030 nm FS laser as a glucose sensor. A single CuNW glucose sensor on a flexible paper substrate was successfully demonstrated with a detection limit of about 10^{-6} M.

5.2 Nanowire Synthesis and Laser Welding

5.2.1 Cu Nanowire Synthesis

In this study, CuNWs were prepared with a modified hydrothermal method according to Ref. [338]. 1.348 g octadecylamine (ODA) was added to 100 ml of copper chloride (0.426g) solution and vigorously stirred for 5 hours to form a blue emulsion. Then, the solution was transferred into a Teflon-lined autoclave of 125 ml capacity and heated at 150°C for 72 hours. After cooling down the autoclave to room temperature, the supernatant was poured away, and the CuNWs solution was kept at the bottom. Finally, CuNWs were washed with ethanol for 2-4 times to

remove ODA. Figure 5-1(a-c) show the SEM images for synthesized CuNWs. The self-joined phenomenon was observed between CuNWs, which is due to the inhomogeneous removal of surface capping layers. In Figure 5-1(c), two CuNWs are head-to-head joined and form an angle for 132° . An organic compound, Octadecylamine (ODA) was used for the synthesis of CuNWs. To remove ODA from CuNW solution, the CuNW solution was washed with ethanol for 2-4 times. It is founded that ODA films at the end of CuNWs were thinner than the sidewall. The diffusion between two adjacently exposed wires leads to an end-to-end joining. The average length for CuNWs is around $28.4\text{ }\mu\text{m}$ with 250-350 nm of diameter. Figure 5-1(f) demonstrates that the statistic distribution of the joined angles. The dominant angles are mainly distributed in a range of 110° - 160° . Although this self-joined nanowire has been selectively for simple plasmonic circuits through lithographic manufacturing, it is certainly not suitable for complicated nanoelectronics with the desired function.

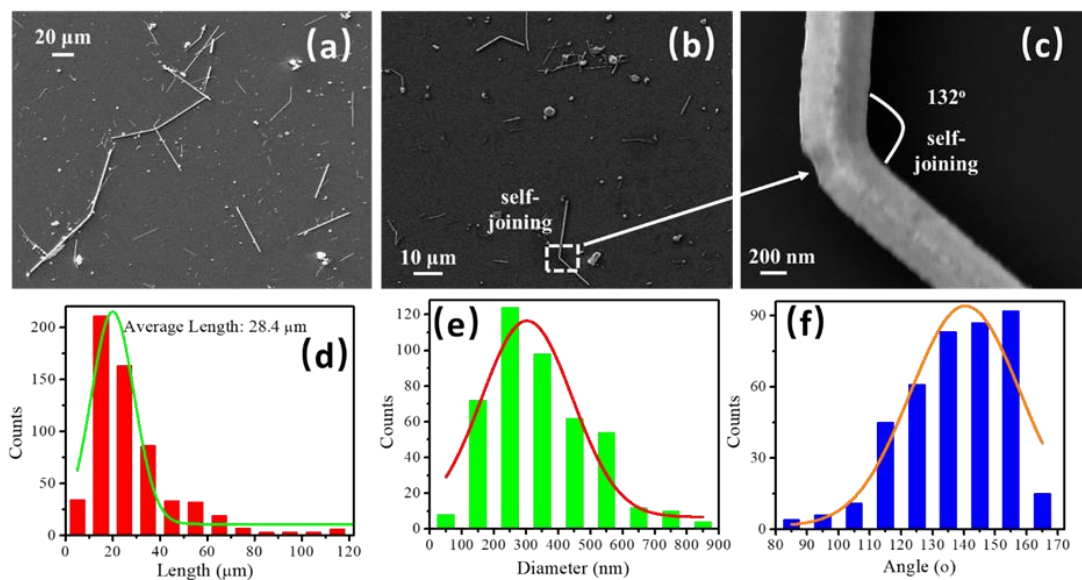


Figure 5-1 (a) SEM images of synthesized CuNWs, (b) SEM images of self-joined CuNWs, (c) enlarge the image of self-joined CuNW for angle measurement, (d) length distribution of CuNWs, (e) diameter distribution of CuNWs, and (f) angle distribution of self-joined CuNWs.

5.2.1 Laser-Induced Welding of a Cu Nanowire

In order to elucidate the laser-induced melting of a Cu nanowire, two types of laser (1030 nm femtosecond (FS) laser and 532 nm continue wave (CW) green laser) have been compared. Figure 5-2 shows SEM images of laser irradiated CuNWs. The experiments were accomplished at room temperature and ambient atmosphere. The laser beam was focused by a long working distance 100 x microscope lens with an NA of 0.8. After focusing, the diameter of the laser beam spot applied to the substrate was around 1 μm. Figure 5-2 (a-c) represents an experiment result for FS laser with an average laser power of 35 mW, and Figure 5-2 (d-f) represents experiment results for CW laser at the same average power of

35 mW. Obviously, at the same laser power condition, two laser irradiations create significant differences. For the FS laser, explosive deformations can be observed on both substrate and CuNW after laser process Figure 5-2 (b-c) compared with Figure 5-2 (a). The silicon wafer substrate is damaged, and a large number of Si and Ag nanoparticles splash around at the irradiation area. A large particles-aggregation appears on top of the NW. However, there is no structural and surface deformation on other parts of the nanowire. On the other hand, at the same laser power condition, the CW laser produced a different effect from that with the FS laser. Comparing Figure 5-2 (e) to (d), CW laser does not break a CuNW at all but provides a very clear surface deformation on the nanowire. As shown in Fig. 1(f), at the laser-focused position, a recyclized structure is observed. This phenomenon can be explained by a local high thermal effect that is induced by the CW laser. CuNW is partially melted at high temperatures induced by laser irradiation, and the melted wire crystalized again after the laser is off. Furthermore, this thermal effect is propagated along the CuNW, and this melting-resolidification occurs entire nanowire. In Figure 5-2 (f), it is obvious that the surface roughness increases after laser irradiation. Because the CuNW was exposed to air, serious oxidation could occur on the surface due to the heat induced by CW laser, which will be further confirmed by the chemical analysis later. FS laser is an ultra-fast high repetition pulse laser, with an average laser power of 35 mW, it can generate a peak power density of $1.24 \times 10^{14} \text{ W/cm}^2$. On the other hand, with 35mW power, CW laser generates a power density of $4.46 \times 10^6 \text{ W/cm}^2$. Meanwhile, for an ultrafast

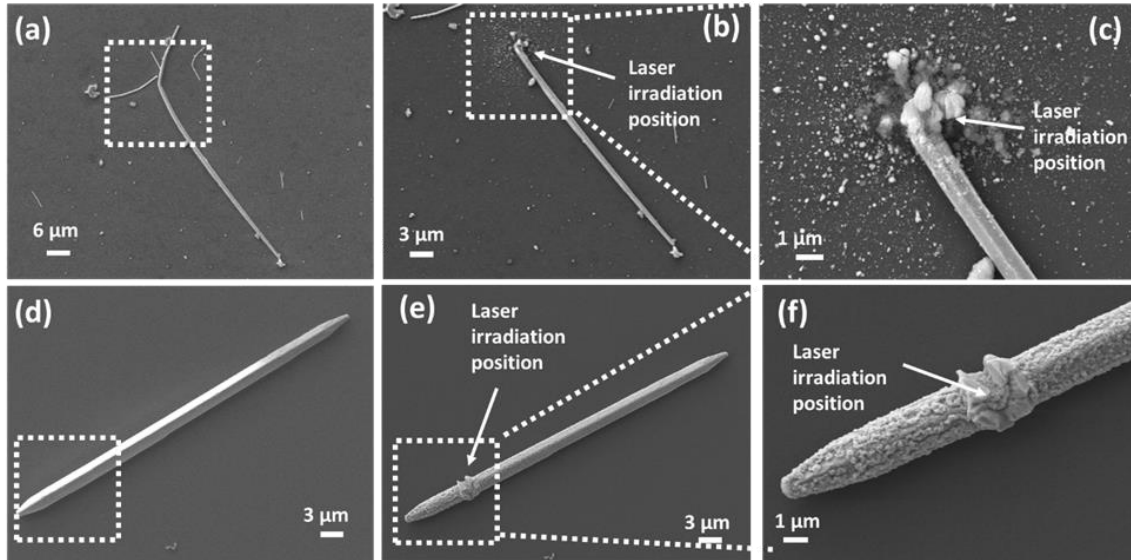


Figure 5-2 SEM images of CuNW (a) before and (b) after FS laser irradiation, and (c) enlarged image of FS laser irradiation area. CuNW images (d) before and (e) after CW laser irradiation and (f) enlarged image of the CW laser irradiation area.

interaction, the absorption of photons stimulates electrons within a hundred femtoseconds (fs), which is too short to disturb lattice. The absorbed energy was thus transferred from electrons to the lattice by electron-lattice scattering after the laser pulse[91, 92]. The thermal coupling between free electrons and lattices typically occurs within 100 ps, depending on the electron-phonon coupling strength of different materials. The typical electron-phonon coupling time of hundred femtoseconds is much shorter than the heat transfer period by thermal conduction. Therefore, the thermal diffusion to the laser-irradiated surrounding area is very limited[93].

To elucidate the origin of that the surface deformation on CuNW, energy dispersive X-ray spectroscopy (EDS) analyses was conducted through element mapping. Figure 5-3(a) and Figure 5-3(b) represent EDS results of CuNWs irradiated by CW laser and FS laser at ambient atmosphere. As Figure 5-3(a) shows, a clear oxygen response is observed on the surface of the CuNW after the CW irradiation, and it is especially stronger at the recrystallized area marked with a white arrow. In contrast, as shown in Figure 5-3(b) the oxygen response on the CuNW surface irradiated by the FS laser is within the detection error of EDS analyses under the same condition. These results infer that the surface structural change is introduced by oxidation of Cu, which is caused by local, high temperature by laser and oxygen in the air. To further testify this, the same experiments were carried out in a glove box with Ar buffer gas and both oxygen and water concentrations lower than 0.1 ppm. Experiment results and EDS analysis results are shown in Figure 5-3(c) and (d). From Figure 5-3(c), we observed that at the end of the nanowire, where the CW laser is irradiated, there is a critical indication of melting. The shape and surface changes of CuNW (from a pentagon to a rounded shape with a smooth surface) can be observed.

Different from Figure 5-3(a), other nanowires that irradiated by FS laser and CW laser irradiation operated in a protective gas do not display surface roughness change; i.e., the nanowire surface remains smooth and clean. The EDS analysis also shows no remarkable change of the oxygen element distribution. Additionally, for FS laser sample, no discernible difference has been detected between two different environmental conditions. Both samples that processed in air and Ar

conditions present very similar results, explosive deformation on laser irradiation positions and clean and smooth surface at the entire unaffected area. At this point, it can be concluded that the surface deformation on CuNW processed with CW laser is due to oxidization. The CW laser induces significant thermal diffusion, which leads to oxidization on the entire nanowire. In contrast, the diffusion of the thermal effect induced by the FS laser to the non-irradiation area is minimized. The dynamic procedures of these experimental results are further investigated by computational simulation. These results not only evidence the FS laser as an ideal tool for precise processes but also show the advantage of FS laser to process an easily oxidized material in air.

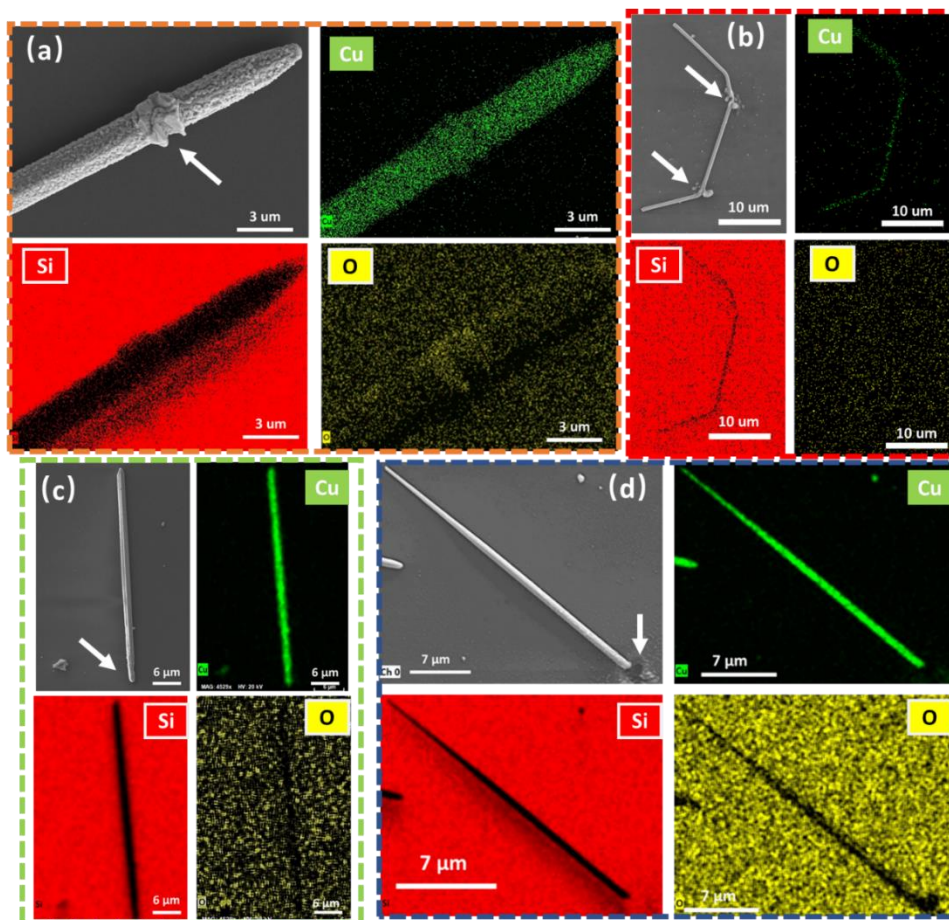


Figure 5-3 EDS mapping results for (a) CW laser processed in air, (b) FS laser processed in air, (c) CW laser processed in Ar and (d) FS laser processed in Ar.

On this basis, studies on the effects of laser power with the FS laser and the CW laser were accomplished. For the FS laser, it is clear that explosive deformations will occur at an average laser power of 35 mW. Thus the laser power has to be reduced to avoid damage to the NWs and Si substrate. Ultimately, the laser power was decreased from 35 mW to 4 mW. Laser powers of 5 mW and 4 mW were also used to determine the minimum laser processing power. For the CW laser, the experiment shows that with 35 mW laser power irradiation, laser only melts a limited area of the CW surface. From the point of laser microprocessing, such limited surface melting cannot provide enough contribution to the nano welding or nano join process. For a better understanding of CW laser effects on CuNW, the laser power was increased from 35 mW to 45 mW. All the experiments were operated in a glove box to protect CuNWs from oxidization. Figure 5-4(a-c) shows the SEM images of CuNWs after processed with the FS laser with different laser powers. From the images, as the laser power decreased from 10 mW to 4 mW, the size of holes induced by laser ablation on the substrate was reduced from about 4 μm to about 2.5 μm . It is worth to note that at 5 mW laser power, the agglomeration of large particles did not occur on the end nanowire. Instead, a clean and sharp cutting edge is formed. As laser power decreases to 4 mW, a clear ablation is observed on Si substrate, but no critical ablation is found on CuNW. We attribute this phenomenon to two reasons. First, it is because the ablation threshold value of silicon is lower than copper. At a similar pulse width of 250 fs, the ablation threshold of Si is about half of Cu, 0.405 J/cm²

and 0.86 J/cm^2 , respectively[339]. Another reason is that due to the optical coupling of the laser beam, which leads to focus the laser beam under the CuNWs.

The CW laser yields different effects on CuNWs. Figure 5-4(d) shows the laser illumination results for 35 mW power with the CW laser. It clearly indicates a melting of the end of CuNW while there is no obvious change for the length and width of CuNW. As further increase the laser power to 45mW, as shows in Figure 5-4(e), a ball-like structure is formed at the laser irradiated area. The diameter of the ball is about $1.2 \text{ }\mu\text{m}$, which is significantly larger than the wire diameter. The blue dash line presents the original nanowire shape. By comparing the CuNW before and after laser processing, the length of CuNW shrinks from $28.6 \text{ }\mu\text{m}$ to $23.7 \text{ }\mu\text{m}$. The approximated total volume of the CuNW changed form $18.2 \text{ }\mu\text{m}^3$ to $15.9 \text{ }\mu\text{m}^3$. It can be inferred that the ball structure is a result of vaporization and shrinkage due to a high temperature melting inducted by CW laser heat. The process for forming this ball structure can be further explained by the location of peak temperature (determined by the beam center position). This melted amount of Cu tends to form a ball-like structure in order to obtain a minimum surface energy state, shortening the CuNW. The location of the peal temperature is decided by the position of the beam center. Once the temperature of the laser irradiation area is above the melting temperature of CuNWs, it transforms into a liquid phase. At the same time, for the rest of the parts of CuNWs, the temperature is below the melting point. The shrinkage direction is determined by this temperature gradient. This process happens on the microsecond time scale[133, 340].

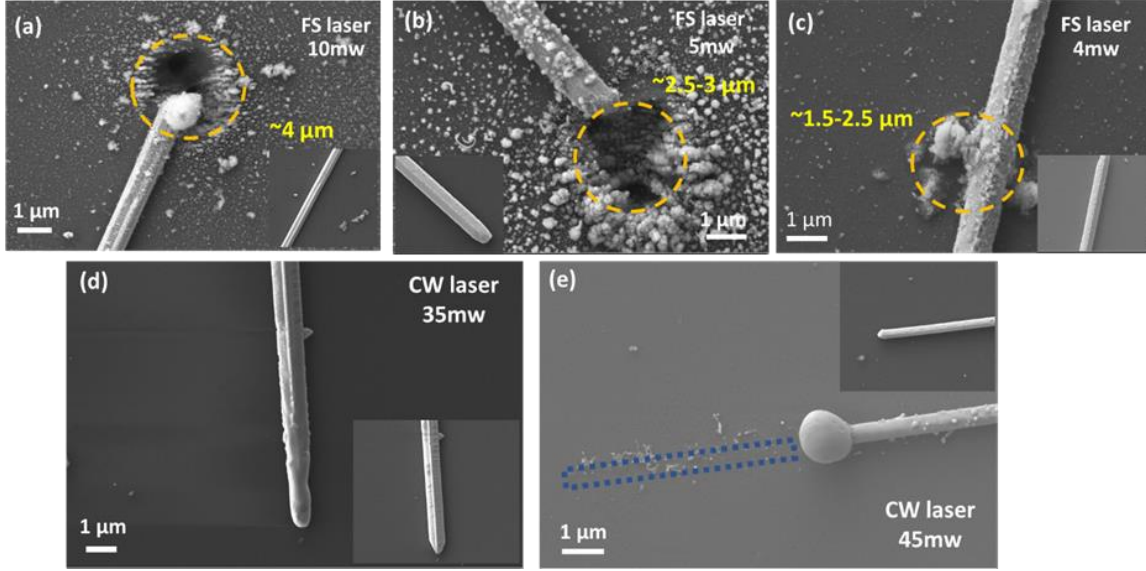


Figure 5-4 SEM images for FS laser irradiated nanowires with (a) 10 mW, (b) 5 mW, (c) 4 mW, and CW laser irradiated nanowires with (d) 35 mW and (e) 45 mW. Inserts show the original nanowires before laser processes.

5.2.2 Simulations using 1-D Heat Diffusion Equation and Finite Difference

Method

5.2.2.1 Single-Temperature 1-D Heat Diffusion Model

The temperature distribution in CuNW and its evolution during the CW laser heating are calculated by using the single-temperature 1-D heat diffusion model and the finite difference method. The energy balance in control volume of each nodal point (m) is used as the governing equation[341-343]:

$$Q_{laser} + Q_{cond} - Q_{conv} - Q_{rad} = \Delta E_{st}, \quad (2)$$

where Q_{laser} is the heat addition by laser and considered for the first nodal point ($m = 1$ or $x = 0$) only, Q_{cond} is the net heat conduction flow to the neighboring nodes, Q_{conv} and Q_{rad} are the convection and radiation heat loss through the CuNW

surface, and ΔE_{st} is the change of stored heat in the control volume of each node. Here, this analysis excludes heat dissipation through the substrate. This omission of the CuNW/substrate conduction heat transfer is because its inclusion can impose excessive complexities (from contact shape, roughness, and interfacial transport) although their influence is not significant (due to roughness and smaller actual contact area) and can be included in other surface heat dissipation terms (Q_{conv} and Q_{rad}). Q_{laser} is given as the product of laser heat flux q_{in} , absorptance (ratio of the absorbed to the incident radiant power) β , and the first node surface area, i.e., $Q_{laser} = q_{in} \beta A$, and our simulations employ $q_{in} = 4.46 \times 10^{10} \text{ W/m}^2$ for CW laser (see S.I. Sec. V) and $\beta = 0.5$ at the wavelength of CW laser (532 nm) [344]. Q_{cond} is calculated using nodal temperatures (T_m) and Cu thermal conductivity, $k = 400 \text{ W/m-K}$ with 1-D Fourier heat conduction equation[345]. The convection and radiation heat transfer are calculated as $Q_{conv} = hA(T_m - T_\infty)$ and $Q_{rad} = \epsilon \sigma A(T_m^4 - T_{surr}^4)$ [345]. Here, σ represents the Stefan-Boltzmann constant, and we use room temperature for the surrounding and ambient air temperatures ($T_{surr} = T_\infty = 303 \text{ K}$), convection coefficient of $h = 2,000 \text{ W/m}^2\text{-K}$, and Cu emissivity of $\epsilon = 0.07$ [346]. Lastly, specific heat capacity, $c = 385 \text{ J/kg-K}$ and density $\rho = 8,960 \text{ kg/m}^3$ of Cu are used for the calculation of the stored thermal energy change, i.e., $\Delta E_{st} = \rho V c (\partial T_m / \partial t)$, where V is the control volume of nodal point m .

5.2.2.2 Two-Temperature Model

With a short pulse of high-intensity laser irradiation, nonequilibrium between electron and lattice systems dynamically changes, and to address this

nonequilibrium dynamics, electron and lattice temperatures of CuNW (T_e and T_l) are separately calculated. As in the analysis of CW laser, 1-D model and FDM are employed, but for each nodal point, the thermal energy balances for electron and lattice are considered, given by[347]:

$$\text{for electron } T_e, \quad Q_{laser} - Q_{el \rightarrow latt} + Q_{el,cond} = \Delta E_{el}, \text{ and} \quad (3)$$

$$\text{for lattice } T_l, \quad Q_{el \rightarrow latt} + Q_{latt,cond} - Q_{conv} - Q_{rad} = \Delta E_{latt}. \quad (4)$$

Here, the laser heat addition ($Q_{laser} = q_{in}\beta A$) is applied to the first node as in the CW laser simulation but considered only in T_e analysis[91] [348]. At the wavelength of FS laser (1,030 nm), β has been reported as 0.06[344]. During a pulse with 300 fs of duration, we assume a constant laser heat flux, $q_{in} = 1.77 \times 10^{17}$ W/m² (S.I. Sec. V), which ensures the employed average power of FS laser (5 mW) considering 1 μ m of laser beam diameter and 120 kHz of pulse repetition rate. Heat flow from electron to the lattice, $Q_{el \rightarrow latt}$ is calculated using the electron-lattice coupling coefficient (g , W/m³-K) from the literature[349] and the difference between T_e and T_l , i.e., $Q_{el \rightarrow latt} = gV(T_e - T_l)$. Conduction heat flow and stored thermal energy change for electron and lattice [$Q_{el,cond}$ and ΔE_{el} in Eq. (2) and $Q_{latt,cond}$ and ΔE_{latt} in Eq. (3)] are calculated using the electron thermal conductivity, $k_e = 385$ W/m-K, lattice thermal conductivity, $k_l = 17$ W/m-K,[350] temperature-dependent electron volumetric heat capacity C_e (J/m³-K) from Ref.[349] and lattice volumetric heat capacity, $C_l = 3.45 \times 10^6$ J/m³-K for Cu.[350] Convection and

radiation (Q_{conv} and Q_{rad}) are included in the T_l analysis only and calculated as the single-temperature modeling using the same properties.

5.2.2.3 Simulated System

CuNW is modeled as a cylinder with 30 μm of length and 200 nm of diameter for the thermal analysis with the 1-D heat diffusion model and the finite difference method (FDM). The modeled CuNW is subdivided along the length of CuNW (i.e., in the x direction) as in Figure 5-5. Different grid sizes are tested, and a small difference is observed in the results. Here, we select 41 equally spaced nodal points with the distance between two nodes of 0.75 μm . The time step is set at 100 ps for the single-temperature model and 0.1 ps for the two-temperature model.

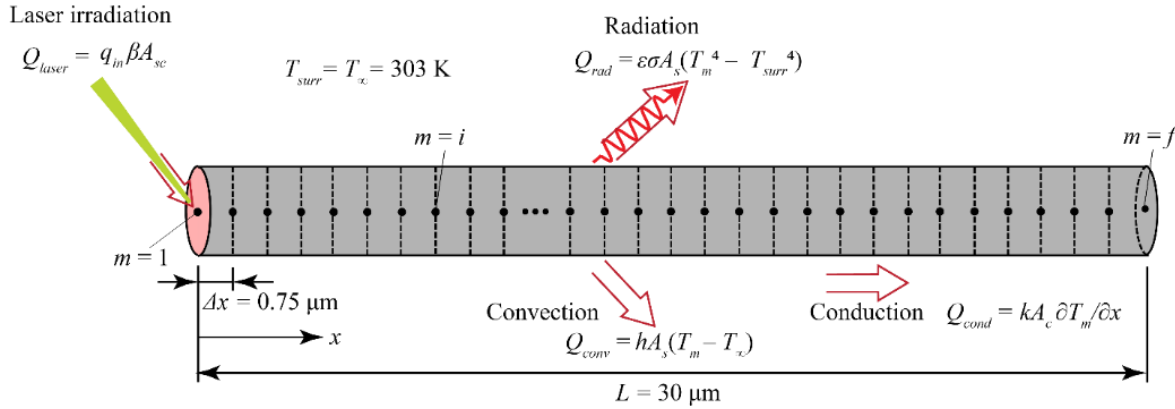


Figure 5-5 Computational model of 30 μm long CuNW for 1-D heat diffusion equation solved with finite difference method simulation. Convection and radiation heat transfer are considered as the experiment occurred in the ambient atmosphere. The heat source from the laser is considered at the tip (first nodal point) of CuNW.

According to our computational simulations, with the CW laser (35 mW) irradiation (at $x = 0$), heat is accumulated, increasing temperature of CuNW with heating time (t), and the heat is dissipated along the length of CuNW (i.e., in the x direction), as shown in Figure 5-6(a). With the CW laser heating longer than 0.5 μs , the temperature rises beyond the Cu melting point ($T_{m, \text{Cu}} = 1368 \text{ K}$ [351]), and a large portion of CuNW has a temperature above the oxidation temperature (1073 K)[352, 353]. Figure 5-6(b) displays that the thermally affected zone (i.e., the heated portion of the CuNW where the temperature is above the oxidation temperature) extends to 10 μm after 1 μs of heating time. It can be inferred that with the increase of irradiation time, the whole CuNW will be heated above the oxidation temperature. This explains that the oxidization of the entire CuNW with a CW laser observed from the experiment in this study.

With the FS pulse laser irradiation at $x = 0$, the electron temperature (T_e) reaches a very high peak value ($\sim 27.5 \times 10^4 \text{ K}$) within the pulse duration ($\sim 300 \text{ fs}$), and then it decays rapidly, releasing their energy to phonons (or lattice). The electron-lattice interaction causes the rise of local T_l [354], and T_e reaches almost equilibrium with T_l shortly ($< 20 \text{ ps}$) after the pulse at $x = 0$ (Figure 5-6(c)). The lattice temperature (T_l) rises and decreases, and for most of the wire ($> 27 \mu\text{m}$), it stays below the Cu melting point (Figure 5-6(d)). A non-thermal ablation is expected at the beginning of the irradiated zone ($< 1 \mu\text{m}$, close to the focus spot size) as the lattice temperature is above the evaporation temperature of Cu ($T_{ev} = 2840.15 \text{ K}$ [355]), as shown in Figure 5-6(d). It is important to point out that such heat is very localized and maintained in a very short time period; T_l can be above

the melting point less than 100 ns only near the heating region ($x < 3 \mu\text{m}$). FS laser irradiation with an average power of 35 mW as in the CW laser is expected to induce ablation of the much larger area, as Figure 5-6 shows up to $6 \mu\text{m}$ of CuNW with a higher temperature than T_{ev} . With an average power of 5 mW, T_l drops below the oxidation temperature in 150 ns after a laser pulse, and the entire CuNW will be cooled close to room temperature before the next laser pulse comes ($t = 8.33 \mu\text{s}$ with 120 kHz), as indicated by Figure 5-6(f,g). As T_l is maintained below the oxidation temperature in the most region ($x > 4 \mu\text{m}$), we expect no significant oxidation. Even if thermal melting and oxidation exist, they are limited to a very local region (near the irradiated region) less than $3 \mu\text{m}$. This simulation result is identical to the experimental results that are shown in Figure 5-2 and Figure 5-4, which indicate that FS laser irradiation effect zones are about $2.5\text{-}4 \mu\text{m}$ with different laser powers.

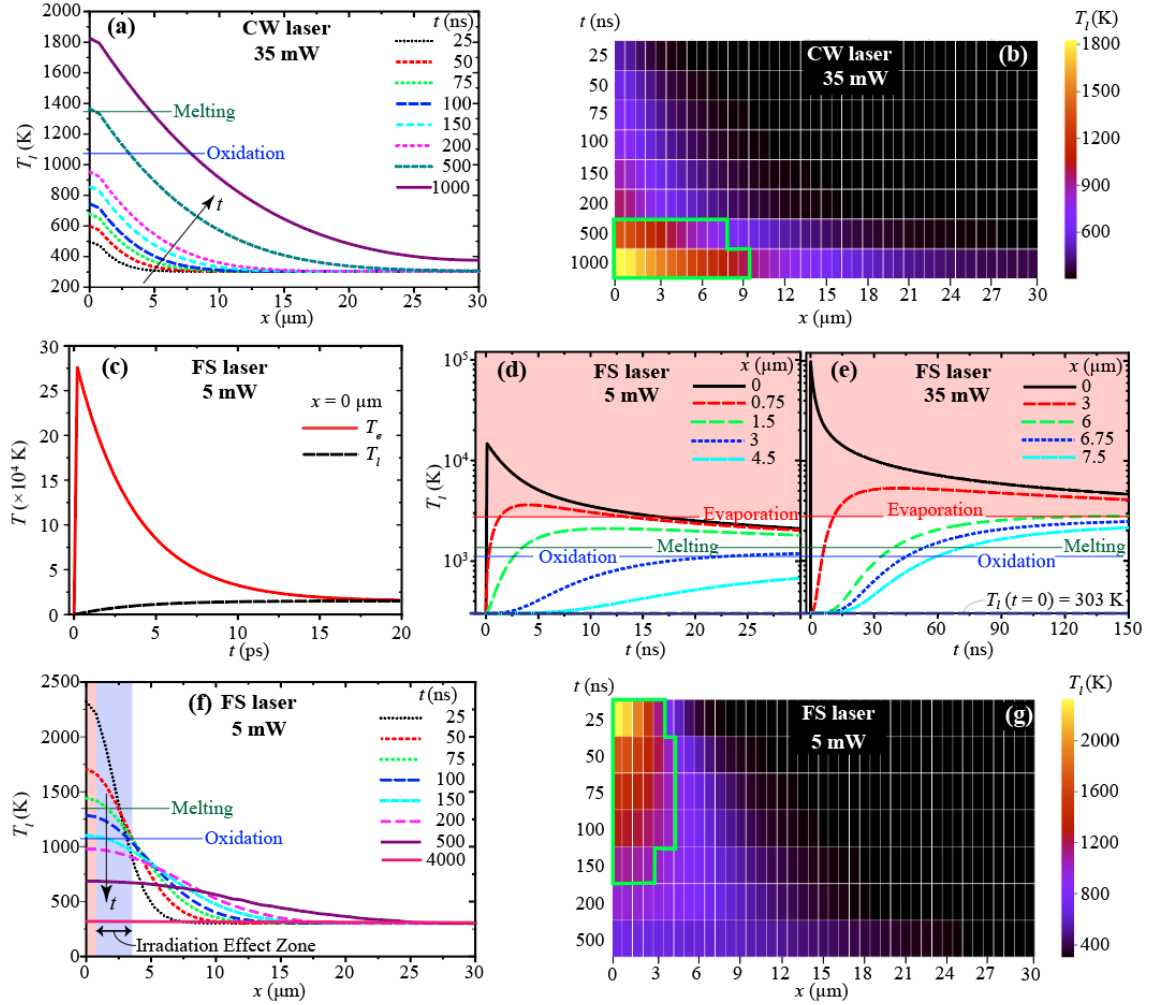


Figure 5-6 (a) Temperature distribution and (b) heatmap of a modeled CuNW with respect to the distance from the heating area at a different heating time. (c) Electron and lattice temperatures of the first nodal point in a short time period after the FS laser pulse (with an average power of 5 mW) starts (< 20 ps). Time evolution of lattice temperature (T_l) from the beginning of a laser pulse (300 fs) at five different locations of CuNW with average FS laser power of (d) 5 mW and (e) 35 mW. (f) Temperature distribution and (g) heatmap of CuNW in the x -direction at different t when using the FS laser with 5 mW average power. The regions surrounded by green lines in (b) and (f) are above the oxidation temperature and vulnerable to oxidation.

5.3 Sensor Development

For the sensing application of welded CuNW with higher electrical conductivity and higher capture efficiency [356-358], a single CuNW glucose sensor is fabricated and demonstrated. The sensor fabrication process including silver electrodes printing, gap cutting with a laser, CuNWs manipulation, and laser welding.

5.3.1 Electrode printing and nanowire manipulation

5.3.1.1 Silver Electrode Fabrication

Silver (Ag) electrodes were printed by an Optomec aerosol jet printing system (AJ 200) with Ag nanoparticle ink (CLARIANT). The diameter of Ag nanoparticles is about 30-40 nm. In this experiment, silver electrodes were printed with 80 μm of line width and 35% of overlap. The printed silver electrodes were cured in a furnace for 1 hour at a temperature of 125°C. Regular photo paper was selected as a substrate due to its relatively high printability and high flexibility. The processing speed was set as 2 mm/s. The thickness of printed Ag electrodes was around 3-4 μm .

Figure 5-7(a) is a schematic diagram of the 3D laser direct writing system. The fiber laser system (Model: Cazadero, Calmar Laser Inc.) generates a femtosecond (fs) pulse chains, of which main parameters are listed as following: pulse width ~ 350 fs, 1,030 nm central wavelength, 120 kHz repetition rate and 2.5 W average power. The fs pulsed laser passed through a shutter, optical isolator, adjustable attenuator, dichroic mirror and microscope objective lens. Then it was

used to cut silver films on the 3D translation stage. The laser beam passed into a vertical microscope system and was focused by a long working distance and high numerical aperture x100 objective lens (0.8 NA). Real-time observation of the laser writing process was performed with a charge-coupled device (CCD). The laser writing process was implemented with a scanning program-controlled design. Figure 5-7 (b) is an SEM image of cutting of silver films at an incident laser fluence of 2.75 J/cm^2 , the corresponding average power is 400 mW, and the gap width is around $3.6 \text{ }\mu\text{m}$. The right picture [Figure 5-7 (c)] is a Liu-plot of ablation areas (D -square) as a function of incident laser fluence[359]. It demonstrated that the D -square gradually increased with an increment of incident laser fluence. The ablation threshold of silver films is 2.53 J/cm^2 . During the cutting of silver films, the laser power was adjusted to 400 mW, and the speed of a 3D translation stage was 20 mm/min . Thus, the silver film was cut to form the trench-structured electrodes with a gap of $2\text{-}4 \text{ }\mu\text{m}$.

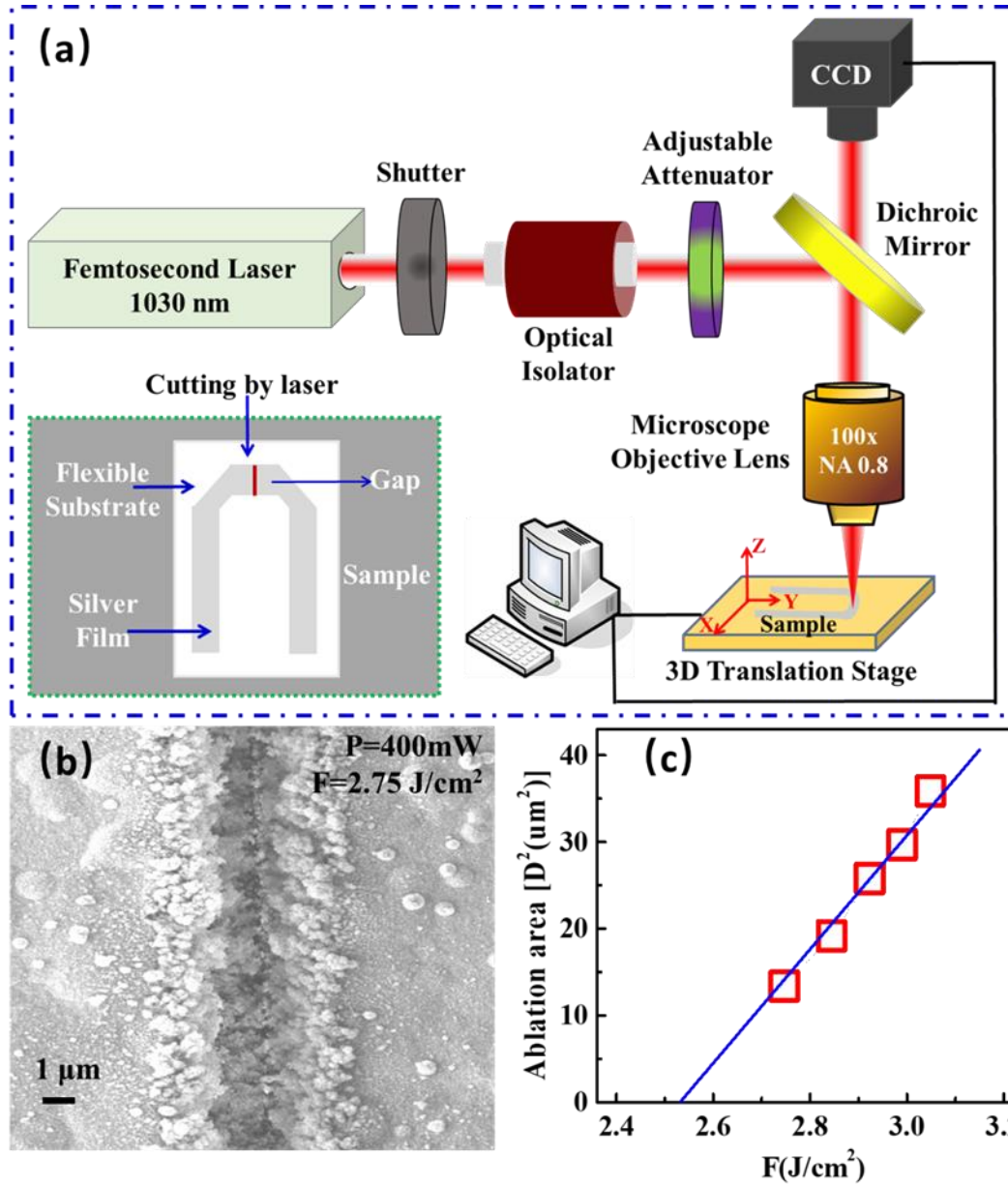


Figure 5-7 (a) Schematic diagram of the 3D laser writing system, (b) SEM image of cutting of silver film at an incident laser fluence of 2.75 J/cm^2 , (c) Liu-plot of ablation areas (D -square) as a function of incident laser fluence.

5.3.1.2 Manipulation of CuNWs with a Dielectrophoresis Method

After the preparation of CuNWs and cutting of silver films, the CuNWs solution was dropped onto the gap and manipulate CuNWs by a DEP method. In this experiment, manipulation of CuNWs was approached by adding alternating current (AC, Model: GWinstek SFG-1013) with different parameters on both sides of the gap, the schematic diagram is presented in Figure 5-8(a,b). Figure 5-8 S4(e) and Figure 5-8(f) show CuNWs solution droplet transfer and CuNWs alignment by a DEP force, respectively. The time-averaged DEP force acting on the CuNWs is estimated based on the equation as [320].

$$F_{DEP} = \frac{\pi r^2 l}{2} \epsilon \kappa \cdot \nabla |E|^2$$

where r is the radius of the CuNWs, l is the length of the CuNWs, ϵ is the permittivity of the suspending medium solvent isopropyl alcohol (IPA), κ is the real part of the Clausius-Mosotti factor, and E is the electric field. In this experiment, the AC frequency is 6 MHz, with 6 V for 1 minute.

5.3.1.3 Nanowire Selecting and Cutting

During the manipulation of CuNWs with AC bias, it is found that several CuNWs well link the gap. Here, the main target of this study is to fabricate a single NW device. So only one CuNW bridging the gap is needed, other CuNWs bridging the gap should be cut off with an FS pulsed laser. For cutting CuNWs, 70 mW laser power was induced to the middle position of these CuNWs. Figure 5-8 (e) shows a CuNW before laser cutting, and Figure 5-8 (f) shows the after cutting with FS laser.

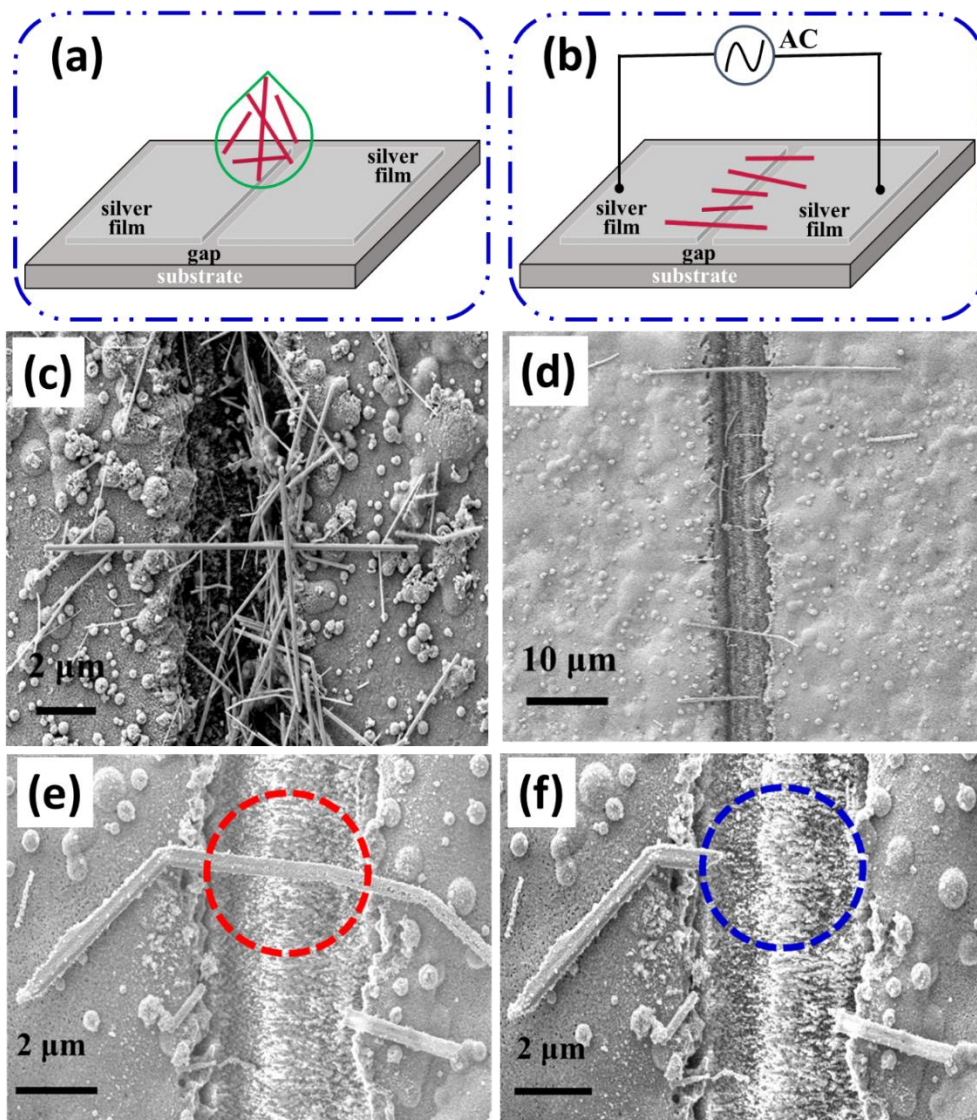


Figure 5-8 (a) Schematic diagram of manipulating CuNWs with a DEP method, (b) schematic of CuNWs alignment by a DEP force, (c) CuNWs bridge the gap without using AC for high concentration of CuNWs solution, (d) CuNWs bridge the gap with AC parameters of 6 V, 6 MHz, and 1 min, and (e) SEM images of CuNW before laser cutting, and (f) after laser cutting with 70 mW.

5.3.2 Nanowire Welding

For the sensing application of welded CuNW with higher electrical conductivity and higher capture efficiency[356-358], a single CuNW glucose sensor is fabricated and demonstrated. The sensor fabrication process including silver electrodes printing, gap cutting with a laser, CuNWs manipulation, and laser welding. In order to make a functional sensor, the joining of CuNW to silver electrodes is needed to decrease the contact resistance. FS laser was selected as for the nano welding of CuNWs to avoid the CuNWs from oxidization and deformation due to the laser-induced thermal effect in air condition. A laser power of 30 mW was used to join a CuNW to the silver film. Figure 5-9(a) displays the SEM image of a CuNW bridging the gap before laser joining. Then the CuNW were illuminated at both sides by tightly focused laser beams at the position marked as the blue and white circle in Figure 5-9(b). Figure 5-9(c) shows a cross-section SEM image of a laser joined area. A Ge Protection layer was deposited during the FIB process for protecting the sample.

To observe the whole CuNW, the laser focus point is slightly away from the CuNW. It is obviously that Ag film was melted at the laser irradiation zone. The melted Ag film partially wrapped around the CuNW and enlarged contacted area, which directly leads to reduce contact resistance. Figure 5-9(d-e) are the enlarged images of the left and right part of Figure 5-9(b), respectively. In Fig. 4(d), the CuNW is partially damaged, and a part of the CuNW is well embedded into the silver film (as the blue circle located). From Figure 5-9(e), it is obviously that partial NW is cut, and a hole is generated in the silver film (see the white circle position).

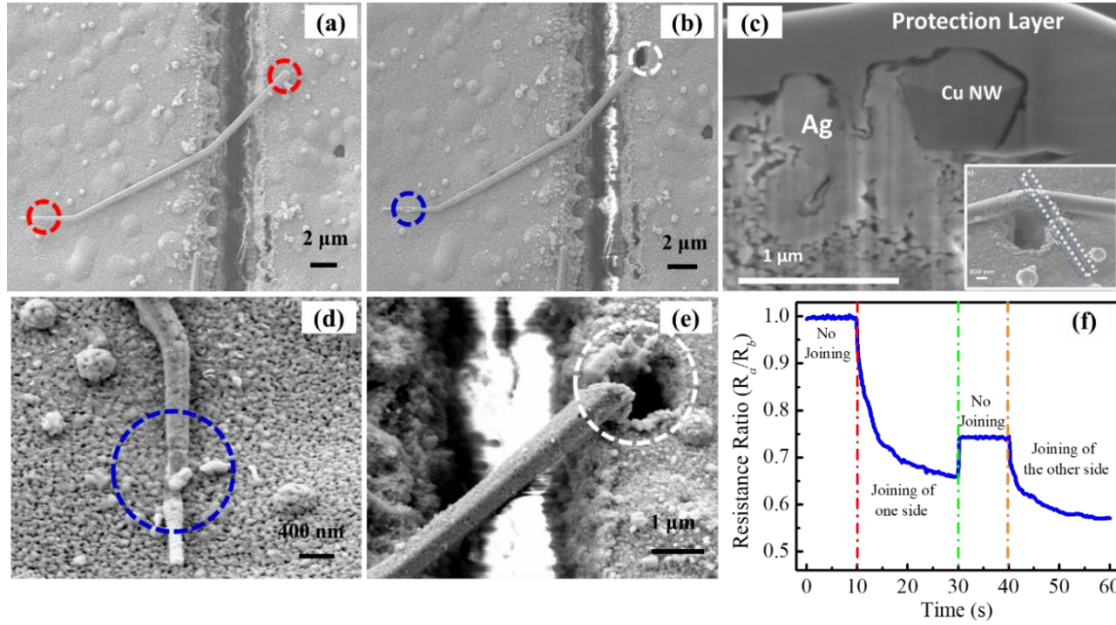


Figure 5-9 SEM images of a CuNW (a) before laser welding and (b) after FS laser welding, (c) cross-section SEM image of laser-welded area, (d) enlarge image of blue welding area, (e) enlarge image of white welding area and (f) real-time resistance change monitoring results during laser welding.

Therefore, it is reasonable to conclude that both ends of the CuNW are well joined to the silver film.

The joining situation is further characterized by in-situ measurement of the resistance variation via a four-terminal method between after laser joining (R_a) and before laser joining (R_b). The measured resistance ratio as a function of illumination time at a laser power of 30 mW is shown in Figure 5-9(f). It is illustrated that the resistance almost keeps unchanged after single CuNW linking the gap. The resistance ratio of R_a to R_b gradually decreases and then becomes flattening during the joining of one side of this CuNW. The resistance ratio increases slightly due to a heterostructure of Cu/Ag before joining the other side, then it also

gradually decreases and then becomes stable in the process of joining the other side. In this experiment, the input electrical current is set as 0.1 μA .

5.3.3 Sensing of Glucose

The welded CuNWs were tested for glucose sensing at different concentrations. The sensor shows stable responses with variable glucose concentrations. The detection limit for this sensor is about 10^{-6} M (1 μM). From Figure 5-10(a)-(b), the resistance gradually decreases with increasing glucose concentration from 10^{-6} M to 1 M [see red circles with error bars and blue squares with error bars]. Moreover, the amperometric detection is carried out by dripping glucose solution with different concentrations onto the welded single CuNW at a voltage of 0.2 V. It is found that the CuNW generates steady-state current for 120 s of a time interval as shown in Figure 5-10(c). The response current gradually

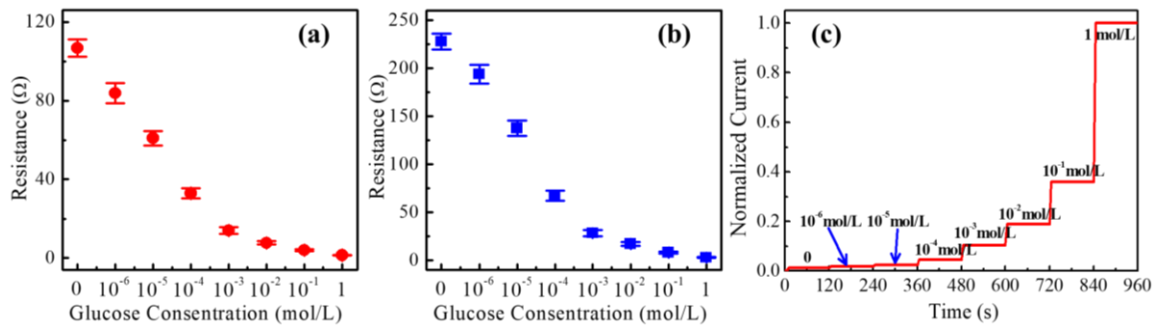


Figure 5-10 (a) Variation of resistance with the concentration of glucose sample 1 and (b) sample 2. (c) Variation of normalized response current with the time at a voltage of 0.2 V under the condition of increasing a glucose concentration

increases with an increment of glucose concentration from 10^{-6} M (1 μ M) to 1 M. This evidences the single CuNW as a sensor for glucose measurement. The dramatic changes in response current after contact with glucose solution is attributed to the oxidation of glucose as the glucose can be oxidized during Cu (III) formation from Cu (II). Thus, the strong oxidization of Cu (III) is responsible for its electrocatalytic behavior[360-362], but the exact mechanism for the oxidation of glucose in alkaline media at Cu based electrodes is still elusive.

5.4 Conclusions

Laser welding of CuNW opens up new possibilities for functional nanodevice development and integration. The simulation and experimental studies demonstrate effective control of material melting and contact welding under laser irradiation. The timescale of laser processing showed a clear impact on the melting and welding of CuNW, and the resultant structural and electrical characteristics. The ultrafast FS laser exposure induced a highly localized non-thermal melting of CuNWs while CW laser led to significant thermal energy diffusion across the entire nanowire. Computational simulations were conducted to gain an understanding of laser-NW interactions to control material melting and develop high performance welded nanoscale electrical contacts. Simulation studies established heat accumulation overtime under CW laser irradiation leading to melting and oxidation of CuNW under ambient conditions. However, the highly localized non-thermal heating by ultrafast FS laser minimized thermal diffusion outside the irradiation zone resulting in superior surface morphology, prevented metal oxidation, and

resulted in reducing contact resistance (contact resistance reduced over 45%), as verified experimentally. Welding CuNWs with a higher electrical conductivity is promising for nanodevice development and integration. To demonstrate a practical application, we successfully manipulated CuNWs to well-bridge the 5 micro silver film gaps under the AC field and join a single CuNW to the silver film with a focused fs pulsed laser. The in-situ observation and resistance variation were used to analyze the join situation. It is evident that the contact resistance significantly decreases after joining. Such a welded Cu single nanowire was used for glucose sensing. The experiments displayed that the measurement resolution of glucose can reach 10^{-6} M. The present laser processing approach provides an effective strategy for fabricating 1D-3D electronic devices through nanoscale welding of diverse metallic and semiconducting NWs.

6. LASER-INDUCED WELDING FOR TELLURIUM NANOTUBE MEMRISTOR

6.1 Motivation and Introduction

With the development of artificial neural networks, biological computation becomes a very promising and highly desired technology in the area of Big data analysis [169]. Comparing to conventional computation technology, which requires arithmetic/logic units and memory units, the configuration of biological computation could simultaneously operate the arithmetic calculation and memory without the burden of data transmission, which provides significantly higher efficacy and computation speed than conventional computation technology. Especially, in recent years, the hardware-implemented neural network computation system has attracted much interest due to the potential inherent in machine learning, pattern recognition at low power consumption[363, 364].

Conventionally, transistor devices were used as a calculation unit to simulate biological synapse, however, the three-terminal structure of transistors increases the difficulty for large-scale integration. As a neuromorphic computation system, large-scale parallel logic and switching cells are required while the complicated structure of conventional semiconductive transistors is suffered from high power consumption and complex structural configuration[365, 366]. The memristor is a two-terminal device, with structural similarity to the biological synapse. Additional to geometric similarity, the working property of the memristor also can mimic biologic synapse; Figure 6-1 presents the working principle of a

bio-synapse and typical two-channel memristor devices. In a bio-synapse, the presynaptic sites are located either on a dendrite or on the cell body, signals/pulses are transferred from presynaptic neuron to receptor through the synaptic cleft mediated by endogenous messenger chemicals. In brief, information flow as an action potential and/or a pulse current. And this pulse triggers the release of a neurotransmitter from a vesicle, whereupon a receptor binds these neurotransmitters following by single transmission on the postsynaptic neuron (as shown in Figure 6-1(a)). In a memristor, the channel material remains at high resistance status for low voltage range. Thereupon the current flowing through the channel material once the applied voltage is larger than the threshold value. The resistance of a memristor is adjusted by current flowing through it. The signal transition principle is highly mimic the bio-synapse. This property makes the memristor as an ideal device for simulating bio-neural network system in electrical circuits. Moreover, the memristor has more advantages compared to the conventional transistor in computational ability, switching speed, power consumption, and complexity[367]. As an estimation, the functionality offered by one memristor can be used to replace up to ten transistors on a chip[368]. A hybrid CMOS/memristor circuit with five layers of 30-nm-pitch crossbars, two memristors per synapse, and 10^4 synapses per neural cell would have an areal density of about 25 million cells per square centimeter, which is higher than that in the human cerebral cortex[369]. Estimates show that such hybrid neuromorphic networks may also provide high power efficiency (about $1\text{W}/\text{cm}^2$), at a high operation speed

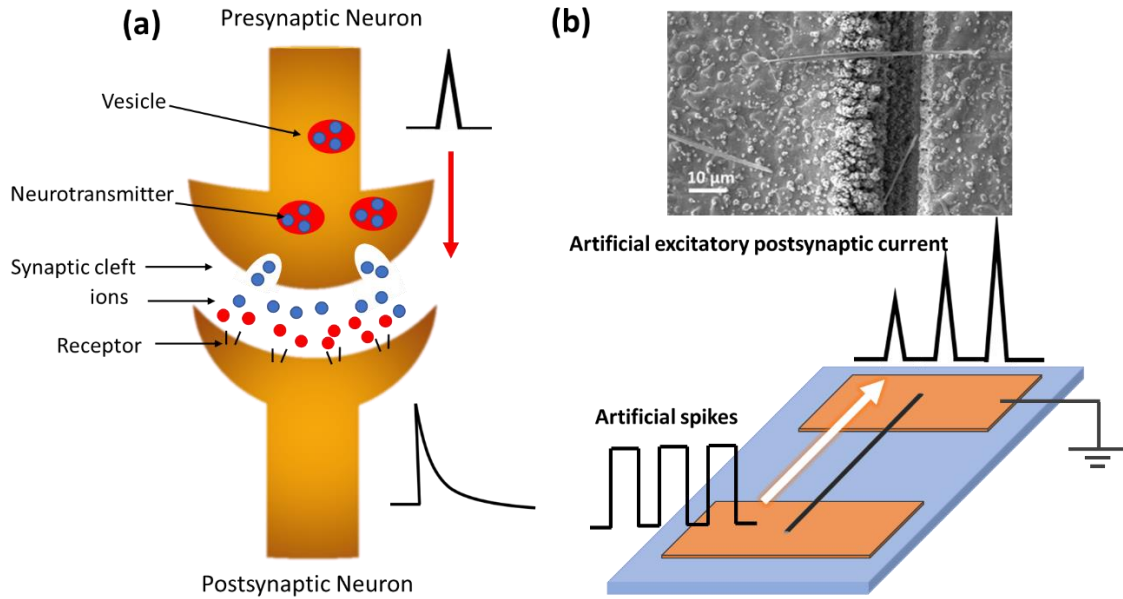


Figure 6-1 (a) Schematic of a bio synapse (b) Schematic of single Te nanotube device for the synaptic response study and SEM image of Te nanotube device

(0.02ms signal transfer delay)[370]. These highlight the significance of memristor-based neuromorphic computation.

In this chapter, we report a tellurium nanotube threshold switching memristor device. A symmetrical voltage-dependent threshold switching behavior was obtained. As the best of our knowledge, this is the first research that reports the tellurium nanotube-based memristor. More importantly, in this research, a clean-room free fabrication process was established. The process temperature for the entire fabrication was controlled to less than 190°C. Additionally, it was found that the FS laser welding process could adjust memristor characteristics. A capacitor coupled memristor behavior was observed after the laser process. Also, the laser-welded devices showed a multistage memory characterization.

6.2 Experiments and Measurements Setup

6.2.1 Nanotube Syntheses

Te nanotubes (TeNT) were synthesized by a hydrothermal process. 0.1 mmol TeO_2 and 0.23 g cetyltrimethylammonium bromide (CTAB) were added into a 25 ml Teflon-lined stainless-steel autoclave. Then the autoclave was filled with Ethylene glycol (EG) up to 80% of the total volume of autoclave and maintained at 180°C for 24 hours, then naturally cooled to room temperature. Silver-gray solids were collected by centrifuging the reaction mixture at 5,000 rpm for 30min. CTAB residuals were removed by washing the particles alternatively with distilled water and ethanol several times. Figure 6-2 (a) shows SEM images of synthesized Te nanotubes, and an enlarged image is shown in Figure 6-2 (b). The average length of Te nanotube is about $20\text{ }\mu\text{m}$ with a diameter of approximately 800 nm.

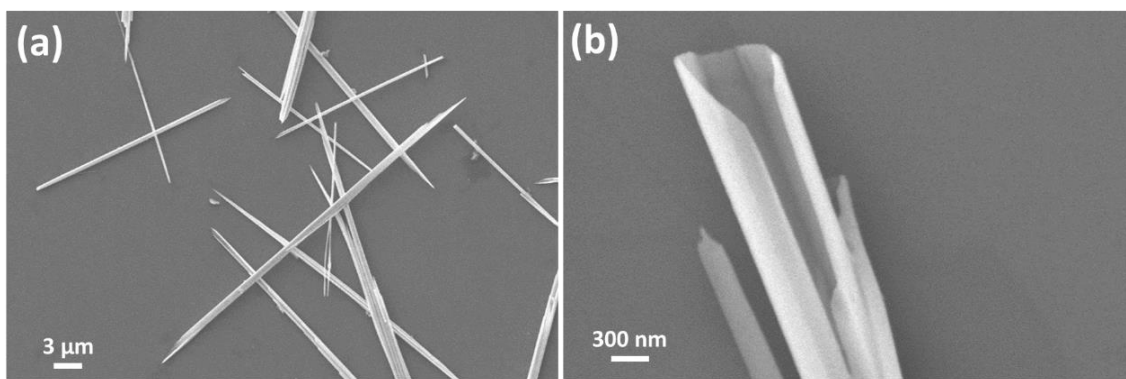


Figure 6-2 SEM images of (a) synthesized Te nanotubes, and (b) an enlarged image of Te nanotube

6.2.2 Silver Electrode Fabrication and Nanotube Manipulation

Silver electrodes were printed by an Optomec aerosol jet printer on a photo paper. A 300 μm nozzle was used during the printing process. The silver electrodes were printed by 80 μm printing paths with a 35 % overlap. The printing process is similar to what we have been introduced in chapter 5. Printed silver electrodes were cured in an oven with 125 $^{\circ}\text{C}$ for 60 min. FS laser was involved in cutting a gap on printed electrodes and then formed the interdigitated circuit. The laser beam was focused by a 100x microscope objective lens on the photo paper surface. And the size of the gap is controlled to around 5 μm .

DEP method was applied for nanotubes and nanowires manipulation. Figure 6-3 shows SEM images of nanotube manipulation results by the DEP process. 5 μl nanowire solution was dropped to the electrode surface. An AC current was applied to the electrode. In an ideal case, nanowire or nanotube should be vertically aligned to the gap. In order to study the ideal perimeter for the process, different AC amplitudes and frequencies were applied. As Figure 6-3 shows, by increase the AC signal frequency, nanotubes show better alignment. However, it is needed to mention that a high AC voltage will break nanotubes during the DEP process (as shown in Figure 6-3(d)). In this study, an AC signal with a 5V peak to peak amplitude and 5MHz frequency was chosen for all the DEP process.

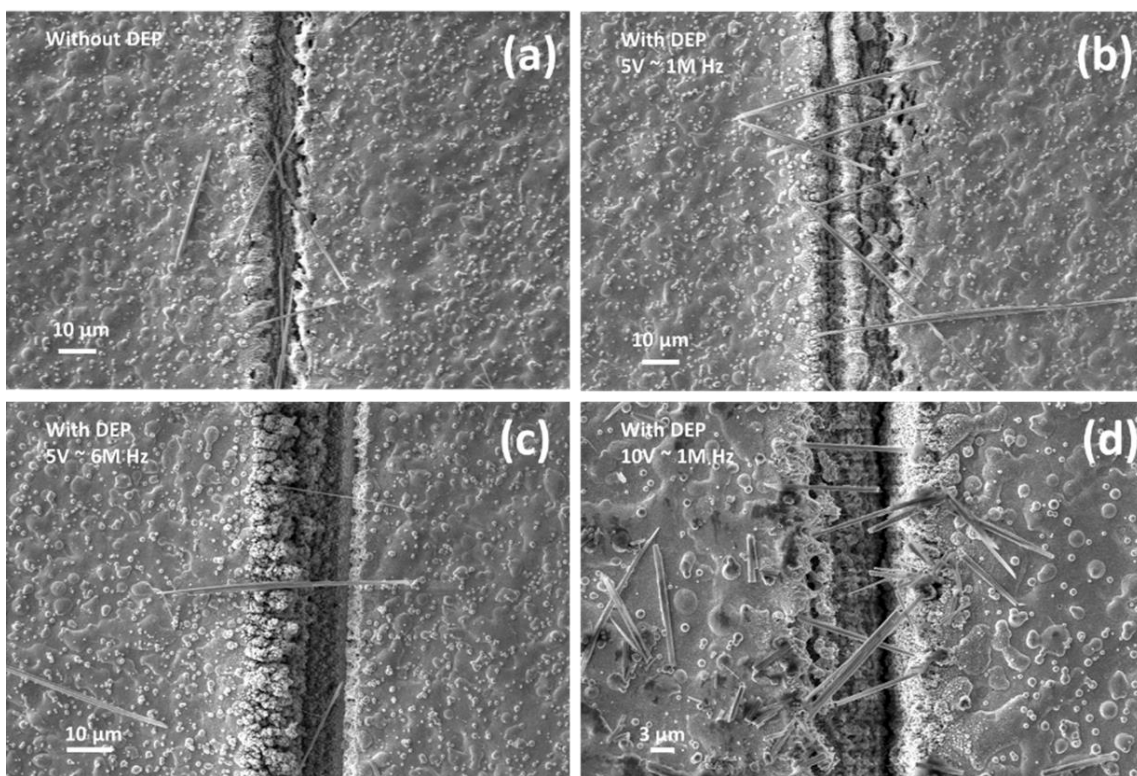


Figure 6-3 SEM images of TeNWs manipulation with a DEP method, (a) with and without manipulation, at (b) 5V 1M Hz, (c) 5v 6M Hz, (4) 10V 1M Hz.

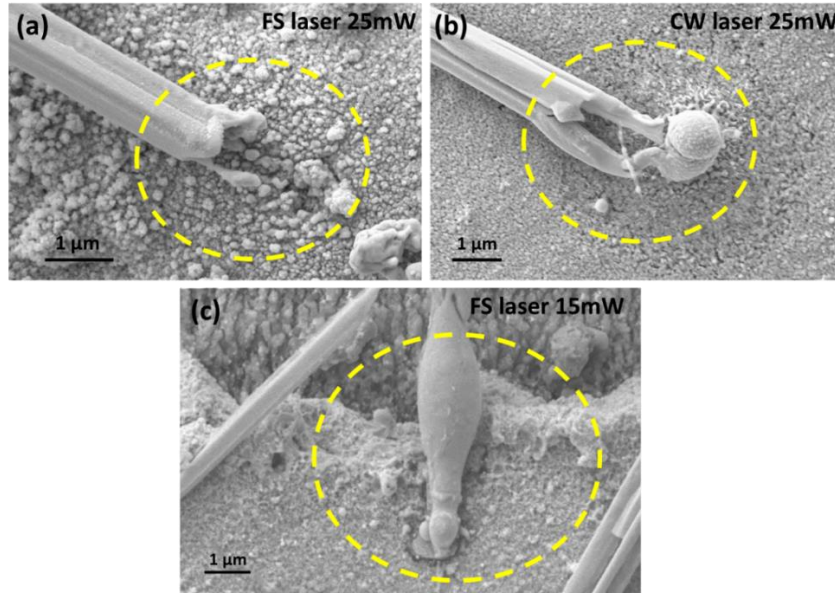


Figure 6-4 SEM images of interface between Te nanotubes and silver film substrate at different laser processing parameters: (a) 25mW FS laser for a short period (<1s), (b) 25mW CW laser for a short period (<1s), and 15mW FS laser for a long period (> 2s).

6.2.3 FS Laser Welding

In order to improve the electrical connection between Te nanotube and Ag electrodes, FS laser was focused on the joint point of nanotube and silver electrode. A 15mW laser beam was focused by a x100 objective lens, which provides a focal spot with approximately 1 μm diameter. Figure 6-4 shows SEM images of welded Te nanotubes by FS laser and CW laser with different laser powers. As an initial experiment, a comparison study of FS laser and CW laser was accomplished. Figure 6-4 (a) and (b) present a laser welding result by 25mW FS laser and 25mW CW laser, respectively, yellow circles represent laser affected

areas. It can be observed that, there is a critical melting phenomenon on CW laser-welded sample. A sphere structure was formed due to the melting of Te nanotube (Figure 6-4(b)). For FS laser-welded sample, a small amount of melted nanotube can be observed at the end of the nanotube. However, compared to the CW laser-welded sample, the thermal melting effect is limited. Based on this experiment result, laser welding parameters were adjusted. Figure 6-4 (c) shows the final welding with 15mW FS laser.

6.3 Memristive Features and Discussion

In this study, all measurements were carried by Bio-Logic SP-200 electrochemical working station. Figure 6-5 presents I-V sweeping performance for a Te nanotube memristor. Symmetrical hysteresis curves are observed in Figure 6-5, and the loop implies clear resistive switching behaviors. When voltage sweep from 0 to 1.5V, the current response remains at a low level for voltage lower than the turn-on voltage (around 0.7v for this device). After the voltage is larger than the turn-on voltage, the current response shows a sudden increase. This implies a typical diode behavior created between the nanotube and the electrode. When sweeping back from 1.5v to 0v, the current recovers to its initial value of zero along the high conductive path, which is a typical feature of volatile switching behavior. The device also demonstrates a symmetrical behavior for both positive and negative sweepings, implying the threshold switching behavior for both polarities [371]. As the best of our knowledge, this is the first time that the tellurium nanotube has been reported as a memristor material.

Moreover, FS laser welding was accomplished for tuning the features of nanotube memristors. Figure 6-5 (c) and (d) present I-V sweeping performances for memristor after laser welding. The main characteristic of the memristor remained the same as before laser welding. However, the threshold voltage showed a critical change after laser welding. Before laser welding, the HRS and LRS state switched at 0.6V. After laser irradiation, the switch voltage increased to over 1V (shown in Figure 6-5 (e) and (f)). This switching voltage is much higher than the working function difference between Te and silver, which are 4.95eV and 4.5eV, respectively. The voltage shift can be led by either thickening of diffusion layers or oxidization of silver electrode and interface changes between Te nanotube and silver. The detailed microstructure is needed to further elucidate this point.

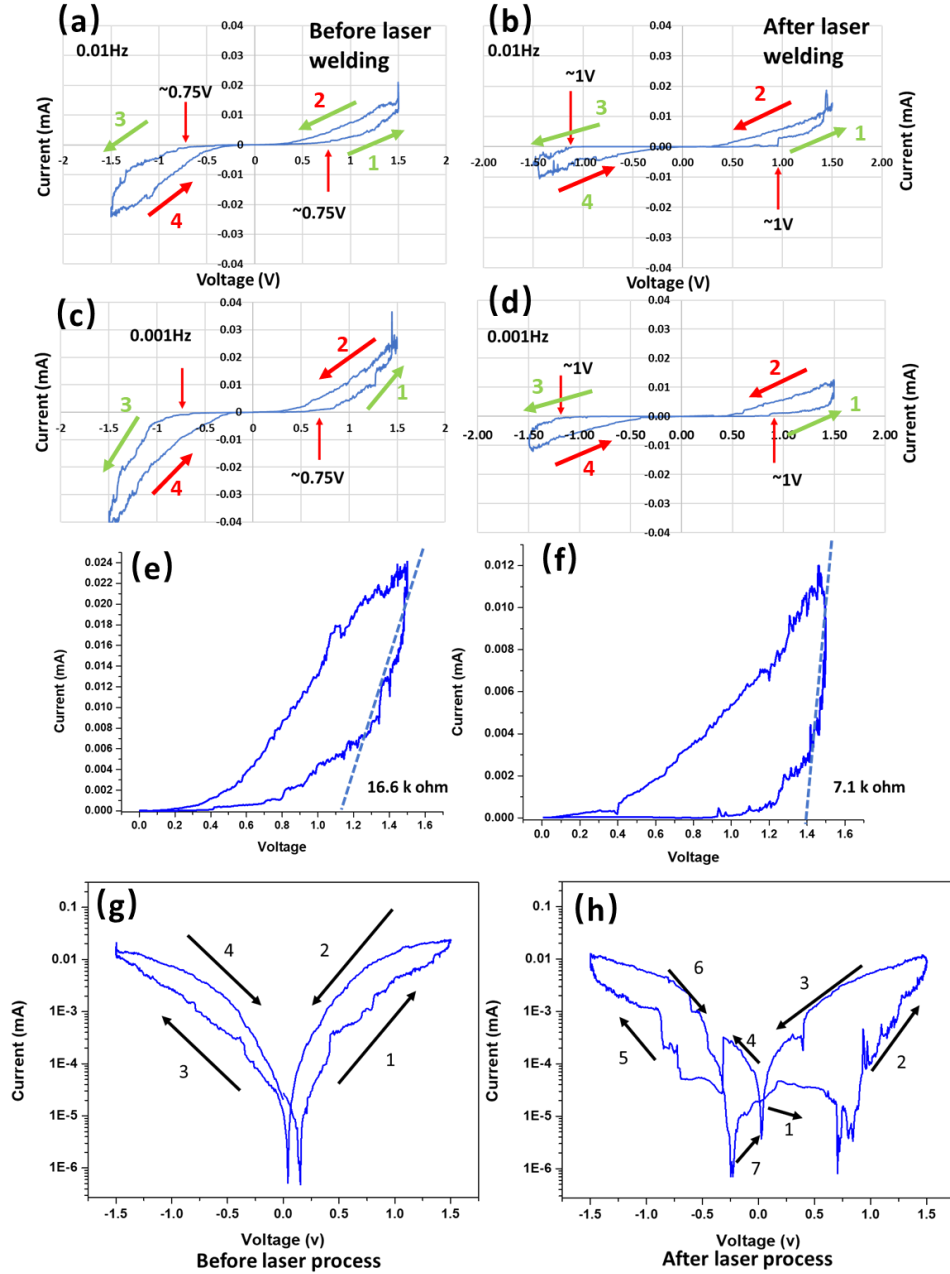


Figure 6-5 CV measurements of Te Nanotube memristors at a sweeping rate of (a) 0.01Hz, or (b) 0.001Hz. CV measurements of laser-welded Te nanotube memristors at a sweeping rate of (c) 0.01Hz, or (d) 0.001Hz, enlarged I-V curve of 0.001Hz sweeping rate for (e) before laser welding, (f) after laser welding, corresponding I-V curve plotted on a semi-logarithmic scale for (c) before laser welding, and (d) after laser welding. And semi-logarithmic scale of the I-V curve for (g) before laser welding and (h) after laser welding.

For verifying and understanding the threshold voltage shift, corresponding I-V curves were plotted on a semi-logarithmic scale (shown in Figure 6-5 (g) and (h)). Figure 6-5 (g) presents that before laser welding, the current shows a clear voltage dependence; the current increase/decrease along with the voltage increase/decrease. After laser welding, the current shown a significant drop when the voltage increased over 0.5v. The same phenomenon is observed for both positive and negative sweeps. More importantly, when sweep voltage swept from 1.5v back to 0v (end of stage 3), a small amount of current remained in the laser-welded device, which implies that a capacitive-coupled memristive effect was introduced by laser welding [372]. Typical, a capacitive-coupled memristive effect can be observed for metal-oxide memristor [373, 374]. This phenomenon probably implies that a thin oxidization layer was induced during the laser welding process and led to create a capacitive coupled memristive effect to the device.

In addition, in the conductive state, a higher conductivity is achieved in the laser-welded device than that of the non-welded device (Figure 6-5 (e) and (f)). During the laser welding, laser irradiation partially melted the nanotube, and the enlarged contact area between nanotube and electrode (as shown in Figure 6-5 (c)). When the applied voltage higher than the threshold voltage, the interact between nanotube and electrode turned to a conductive state. Enlarged contacted area has a significant advantage in reducing contact resistance and can allow more current to pass through. Therefore, the device shows a higher conductivity after laser welding. Besides, the interdiffusion between Ag and Te may occur. This

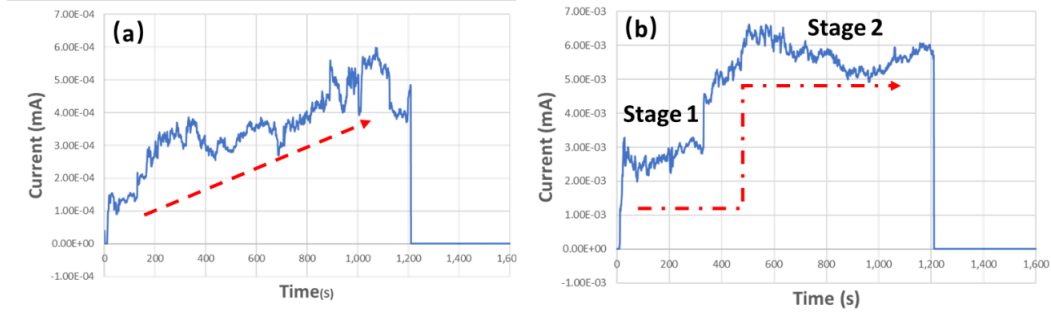


Figure 6-6 Constant voltage measurement for Te nanotube memristors (a) before laser irradiation and (b) after laser irradiation.

interdiffusion may also lead to the current increase. Further microstructure characterization can elucidate this point.

Figure 6-6 presents constant voltage measurements for Te nanotube memristors. A 1V constant voltage was applied for 20 min. Figure 6-6 (a) displays that before laser welding the current passed through the nanotubes increases for the entire measurement period. Owe to the joule heat of DC current, nanotubes were heated and led to reduce conductivity for a semiconductor [375]. On the other hand, for the laser-welded sample, two stages of current response are observed (shown in Figure 6-6 (b)). From 0-300s, the current behaved at a relatively low stage and remained at a stable status. After the 300s, the current showed a rapid increased and then remained at a high current stage. The current is almost double. This phenomenon implies that for the laser-induced device, additional to LRS and HRS, multiple resistance stages can co-exist in HRS.

In order to further clarify the multistage behavior a large-amplitude sinusoidal voltage was applied to the memristor and the current response was measured.

Figure 6-7 presents the current response under continues excitation with forward (0-5v) voltage cycles. Captiously amplified multilevel current is observed in the figure. For both laser-irradiated and unirradiated samples, the current response could be amplified to 4 different levels, which represents that for this type of memristor there are 4 different memory stages for this memristor system. From the figure, it refers that a conductive path is created between electrode and nanotube by applying a high forward voltage, which provides a low resistance statue. This statue will be held and after applying another forward voltage, more conductive paths are created and further amplifies the current response. For the unirradiated sample, the current response is able to be amplified for the first 4 cycle, and the peak current is around 45 μA . but after the 5th cycle, the current response shows a large vibration and peak current response drops to 20-35 μA . The unstable current response could be led by unusable contact resistance between nanotube and electrode. Also, an unstable peak current can be due to the high instability of conduction paths under high current flow. For the laser-irradiated unit (Figure 6-7(b)), the current response can be amplified to 4 different levels. The amplitude of each amplified level is in a range of 50 - 70 μA . And current response amplitudes are higher than the unirradiated sample, which represents a lower contact resistance between nanotube and electrode after laser irradiation. Additionally, after the 5th cycle, the current response presents more stable than the unirradiated sample.

Figure 6-8 demonstrates the multilevel current amplification memory effect for 0-10V voltage cycles with periodic application of a reverse rest bias of -8 V. By comparing before and after laser irradiation, it is clear to see that current response of unirradiated sample are very noising and lots of current spikes could be observed. On the other hand, after laser irradiation, the current response becomes stabilized and current overflow has been reduced significantly. As presented in Figure 6-8 (b and d), the current response is amplified to a different level depending on different voltage cycle numbers. Furthermore, the high current response is reset to the initial level immediately after the bias voltage is applied. This suggests that the memory state defined by the previous voltage cycle number and it appears that the reverse bias of -8V is able to erase the previous history and providing a controllable multilevel current response. The mechanism of this multistage memory behavior could be due to the oxygen vacancy accumulation, which is typically observed in metal oxide material [329]. It also can be a result of electrochemical metallization, which typically happens between two types of metal materials, such as Ag/Pt [376]. However, the detailed mechanism for this system still needs further clarification.

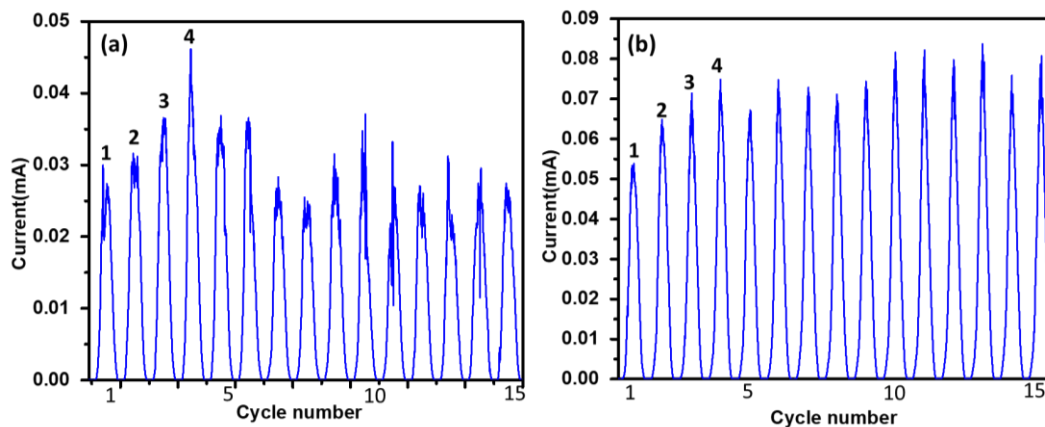


Figure 6-7 current response under repeated voltage cycles with sequences of 0v -5v-0v for (a) unirradiated sample, and (b) laser-irradiated sample.

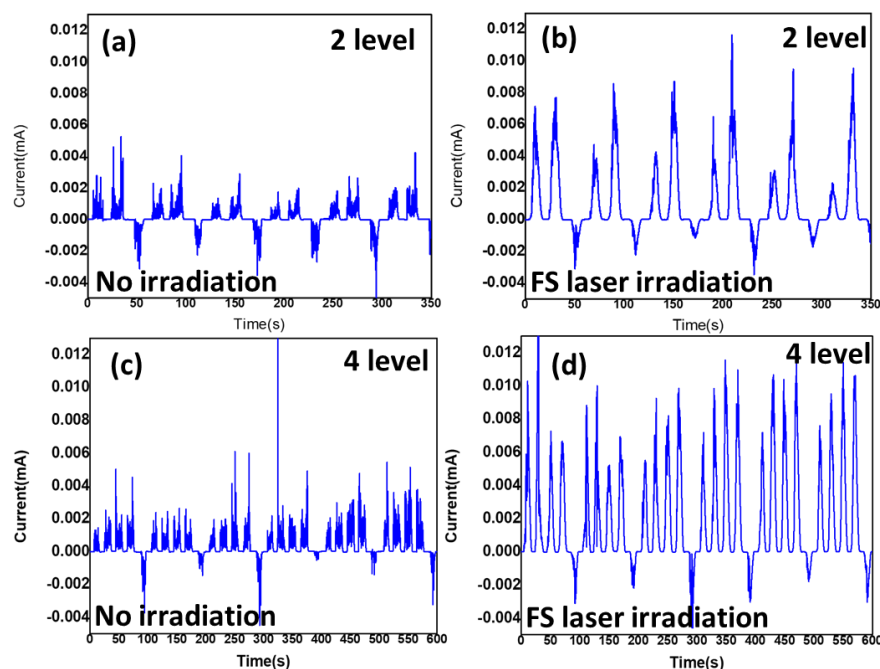


Figure 6-8 Memory level profiles for unirradiated sample and FS laser irradiated sample. The single forward voltage loop in a sin profile was 0v-10v-0v. The reverse bias used was -8v.

Figure 6-9 presents a semi-logarithmic scaled current response of the red dash line range in the inset. The sweeping voltage range is -8V to 10 V. The figure shows that the current response drops in the first stage. After that the current response shows a clear voltage dependence (stage 2 and 3), but once the voltage is lower than 1V, the current response increased suddenly (stage 4). And the same phenomena are observed with both the forward (0 $\rightarrow$ 10 V) and backward (0 $\rightarrow$ -8 v) voltage sweeping. Meanwhile, when the applied voltage is 0V, there are a small amount of current remaining could be observed. The same phenomenon is also shown in -1.5-1.5V range sweeping, as shown in Figure 6-5 (h). At the beginning, the applied voltage starts to charge the coupled capacitor, which drops the current amount that passes through the nanotube at stage 1. Once the capacitor is fully charged (acts as a large resistor), the current starts to flow along the nanotube and the current response shows a clear voltage dependence and switching (stage 2, 3). When the voltage sweeps to lower than 1V in this case, the coupled capacitor starts to discharge and leads to an increase in current response (stage 3-4). Therefore, the capacitive-coupled memristive effect still exists for large-amplitude voltage sweep. This kind of capacitive-coupled memristive feature is a brand new phenomenon and may find innovative application is self-learning and computation.

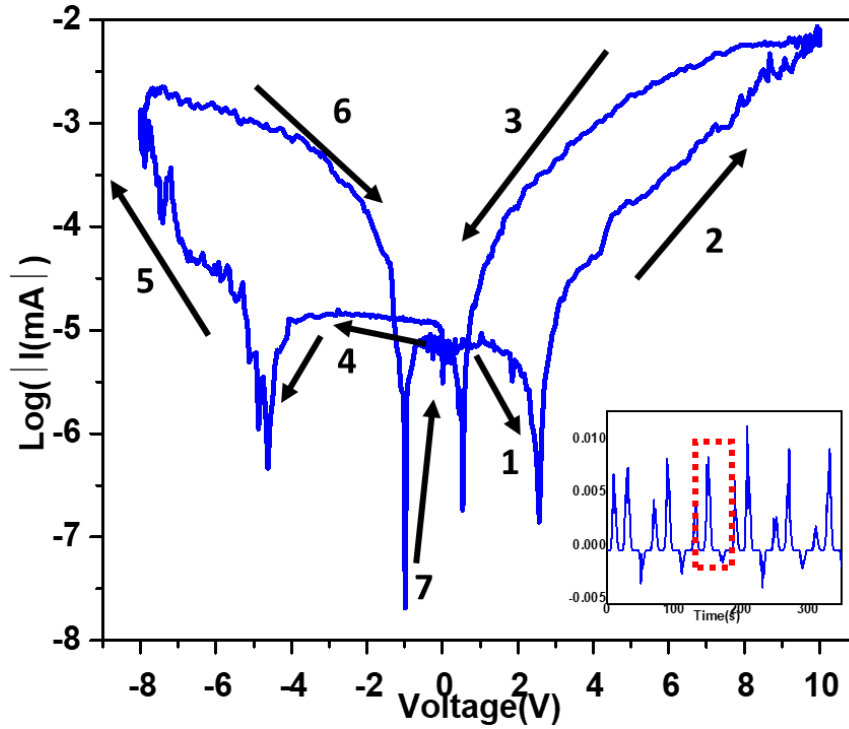


Figure 6-9 Semi-logarithmic scaled I-V curve for a -8-10 V voltage range. Inset: red dash line presents the data that used in the plot.

6.4 Conclusions

In this chapter, we reported a printed tellurium nanotube memristor on a flexible substrate. The devices provide a symmetrical voltage-dependent threshold switching behavior. A laser-induced welding process was involved. And noticeable changes in memristor behaviors were observed after laser processing. A capacitor coupled memristor behavior was discovered and induced by the FS laser welding process, which is considered due to the possible thin oxidization layer that created during the welding. More importantly, this capacitive-coupling devices displayed a multi-stage resistance in the high resistance stage. This multilevel response can

be repeatedly selected by introducing a reviser bias, which performs as a “reset” function and erases the effect of previous voltage cycles and reset the resistance to an initial statue. Although the detailed microstructure characterizations need to elucidate the underlying physical mechanism, this switchable multi-stage resistance and capacitance phenomenon provides a feasible and very attractive basis for applying devices in a complex neural network system.

7. CONCLUSIONS AND OUTLOOK

7.1 Conclusions

In this dissertation, different laser processing methods and printing methods were combined for producing a high-performance electrical device. At the same time, for different applications and different materials, we selected and studied different laser processing methods as approaches to reduce resistance, adjust material properties, and improve machining precision. For nanoparticles, a pulse laser was selected as a tool for selective sintering to reduce the resistance. A nanosecond pulse laser was used to sinter a printed 3D structure with Al nanoparticles for Al-air battery. Taking advantage of high-power density and relatively low heating affecting zone of the pulse laser, we successfully sintered printed structure and removed the organic component that was contained in Al nano ink without damaging the substrate. In this study, the battery performance showed significantly improved due to the reduction of overall anode resistance. For polymer material, two types of laser were selected for different purposes. A CW laser was selected to cut or machining the thick polymer material sheet and created a specified pattern on a PI substrate which has pre-printed electrodes on it. Because of this, the cutting requires a high-resolution machine process on a soft material, which is difficult to accomplish by other cutting processes. By using a CO₂ CW laser, we created 100 μm cutting trace on a 70 μm thick PI sheet. This process reduced overall sensor fabrication time, but more importantly, it shows a possibility to further develop a roll-to-roll fabrication process. A laser induce

graphene sensor array is another polymer-based application in this dissertation. In this study, an FS laser was used to carbonize the polymer substrate and created graphene band interdigit structured directly on a flexible substrate. A highly focused ultra-fast pulse laser beam produces an extremely high-power density to the polymer surface, which breaks the C-O, C=O, and N-C bonds that contain in polymer and lead to their rearrangement to form prophetic structures. The rearranged carbon structure is very similar to the multi-layer graphene, with high surface-volume ration. Taking advantage of this characteristic, a sensor array was fabricated on a flexible substrate. Additionality, by applying a machine learning concept, principal component analysis (PCA), we reported a first e-tongue sensing unit for multi-target detecting, which fabricated by laser direct writing process. The sensing system not only provides high sensitivity but also shows a nice selectivity. Lastly, as a high precision machines tool, ultra-fast pulse laser not only able to provide an extremely high power density but more importantly, due to the laser principle, it provides a very limited thermal effect for the non-irradiated zone, which allows the laser to perforin micron or submicron scale machine and process. Taking advantage of this property, studies of FS laser-induced nonthermal welding for 1D nanomaterials have been accomplished in this dissertation. We started with a metal nanowire, which has less complexity than other nanomaterials, such as alloy and semiconductive material. Cu nanowire was selected not only because Cu nanowire is an excellent material for a glucose sensor, but also it is an oxygen-sensitive material, which is very challenging for thermal welding/processing in an air environment. Two types of laser were selected for comparison study; a 532 nm

CW laser and 1030 FS laser. By comparison, it shows clear evidence that FS laser has a very limited thermal effect for Cu nanowire, which leads to avoiding oxidization of Cu during the welding process. Also, due to the minimized thermal effect, the fabrication accuracy is higher than the CW laser. At the same time, by laser welding, the contact resistance between nanowires and electrodes was dropped over 40%. 1D semiconductor material was selected as the second topic in this study. From our study, Te nanowire shows a promising semi-conductive property that can be used as a channel material for P-type field-effect transistor. Additionally, it shows a memristor property, which could be used as a memory and computational unit. The laser irradiation effect of 1D semiconductive material is still in progress and will be accomplished in future work. By combining printing technology and laser processing, we developed a cleanroom free single nanowire device fabrication process. This study could be a breakthrough in nanomaterial devices development.

In summary, my main contributions are listed as follows

1. Developed a 3D printed Al anode for Al-air battery. And laser selective sintering was applied to the printed structure. By laser sintering, the conductivity of anode electrodes had an essential improvement, which led to battery performance improvement. Additionally, a KOH gel style electrolyte was developed in this study.
2. A current sensor coil was printed by the aerosol jet printing method on a flexible substrate. And a 40W CO₂ laser was applied for precision cutting during the fabrication process.

3. A Laser-Induced carbon-based flexible sensor array for a multiflavors detection system was developed by the laser direct writing process. Different surface treatments and relative characterizations were accomplished. Additionally, a principal component analysis (PCA) was performed in this research.
4. Synthesized copper (Cu) nanowires for the single nanowire glucose sensor. laser welding of Cu nanowires with printed Ag electrodes was accomplished to reduce the contact resistance. Also, a laser sintering system was built in a glove box for studying the oxidation behavior of Cu nanowires during the laser irradiation.
5. Synthesized Tellurium (Te) nanotubes for studying the memristor. FS laser welding was performed to study the property changes of Te based memristor. A multistage memristive switch is confirmed in welded Te nanotube devices.

7.2 Outlook

From our accomplished works, it shows a very critical result that by combining laser processing and printing methods is a promising approach for fabrication high-performance printed electrode devices. laser processing plays an important role in increasing fabrication accuracy, lowering cost, and improving performance, specialty in reducing contact resistance for nanowire devices. However, there are still some further works that need to be approached.

1. For Metal-Air battery, a primary Al-Air battery has been developed in this dissertation. This study could be extended to more extensive materials, such as nickel, zinc, and magnesium [377, 378]. Also, composite alloy metal materials are gained huge attention in recent years as an anode material for metal-air battery

applications [379]. More importantly, some literature has been reported that Al can be used as an anode material for rechargeable batteries [380, 381].

2. For printed electronics applications, in this dissertation, all printings were accomplished with single element printing (silver and aluminum). And most of the printed structures were commutable as conductive electrodes. which means the printed structure itself does not perform as a sensing material, and functionalization is required to perform as a sensor. Therefore, for fully printed devices multi-elements and multi-layer printing are necessary. Therefore, developing more function printable materials will be a key factor for printing functional electronics.

3. For smart sensing application, the printing process could achieve a low cost and fast sensor fabrication. But in most of the case, to fabricate a highly sensitive and selective sensor, a specific surface functionalization is needed. Especially, selectivity is one big challenge in sensor development. However, by using the machine learning process and integrating responses from different sensing unites, different measurement units enable cross-sensitivity, namely the ability of the system to respond to a wide number of different analytes without functionalization with probe molecules. some preliminary works based on this concept has been accomplished in this dissertation. This concept further developed by applying this method to different applications, such as organophosphorus, bio-chemical, or toxic gas sensing applications. Additionally, PCA that has been done in this dissertation is a very powerful tool, but it has limitations such as the veracity of data mapping. Based on this consideration, other machine learning processes, such as KNN,

ANN, et al., could be combined and it could provide a more comprehensive analysis.

4. Our accomplished works show that laser welding can significantly reduce the contact resistance between the metal nanowire and electrodes. However, more research works are needed to fully understand the effect of laser irradiation for metal-metal/ metal-semiconductor welding. Especially for metal-semiconductor welding, the junction between two different materials can form Ohmic contact or Schottky contact. How the laser irradiation will affect these two types of contact are still need more works to clarify. Additionally, based on this research, how it will affect to FET performance and memristor performance have great research value.

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APPENDIX

VITA

Yongchao Yu was born in china. He began attend University of Tennessee, Knoxville in 2008 and revised B.S and M.S degree in electrical engineering in 2013 and 2015 respectively. He started his Ph.D. study in Mechanical Engineering at 2016. During his four years Ph.D. work, he published 5 publications, 1 conference proceeding and in addition to totally twenty-one first/co-authored publications.